SYNTHESIS OF NEW MONOMERS STARTING FROM RENEWABLE RESOURCE MATERIALS AND POLYMERS DERIVED THEREFROM

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CHEMISTRY

by

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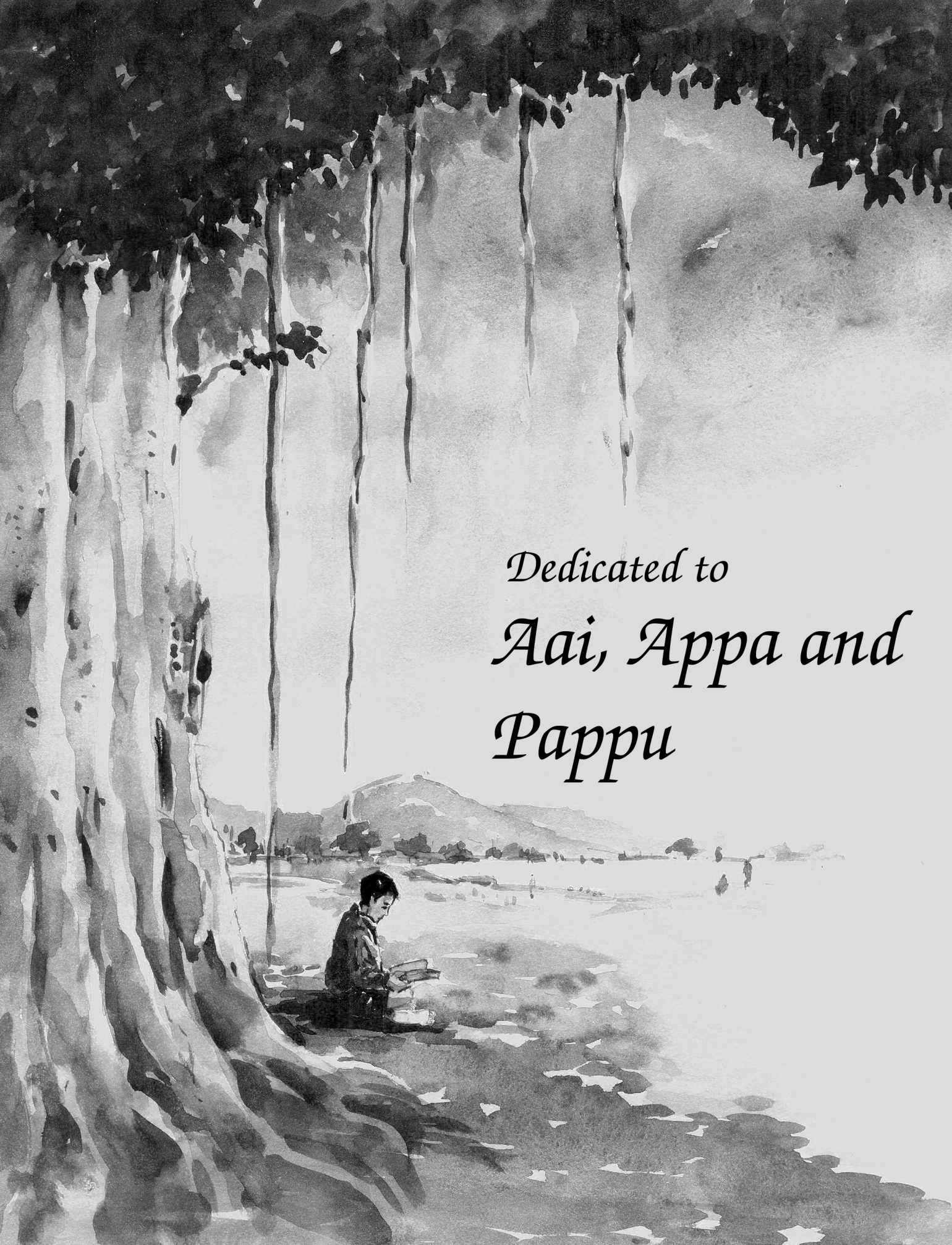

Dedicated to

Aai, Appa and Pappu

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Certificate of the Guide

Certified that the work incorporated in the thesis entitled: **"Synthesis of New Monomers Starting from Renewable Resource Materials and Polymers Derived Therefrom"**, submitted by **Mr. Arvind S. More** was carried out under my supervision/ guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

July 2009
Pune

Prakash P. Wadgaonkar
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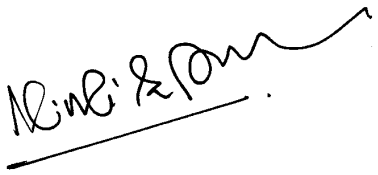
DECLARATION

I hereby declare that all the experiments embodied in this thesis entitled **"Synthesis of New Monomers Starting from Renewable Resource Materials and Polymers Derived Therefrom"**, submitted for the degree of Doctor of Philosophy in Chemistry, to the University of Pune has been carried out by me at the Polymer Science and Engineering Division, National Chemical Laboratory, Pune, 411008, India, under the supervision of Dr. Prakash P. Wadgaonkar. The work is original and has not been submitted in part or full by me, for any degree or diploma to this or to any other University.



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My dissertation has always been a priority, but as most know, there are several priorities in a person's life at any one time. Unfortunately, due to life's confronts and the changes that followed, my dissertation could not always be the number one priority. At any rate, I have finished, but not alone, and am elated. I could not have succeeded without the invaluable support of several. Without these supporters, especially the select few I'm about to mention, I may not have gotten to where I am today, at least not sanely.

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I am indebted to my Father and Mother all my life; whatever I am today is because of them. Both have instilled many admirable qualities in me and have given me a strong foundation to establish myself in real life. They've taught me the value of hard work, self-respect, being persistent and independent. Due to their unrelenting love, tremendous patience, inexorable support and unwavering belief in me, I was able to complete my long dissertation journey. My mother, especially, is a great role model of resilience and strength. Both have always been a constant source of love and always taken pride in me. I would like to place my sincere thanks to my brother, Pappu, for his unconditional love and support.

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Abstract

Sustainability, industrial ecology, eco-efficiency and green chemistry are guiding the development of the next generation of advanced materials, products and processes. World-wide potential demands for replacing petroleum-derived raw materials with renewable plant-based ones in production of valuable polymeric materials are quite significant from the societal and environmental view points. Therefore, using inexpensive renewable resources has greatly attracted the attention of many researchers.

Most of the monomers that are used to prepare polymers are derived from petroleum sources. Due to the depletion of petroleum sources and their escalating prices, polymer chemists have turned their attention to obtain monomers and polymers from renewable resource materials. The field of polymers derived from non-petrochemical feedstocks is gaining a great deal of momentum from both commercial and academic sense. Fundamental research in the production, modification, property enhancement, and new applications of these materials is an important undertaking. The new materials, concepts, and utilizations that result from these efforts will shape the future of polymers from renewable resources.

Biomass constitutes a renewable source of natural products able to be used as unfailing starting materials for access to new compounds and able to substitute petroleum derivatives. Among them, natural oils are expected to be ideal alternative chemical feedstocks. Oleochemicals are abundantly available throughout the world and offer an exceptional variety of chemical building blocks for the design of materials with a strong added value.

The main objective of the present research was to design and synthesize difunctional condensation monomers for high performance polymers starting from renewable resource materials. Another objective was to utilize these difunctional monomers to obtain high performance polymers with improved solubility/ processability.

Thus, our synthetic research efforts were directed towards design and synthesis of difunctional monomers with features that disturb chain packing and structural regularity in the polymer backbone. The approach involved making use of 3-pentadecyl phenol as a starting material which in turn is obtained from cashew nut shell liquid (CNSL)-a renewable resource material. The monomers were designed with a view to incorporate structural features such as: i) the presence aromatic ether linkage to provide lower energy of internal rotation to the polymer chain, ii) the presence of pentadecyl chain in the polymer structure for improving processability *via* internal plasticization effect, and iii) the presence of flexibilizing pentadecyl chain on only one phenyl ring to introduce asymmetry to the polymer backbone. A series of difunctional condensation monomers *viz;* aromatic dibromide, diacid, diacylhydrazide, diamines, diisocyanate and bisphenols containing pendant flexible pentadecyl chain was designed and synthesized starting from CNSL.

Another objective of the present work was to synthesize and characterize step-growth polymers *viz;* polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(ether ketone)s and poly(ether sulfone)s containing pendant flexible pentadecyl chains and to investigate the effect of incorporation of pentadecyl chains on the solubility and thermal properties of the polymers

The thesis has been divided into following seven chapters:

Chapter 1 gives a comprehensive review of literature on polymers derived from renewable resource materials, with emphasis on monomers, polymers and chemicals derived from CNSL. A comprehensive review of literature on polymers, *viz*., polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(ether ketone)s and poly(ether sulfone)s covering methods of synthesis, structure-property relationship, etc., is also presented.

Chapter 2 discusses scope and objectives of the present thesis.

Chapter 3 presents a brief literature review on CNSL chemistry, monomers and polymers starting from CNSL, additives based on CNSL, etc. Further, this chapter describes synthesis of difunctional monomers containing pendant pentadecyl chain starting from CNSL *viz;*

a. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene,
b. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid,
c. 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide,
d. 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine,
e. 4-(2'-Aminophenoxy)-2-pentadecylbenzenamine,
f. 1-Isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene,
g. 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, and
h. 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane.

The difunctional monomers and the intermediates involved in their synthesis were characterized by FTIR, ^{1}H-NMR, and ^{13}C–NMR spectroscopy.

Chapter 4 is sub-divided into two sections:

Chapter 4a describes synthesis of (co) polyazomethines containing flexible ether linkages and pendant pentadecyl chains by solution polycondensation of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with commercially available aromatic dialdehydes, *viz.,* terephthaldehyde, isophthaldehyde and a mixture of terephthaldehyde and isophthaldehyde in various molar proportions. Inherent viscosity of (co) polyazomethines was in the range 0.50-0.70 dL/g. Medium to reasonably high molecular weight (co) polyazomethines soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine, *m*-cresol, etc. were obtained. The presence of C_{15} alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. Transparent and stretchable films of (co)

polyazomethines could be cast from chloroform solutions. This chapter also presents another series of (co) polyazomethines obtained by solution polycondensation of a mixture of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and 4,4'-oxydianiline with terephthaldehyde. However, the derived copolyazomethines were insoluble in common organic solvents. All (co) polyazomethines showed broad halo in the wide angle region ($2\theta = \sim 19^{o}$). In the small-angle region ($2 = \sim 3^{o}$), a reflection was observed for (co) polyazomethines. These peaks were characteristics of a typical layered structure resulting from packing of the pentadecyl side chains. T_{10} values obtained from TG curves for (co) polyazomethines were in the range 434-443 ^{o}C indicating their good thermal stability. All these polymers manifest a T_g value in the range 21-59 ^{o}C. The depression in glass transition temperature of (co) polyazomethines due to the presence of pendant pentadecyl chain demonstrated it's plasticizing ability. A large difference between glass transition (21-59 ^{o}C) and initial decomposition temperature (346-380^{o}C) was observed. This offers (co) polyazomethines a wide processing window.

Chapter 4b deals with synthesis of polyamides containing pendant pentadecyl chains by Yamazaki-Higashi reaction (phosphorylation reaction) of 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid with aromatic diamines, *viz.,* 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylene dianiline, 4,4'-(hexafluoroisopropylidene) dianiline and 4-(4'-aminophenoxy)-2-pentadecylbenzenamine. The obtained polyamides had inherent viscosities in the range 0.45 to 0.66 dL/g and could be cast into tough and transparent films from N,N-dimethylacetamide solution. Most of the polyamides were soluble in polar aprotic solvents such as N,N-dimethylacetamide and 1-methyl-2-pyrrolidinone at room temperature or upon heating. Wide angle X-ray diffraction patterns exhibited broad halo at around $2\theta = \sim 19^{o}$ indicating that the polymers are amorphous in nature. X-ray diffractograms showed a reflection in the small-angle region ($2\theta = \sim 2\text{-}5^{o}$) for all polyamides characteristics of formation of layered structure arising from packing of pentadecyl chains. T_{10} values obtained from TG curves of polyamides were in the range 425-455 °C indicating good thermal stability of polyamides. The derived polyamides showed glass transition temperatures in the range 148-189 ^{o}C. The lowering of T_g could be attributed to the fact that the long alkyl chains acts as a bound solvent or internal plasticizer, also increase the free volume, thereby increasing segmental mobility. A large difference between glass transition (148-189 ^{o}C) and initial decomposition temperature (335-376^{o}C) offers polyamides a broad processing window.

Chapter 5 is divided into two parts:

Chapter 5a provides study on synthesis and characterization of poly(amideimide)s containing pendant pentadecyl chains obtained by two-step polycondensation of 4-[4'-(hydrazino carbonyl)phenoxy]-2-pentadecyl benzohydrazide with commercially available aromatic dianhydrides, *viz.*, benzene-1,2,4,5-tetracarboxylic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic

dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. Inherent viscosities of poly(amideimide)s were in the range 0.60-0.64 dL/g indicating formation of reasonably high molecular weight polymers. Poly(amideimide)s were found to be soluble in N,N-dimethylacetamide, 1-methyl-2-pyrrolidinone, pyridine and *m*-cresol at room temperature or upon heating. The presence of pendant flexible pentadecyl chains brought about significant improvement in solubility of poly(amideimide)s. Tough, transparent and flexible films of poly(amideimide)s could be cast from N,N-dimethylacetamide solution of poly(amideimide)s. Wide angle X-ray diffraction patterns of poly(amideimide)s showed typical broad halo at around $2\theta = \sim 19^{o}$ suggesting that all polymers were amorphous. In the small-angle region ($2\theta = \sim 3^{o}$), a reflection was observed for poly(amideimide)s. These reflections are characteristics of a typically layered structure resulting from the packing of the pentadecyl side chains. T_{10} values obtained from TG curves were in the range of 388-410^{o}C for poly(amideimide)s indicating their good thermal stability. Glass transition temperatures of poly(amideimide)s containing pendant pentadecyl chains and ether linkages were in the range of 162-198^{o}C. It was observed that the plasticization effect of the attached pentadecyl side chain induced the depression of T_g. A large difference between glass transition (162-198^{o}C) and initial temperature (340-356^{o}C) was observed. This offers poly(amideimide)s a wide processing window.

Chapter 5b deals with a) synthesis of polyhydrazides by polycondensation of 4-[4'-(hydrazino carbonyl)phenoxy]-2-pentadecyl benzohydrazide with aromatic diacid chlorides, *viz.*, terephthalic acid chloride and isophthalic acid chloride and b) synthesis of polyoxadiazoles through cyclodehydration of synthesized polyhydrazides. Medium to reasonably high molecular weight polyhydrazides and polyoxadiazoles were obtained as indicated by their inherent viscosities which were in the range 0.53-0.66 dL/g and 0.49 to 0.53 dL/g respectively. Polyhydrazides exhibited excellent solubility in polar aprotic solvents such as N,N-dimethylacetamide, 1-methyl-2-pyrrolidinone, N,N-dimethylformamide and were also found to be soluble in solvents such as *m*-cresol and pyridine at room temperature or upon heating. Polyoxadiazoles showed solubility in polar solvents such as N,N-dimethylacetamide, 1-methyl-2-pyrrolidinone, N,N-dimethylformamide upon heating. Polyoxadiazoles were even soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine and *m*-cresol either at room temperature or upon heating. The presence of C_{15} alkyl chain in polyoxadiazoles disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. Wide angle diffraction patterns showed that all of the polyhydrazides and polyoxadiazoles exhibited broad halo at around $2\theta = \sim 20^{o}$ revealing an essentially amorphous nature. A reflection peak was observed at small-angle region ($2\theta = \sim 3^{o}$) both in polyhydrazides and polyoxadiazoles, indicating formation of layered structure due to the packing of pentadecyl chains. Polyhydrazides showed a

weight loss at around 300°C which may be attributed to the loss of water due to thermally activated cyclodehydration reaction leading to *in-situ* formation of corresponding polyoxadiazoles. T_{10} values obtained from TG curves for polyoxadiazoles were in the range 433-449°C indicating their good thermal stability. A decrease in glass transition temperature was observed, both in polyhydrazides (143-166 °C) and polyoxadiazoles (90-102 °C) due to internal plasticization effect of pentadecyl chain.

Chapter 6 is divided into two sections:

Chapter 6a describes synthesis and characterization of polyesters containing pendant pentadecyl chains obtained by interfacial polycondensation of a bisphenol, *viz,* 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane with aromatic diacid chlorides, *viz,* terephthalic acid chloride and isophthalic acid chloride. This section also elaborates a series of copoplyesters by polycondensation of mixture of bisphenols, *viz.,* 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and 4,4'-isopropylidene diphenol (bisphenol-A) with terephthalic acid chloride. Inherent viscosities of (co)polyesters were in the range 0.72-1.65 dL/g indicating formation of high molecular weight polymers. Tough, transparent and flexible films of (co) polyesters could be cast from chloroform solutions. Homo-polyesters and co-polyesters obtained from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane exhibited good solubility in common organic solvents such as chloroform, dichloromethane, pyridine, *m*-cresol, etc. The presence of C_{15} alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. The broad halo at $2\theta = \sim 19^{o}$ was observed for (co)polyesters in the wide angle X-ray diffraction patterns, which could be mainly because of the presence of long pentadecyl chain, which hinders the packing of the polymer chains making them amorphous. In the small-angle region ($2\theta = \sim 3^{o}$), a strong reflection was observed which could be attributed the formation of layered structures due to the packing of pentadecyl side chains. T_{10} values obtained from TG curves of (co)polyesters were in the range 400-460°C indicating their good thermal stability. The glass transition temperature for homopolyesters were in the range 63-82°C and for copolyesters were in the range 177-183°C. The data clearly indicate that there is remarkable drop in glass transition temperature of polyesters by the incorporation of long pentadecyl chain which acts as an internal plasticizer. A large difference between glass transition (63-183°C) and initial decomposition temperature (368-417°C) was observed. This offers copolyesters a wide processing window.

Chapter 6b deals with poly(arylene ether)s *viz*; a) poly(ether ether ketone)s and poly(ether ether ketone ketone)s containing pendant pentadecyl chains or cyclohexylidene moiety with flexible pentadecyl substitutent and b) poly(ether ether sulfone)s containing pendant pentadecyl chain or cyclohexylidene moiety with pentadecyl substituent. Inherent viscosities of poly(arylene ether)s were in the range 0.64-1.27 dL/g indicating formation of high molecular weight polymers.

It is well known that conventional PEEK and PEKK can not be dissolved in most known organic solvents. In sharp contrast, these polymers were soluble at room temperature in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine and *m*-cresol. Most of the poly(ether ketone)s were soluble on heating in polar aprotic solvents like 1-methyl-2-pyrrolidinone, N,N-dimethylacetamide and N,N-dimethylformamide. Poly(ether sulfone)s exhibited excellent solubility pattern and were found to be soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, N,N-dimethylformamide, 1-methyl-2-pyrrolidinone, N,N-dimethylacetamide, pyridine and *m*-cresol at room temperature or upon heating. The good solubility of the polymers could be attributed to the introduction of the pendant phenyl group with pentadecyl chain and cyclohexylidene moiety, which disturbed the close packing of the polymer chains and led to the increased free volume. The presence of C_{15} alkyl chain provided the additional 'handle' for interaction with solvents. In wide angle X-ray diffractograms, all poly(arylene ether)s were exhibited a broad halo at $2\theta = \sim 19^{o}$, indicating their amorphous nature. In the small-angle region (2θ = 2-3^{o}), a reflection is observed for all poly(arylene ether)s. This indicates the formation of layered structure in poly(arylene ether)s due to the packing of pentadecyl chains. T_{10} values obtained from TG curves for poly(arylene ether)s were in the range 416-459 ^{o}C, indicating their good thermal stability. Poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and aromatic dihalides exhibited glass transition temperature in the range 68-93^{o}C; while, those derived from 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane showed T_g values in the range 69-95 ^{o}C. This showed that, plasticization effect of long pentadecyl chain is responsible for the substantial reduction of glass transition temperatures of poly(arylene ether)s. A large difference between glass transition (68-95^{o}C) and initial decomposition temperature (378-417^{o}C) was observed. This offers poly(arylene ether)s a wide processing window.

Chapter 7 summarizes the results and describes salient conclusions of the investigations reported in this thesis.

Glossary

CNSL	Cashew nut shell liquid
DB	Double bond
DS	Degree of substitution
PGE	Polyglycerol esters
PHA	Poly(hydroxyalkanoate)s
PAZ	Polyazomethine
PI	Polyimine
PA	Polyamide
PAI	Poly(amideimide)
PH	Polyhydrazide
POD	Polyoxadiazole
PES	Polyester
PE	Polyether
PTC	Phase transfer catalyst
PEK	Poly(ether ketone)
PCC	Pyridiniumchlorochromate
CPPB	4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid
HPPB	4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide
APPB	4-(4'-Aminophenoxy)-2-pentadecylbenzenamine
BHPE	1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane
BHPC	1,1-Bis(4-hydroxyphenyl)-3-pentadecylcyclohexane
TPA	Terephthaldehyde
IPA	Isophthaldehyde
***p*-PD**	1,4-Phenylenediamine
***m*-PD**	1,3-Phenylenediamine
ODA	4,4'-Oxydianiline
MDA	4,4'-Methylenedianiline
HFDA	4,4'-(Hexafluoroisopropylidene) dianiline
PMDA	Benzene-1,2,4,5-tetracarboxylic dianhydride or pyromellitic dianhydride
BPDA	3,3',4,4'-Biphenyl tetracarboxylic dianhydride
BTDA	Benzophenone-3,3',4,4'-tetracarboxylic dianhydride
ODPA	4,4'-Oxydiphthalic anhydride
6-FDA	4,4'-(Hexafluoro isopropylidene)diphthalic anhydride
TPC	Terephthalic acid chloride
IPC	Isophthalic acid chloride
BPA	2,2-Bis(4-hydroxyphenyl)propane or bisphenol-A
DFB	4,4'-Difluorobenzophenone
BFB	1,3-Bis(4–fluorobenzoyl)benzene
FPS	Bis(4-fluorophenyl)sulfone
HMPA	Hexamethylphosphoramide
NMP	1-Methyl-2-pyrrolidinone
TPP	Triphenyl phosphite
DMAC	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
THF	Tetrahydrofuran
DCM	Dichloromethane
GPC	Gel permeation chromatography
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
WAXD	Wide angle X-ray diffraction

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Chapter 1

Introduction and Literature Survey

1.1 Introduction

Invention of synthetic polymers has revolutionized the world and their invention is an ultimate tribute to man's creativity and ingenuity. The use of synthetic polymers has advanced every facet of our lives by meeting many basic human needs including food, shelter, clothing, health and transportation. It is hard to imagine what the world would be like without polymers.

For synthesis of polymers, monomers are of quintessential importance and many of such monomers are derived from fossil resources. However, excessive use of fossils as fuel for automobile and for other purposes is causing their rapid depletion and it is feared that they will be completely exhausted in a few decades. Expert predictions about the future availability of fossil resources, *viz*., petrol, natural gas and coal which are not renewable within a useful time scale vary between one and three generations.[1,2] Since the industrial revolution in the mid 20th century, use of fossil fuels has been dramatically increased and has recently reached to its peak which is evident from soaring market prices of crude oil. Considering that more than 90% of these resources are used as fuels, their depletion threatens the energy supply. The fact that the vast majority of organic chemicals and monomers which are required for synthesis of polymers are derived from fossils, their depletion is even a major concern to the polymer industry.

The energy issue is being vigorously debated and many alternative solutions are proposed such as nuclear, biomass combustion, aeolian, geothermal, and others. However, for the production of commodity chemicals and polymers, biomass such as vegetable and animal remnants is the only viable alternative to fossil resources. As a consequence, research initiatives to this effect are being implemented ubiquitously with a sense of increasing urgency as witnessed by the growing investments in biomass application in chemical and polymer production by the concerned ministries, supranational institutions (EU, UNIDO, etc.), and the private industrial sectors.[3] This is being evident from the dramatic increase in scientific publications, patents and international symposia covering the topic of the exploitation of renewable resources to produce commodities, alternative to chemicals, monomers, and polymers.

To isolate the chemicals of interest from biomass, an approach of 'biomass-refinery'[4] was put forward which is similar to classical petroleum-refinery in which each of the different components of a given natural resource is isolated by chemical or biochemical means with the aim of turning them into useful products. Thus, interesting chemicals and monomers for industry and medicine, compounds with a specific useful pristine structure, resins, natural fibres and oils (used as such or after adequate modification) as well as polymers produced by bacteria could replace progressively petrol-based counterparts. For example, various components of wood can be separated and valorized namely: (i) cellulose fibres, essentially for papermaking, but also as reinforcing elements in composite materials; (ii) lignin as a macromonomer for novel plastics, or as a source of valuable chemicals like vanillin; (iii) bark tannins for leather treatment and as components for resins

and adhesives, and (iv) specific minor chemicals present in knots for medical applications such as neutraceticals. Application of biomass could replace fossil resources for production of chemicals and monomers required for polymer synthesis and lessen the dependence on fossil fuels. Since biomass is available ubiquitously, virtually any country in the world could profit from their utilization. However, many challenges need to be overcome before biomass could be applied for chemical and monomer production, especially the extraction or separation of such chemicals from biomass and application of other renewable resources in polymer synthesis. Therefore, the concept of the bio-refinery is very vital for utilization of biomass in polymer synthesis especially for separation of its components and their utilization and their suitable chemical modifications for further use. Much advancement in biomass refinery has been recently reported and considerable financial backing for such projects has been provided from both public and private sectors.[4]

The purpose of this thesis is to exclusively examine one topic within this broad issue namely the use of renewable resources as precursors or to aid the novel macromolecular materials synthesis. This chapter will give a general introduction on utilization of renewable resources to generate chemicals, additives, monomers, and polymers. This section will also provide a brief review of chemistry, extraction, and applications of cashew nut shell liquid (CNSL). In addition to that, within the scope of this thesis a concise review on methods of preparation of polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters and polyethers will also be presented.

1.2 The Context

The utilization of renewable resources came into limelight in the mid 19th century.[3] The first such example reported is chemical modification of natural polymers in 1950s, which gave rise to the first commercial thermoplastic materials like cellulose acetate/nitrate and the first elastomers through the vulcanization of natural rubber.[3] Later, these processes were complemented by approaches based on the controlled polymerization of a variety of natural monomers and oligomers including terpenes, polyphenols and rosins.[3] A further development called upon chemical technologies which transformed renewable resources to produce novel monomeric species like furfuryl alcohol.

The beginning of the twentieth century witnessed the birth of a novel class of materials, the synthetic polymers based on monomers derived from fossil resources. Some hybrid materials arising from the copolymerization between both types of monomers were also developed at this stage as in the case of the first alkyd resins.[3] Interestingly, both monomers used in the first process to synthesize nylon in the late 1930s were prepared from furfural an industrial commodity obtained from renewable resources in a joint venture between Quaker Oats and DuPont.[3]

The petrochemical boom of the second half of the 20th century produced a spectacular diversification in the structures available through industrial organic chemistry. Among these, monomers played a very significant role as it transpires from the high percentage of such structures represented in the list of the most important chemical commodities in world production. The availability of a growing number of cheap chemicals suitable for the production of macromolecular materials gave birth to 'the plastic age' in which we still live today with of course greatly enhanced quantitative and qualitative features.

The progressive dwindling of fossil resources coupled with the drastic increase in oil prices has sparked an intense activity in search of alternatives based on renewable resources for the production of energy. Given the predominance of petroleum- and carbon-based chemistry for the manufacture of organic chemical commodities, a similar preoccupation has recently generated numerous initiatives aimed at replacing these fossil sources with renewable counterparts. In particular, major efforts are being conducted in the field of polymer science and technology to prepare macromolecular materials based on renewable resources. Monomers such as terpenes and furans, oligomers like rosin and tannins, and polymers ranging from cellulose to proteins and including macromolecules synthesized by microbes are discussed herein with the purpose of showing the extraordinary variety of materials that can be prepared from their intelligent exploitation. Particular emphasis has been placed on recent advances and imminent perspectives, given the constantly growing interest that this area is experiencing in both the scientific and technological realms.

1.2.1 Wood

Wood, the most abundant plant source constitutes the paradigm of a composite material. It displays on the one hand, a basic universal qualitative composition in terms of its major constituents (cellulose, lignin, hemicelluloses and polyphenols) and on the other hand, species-specific components which can be polymeric like poly-isoprene (natural rubber) and suberin, or small molecules like terpenes, steroids, etc.

Cellulose dominates the wood composition although its proportion with respect to the other main components can vary appreciably from species to species. Conversely, polyphenols are the least abundant components and moreover, can exhibit quite different structures. As for lignins and hemicelluloses, their relative abundance and their detailed structures are essentially determined by the wood family: softwoods are richer in lignins whereas hardwoods are richer in hemicelluloses. These three basic polymeric components represent fundamental sources of interesting materials.[3]

1.2.1.1 Cellulose

Cellulose is the most abundant biopolymer on the earth with an estimated output of over 10^{11} tons per year and historically the most thoroughly exploited natural polymer and still provides

new stimulating avenues for exploration in materials science and technology.[3,5,6]

Cellulose is predominantly produced by plants and to a smaller extent by animals and bacteria.[6] Cellulose can also be produced by chemical and enzymatic modifications. Cellulose fibres have been used for centuries in traditional industries such as papermaking[7] and textile.[3] The interest of cellulose as a source of novel materials is reflected through, (i) the chemical bulk modification for the preparation of original macromolecular derivatives with specific functional properties;[8] (ii) the surface modification of cellulose fibres in view of their use as reinforcing elements in composite materials and as high-tech components;[9] (iii) the processing and characterization of these composites, including the use of nano-fibres[10] and (iv) the technology and applications associated with bacterial cellulose.[3] However, the use of cellulose fibres in materials science has recently gained considerable attention because of three potential advantages they possess, namely: (i) biorenewable character, (ii) ubiquitous availability in a variety of forms, and (iii) low cost. A recent addition to these numerous realms has concerned their surface modification aimed at extending their use to such novel fields as (i) reinforcing elements in macromolecular composite materials, replacing glass fibres; (ii) pollutant traps for organic molecules in a water medium; (iii) metal-coated and magnetically active materials for microwave technologies, (iv) conducting and photo-luminescent materials for electronic and optoelectronic devices, etc.[11,12]

The driving force related to the use of cellulose fibres in these new fields of applications resides additionally in the ease with which they can be recycled at the end of their life cycle, whether through their actual re-employment or through combustion (energy recovery). Finally, cellulose fibres possess additional advantages like low density and modest abrasive impact.

There is a growing trend to use lignocellulosic fibres in applications for which synthetic fibres were traditionally employed which is ascribed to their numerous well-known advantages.[13] The present applications of natural fibre filled composites are in the field of energy and impact absorption such as car fenders and bicycle helmets.[3] They also include markets that target cheaper, renewable and non-recyclable or biodegradable materials such as packaging and structural elements. Other uses of natural fibre-based composites are deck surface boards, picnic tables, industrial flooring, etc. In cars, about 10–15 kg of these composites typically made up of 50 percent natural fibres and 50 percent polypropylene along with other additives are presently being used. Examples are door panels, roof headliners, seat backs, rear decks and trunkliners.[3]

1.2.1.2 Lignins

Lignin is one of the most predominant biopolymers present in plants exceeded only by cellulose.[14] The idea of using these lignin fragments as macromonomers for the synthesis of polymers by introducing them into formaldehyde-based wood resins or by exploiting their ubiquitous aliphatic and phenolic hydroxyl groups began to be explored only in the last quarter of the twentieth century.[3] Given the fact that these industrial oligomers are produced in colossal

amounts, it seems reasonable to envisage that a small proportion could be isolated for the purpose of producing new polymers without affecting their basic use as fuel. Additionally, novel papermaking technologies like the organosolv processes and biomass refinery approaches like steam explosion provide lignin fragments without the need of their use as a source of energy and with more accessible structures in terms of lower molecular weights and higher solubility. Therefore, lignin macromonomers represent today a particularly promising source of novel materials based on renewable resources.[14]

1.2.1.3 Hemicellulose

Hemicelluloses are the second most abundant polysaccharides in nature after cellulose. Hemicelluloses are used as emulsifiers, stabilizers and binders in the food, pharmaceutical and cosmetic industries.[15] Pectin, one of the components present in hemicellulose is widely used in the food industry as a gelling agent to impart a gelled texture to foods, mainly fruit-based foods such as jams and jellies.[16] There are several other uses of hemicelluloses. To name a few, in food industry, in clinical uses such as cell encapsulation, drug delivery, tissue engineering, engineer bones, in cosmetic industry, etc.[17,18]

1.2.1.4 Natural rubber

Turning now to more species-specific components, natural rubber is certainly one of the most important representatives.[19] Different tropical trees produce different forms of poly(1,4-isoprene), which are exuded or extracted as an aqueous emulsion (latex) or as a sap-like dispersion before coagulation. The *cis* -form of the polymer tends to be amorphous and has a glass transition temperature of about ~70°C which makes it ideally suitable for application as elastomers. It's world production in 2004 was estimated at about 8 million tons. The *trans* –form, called *gutta percha* or balata, readily crystallizes forming rigid materials melting at about 70°C.[19]

The use of rubber is widespread ranging from household to industrial products entering the production stream at the intermediate stage or as final products. Tyres and tubes are the largest consumers of rubber accounting for around 56% total consumption in 2005. The remaining 44% are taken up by the general rubber goods (GRG) sector which includes all products except tyres and tubes. Other significant uses of rubber are door and window profiles, hoses, belts, matting, flooring and dampeners (anti-vibration mounts) for the automotive industry in what is known as the "under the bonnet" products. Significant tonnage of rubber is used as adhesives in many manufacturing industries and products although the two most noticeable are the paper and carpet industry.[20,21]

1.2.1.5 Suberin

Suberin, an ubiquitous component of the outer bark cell walls of higher plants represents typically 20−50% of extractive-free outer bark weight but is also present in some of their other organs like the roots.[15] The structure of this macromolecule has been thoroughly investigated.[15,22,23] Structurally, suberin is composed of aromatic domains and is roughly similar in the structure to

lignins. For a polymer chemist, these structures are particularly interesting and their isolation by ester cleavage has provided a detailed map of their specific abundance in terms of chain length and nature, number, and position of their polar groups.

Little has been published on the use of the suberin depolymerization products as monomers for the synthesis of novel macromolecular materials which has so far concentrated on polyurethanes and polyesters using the mixture of aliphatic monomers.[24,25] Undoubtedly, the predominance of long aliphatic moieties in suberin points to applications of the corresponding polymers associated with a relative softness and a highly hydrophobic character.

1.2.1.6 Tannins

Tannins are natural phenolic structures present in numerous wood species; particularly in the southern hemisphere.[3] They are mostly located in their barks although in some instances they are found in the wood itself.[26] Their traditional use in leather manufacturing has been extended to other applications of which the only relevant example in the present context is the formulation of adhesives and more specifically wood adhesives a domain which is steadily gaining importance because of its ecological relevance.[26,27] Tannins are oligomeric compounds characterized by sequences of units bearing two or more OH groups per aromatic moiety as exemplified by the polyflavonoid structures.[28]

Extensive research particularly by Pizzi[29] has optimized formulations for wood adhesives in which tannins together with appropriate cross-linking agents provide materials displaying properties comparable to those of conventional phenol- and urea-formaldehyde counterparts. Given the worldwide massive requirements related to wood adhesives the progressive replacement of the traditional resins by those incorporating tannins and perhaps also starch seems a realistic and welcome feature of the near future. Tannins are well-known to have antimicrobial properties.[30] Additionally, the use of tannins in other pharmaceutical and medical applications have been reported particularly concerning their anti-tumor and anticancer activity.[30]

1.2.1.7 Wood resins

Nature produces a number of monomers which have been a long-time source of useful "resins". Terpenes and rosin (a mixture of unsaturated polycyclic carboxylic acids, of which abietic acid is the major representative) dominates this sector.[31]

The major applications of these wood resins include paper sizing,[32] as polymer latex stabilizers and surfactants,[33] as an adhesive tack,[34] printing inks,[35] and in pharmaceutical and agrochemicals industry.[36,37] Terpenes constitute the logical precursors to polyterpenic materials destined for bulk applications.[38] In recent years, some monoterpenes have attracted some interest as an environment-friendly solvent for polymeric systems.[39] Camphene, which is both harmless and readily sublimed, has been tested as solvent for polypropylene.[39] Limonene was tested as a solvent for recycling polystyrene as well as a renewable polymerization solvent and chain transfer agent in

ring-opening metathesis polymerizations.[40] Finally, poly(αPIN) was used in the nonisothermal crystallization of isotactic polypropylene from blends containing up to 30 percent of this polyterpene.[41]

1.2.2 Plants and crops

The relevant contribution of plants and crops to the realm of polymer synthesis and applications stems instead from some specific products namely starch as a polymer, vegetable oils as triglyceride oligomers and hemicelluloses and monosaccharides as potential monomers or precursors to furan derivatives.

1.2.2.1 Starch

Starch is an extremely abundant edible polysaccharide present in a wide variety of tubers and cereal grains.[3] In most of its manifestations, it is composed of two macromolecules bearing the same structural units 1,4-*D*-glucopyranose in linear (amylase) and highly branched architectures (amylopectin) present in different proportions according to the species that produces it.[42]

Starch is certainly one of the most versatile materials for potential uses in polymer technology.[42] It can be converted on the one hand into chemicals like ethanol, acetone and organic acids which are used in the production of synthetic polymers and on the other hand, it can produce biopolymer through fermentative processes or be hydrolyzed and employed as a monomer or oligomer.[42,43] Finally, it can be grafted with a variety of reagents to produce new polymeric materials used as such or as fillers for other polymers.[44]

1.2.2.2 Vegetable oils

As a general rule, the chemical composition of oils arises from the esterification of glycerol with three fatty acid molecules, as shown in **Figure 1.1**.[45]

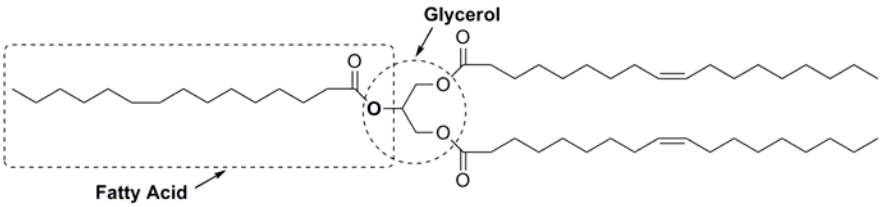


Figure 1.1 The basic structure of natural triglycerides

A vegetable oil is made up of a mixture of triglycerides bearing different fatty acid residues. The chain length of these fatty acids can vary from 14 to 22 carbons and contain 0–5 double bonds (DB) situated at different positions along the chain and in conjugated or unconjugated sequences. **Table 1.1** lists distribution of fatty acids present in commonly available vegetable oils. It should be noted that there are also exotic oils composed of fatty acids with other types of functionalities such as hydroxyl, epoxy, and furanoid groups.[3]

Table 1.1 Main fatty acids contents in different oils

Oils	Fatty Acid					Average number of DB[a] per riglyceride
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
Canola	4.1	1.8	60.9	21.0	8.8	3.9
Corn	10.9	2.0	25.4	59.6	1.2	4.5
Cottonseed	21.6	2.6	18.6	54.4	0.7	3.9
Linseed	5.5	3.5	19.1	15.3	56.6	6.6
Olive	13.7	2.5	71.1	10.0	0.6	2.8
Soybean	11.0	4.0	23.4	53.3	7.8	4.6
Tung	-	4.0	8.0	4.0	-	7.5
Castor	1.5	0.5	5.0	4.0	0.5	3.0
Palm	39	5	45	9	-	-
Oiticica	6	4	8	8	-	-
Rapeseed	4	2	56	26	10	-
Refined Tall	4	3	46	35	12	-
Sunflower	6	4	42	47	1	-

a : double bonds

The traditional uses of vegetable oils (triglycerides bearing a large variety of fatty acid moieties) in paints and inks[46] both as macromonomers in the preparation of alkyd resins[47] and as natural diluents[48] represent standard industrial practices which only undergo periodical upgrading of minor chemical or polymer relevance. The same goes for the mechanism of their oxidative polymerization associated with the interaction of the unsaturations borne by their aliphatic chains with atmospheric oxygen.

Soybean, corn, tung, linseed, castor oil and cashew nut shell liquid (CNSL) are the most common renewable resources used as precursors for the synthesis of oil-based polymers.[3,49] The more stimulating facet of this field is the search for new applications of vegetable oils based on their preliminary chemical modifications aimed at enhancing their specific reactivity in a given type of polymerization process.

Two distinct sites in triglycerides available for chemical modification are (i) the ubiquitous ester moieties which can be readily hydrolyzed or transesterified and if required can be submitted for further transformations[50] and (ii) the possible presence of one or several reactive functional groups along the aliphatic chains the most frequent of which are C=C unsaturations and OH groups.[51,52]

The exploitation of the first approach usually produces the single aliphatic strands with a terminal reactive site unless incomplete modification is preferred in such case one or two OH groups are generated on the glyceric residue. Of course, these processes resemble closely to those associated with the production of "biodiesel" but here the pressing need is to achieve original structures capable of responding adequately to polymerization stimuli.

The second approach is much more versatile in that the unsaturations and/or OH groups are open to a wide variety of rather straightforward modifications, e.g., oxidation to oxiranes but ultimately most of them converge into the formation of hydroxyls which can be exploited as such or turned into other reactive moieties such as polymerizable acrylic or styrenic functions. The most

advanced research and development efforts in this context which in fact have already attained industrial status like Cargill BiOH based on soybean oil (whose triglycerides contain an average of about five unsaturations per molecule) are related to the preparation of polyols for polyurethane production.

A recent investigation in Grenoble[53] is concentrated on appending acrylic moieties onto epoxidized soybean oil and attaining average degree of substitution (DS) as high as eight groups per triglyceride. Already with a DS of about 5, these modified oils displayed an excellent photoreactivity in the presence of conventional photoinitiators suggesting that they can replace adequately the petroleum-based acrylic varnishes currently utilized in fast UV-coating processes. Recent contributions in this area include the work at Domb's laboratory on biodegradable polymers based on fatty acids[54] and the use of vegetable oils as precursors for the preparation of polyurethanes.[55]

There is no doubt that the use of vegetable oils as a source of original polymers will increase progressively in the near future both in quantity and in the variety of novel macromonomers, and this will not constitute a problem with respect to the changes in the global agricultural strategy because contrary to what is being perceived with the much more massive biofuel domain the needs of raw materials will always be very modest relative to the essential food and feed requirements.[56,106]

1.2.2.3 Glycerol

The main secondary product of triglyceride mainly derived from vegetable oils is glycerol.[57] The spectacular rise in glycerol production is associated with the booming biodiesel industry which has resulted in rapid drop in its price down to $0.05/pound. The low low cost of glycerol has accelerated scientific and technological research aimed at multiplying its uses and production of its new derivatives such as diols, diacids, oxiranes, acrylic acid, acrolein, and lactic acid.[58-60] The production of such new derivatives has opened novel perspective of preparing polymers from this renewable resource material. DuPont's Sorona-poly(trimethylene terephthalate)- is among the first industrial materials in which 1,3-propanediol made from glycerol constitutes one of the two starting monomers.[56,61]

The use of glycerol derived from vegetable oils as a starting material in the manufacturing of surfactants represents a convenient strategy for the development of surface-active products.[3] Glycerol itself is not suitable as a primary constituent of the hydrophilic part of the surfactants and polyglycerols are needed to increase the hydrophilicity and to adjust the hydrophilic–hydrophobic balance (HLB) of the products. Fatty acid esters of these polyols called polyglycerol esters (PGE) have been developed leading to the applications in the cosmetic or food emulsifiers. Polyglycerols have been known since the beginning of the 20th century. However, due to the difficulties encountered for the industrial development of high-purity products it is only in the last decade that their uses increased. Solvay is the world-leader in the production of high purity polyglycerols and

manufactures diglycerol a distilled product of 90 percent minimum purity and polyglycerol-3 a grade with a narrow oligomer distribution typically containing a minimum 80 percent of di-, tri-, and tetraglycerol. As a result of their multifunctional properties and harmless nature, PGE's are used in many applications in food and cosmetic industries. They notably function as emulsifiers, dispersants, thickeners, solubilizers and spreading agents. More recently, new industrial applications based on PGEs have been developed. This includes their utilization as antifogging and antistatic additives, lubricants and plasticizers.[59,62-64]

1.2.2.4 Mono- and di-saccharides

Mono- and di-saccharides are produced by different annual plants and interest in using them as precursors for novel material synthesis has increased considerably in recent years. Their applications include (i) conversion of the fructose to hydroxymethyl furfural,[65] (ii) synthesis of poly-condensed materials using sugars as co-monomers,[66] and (iii) preparation of surfactants.[67] The use of sugars as monomers represents an interesting challenge which is being pursued very elegantly and thoroughly.[68] The application of some of these polymers as biomaterials into more conventional domains is debatable mostly because of economic constraints related to the exotic character of both the monomers and their polymerization processes. Sugars, as well as their natural oligomers and polymers also play a fundamental role as precursors to other monomers namely furan derivatives and lactic acid.[3]

1.2.2.4.1 Furans

Hemicellulose is dominantly present in virtually all lignocellulosic materials associated with annual plants and some of their products such as xylan (polysaccharide based on C_5 glycosidic units). The acid-catalyzed depolymerization and dehydration of these residues of agricultural or forestry activities available ubiquitously albeit from different species (sugar cane bagasse, corn cobs, rice hulls, etc.) to produce furfural has been an industrial process for nearly a century and has reached a yearly worldwide output of ~300,000 tons. Some 85% of this chemical commodity whose market price is currently around $1 per kilogram is converted into furfuryl alcohol which is a precursor to different type of resins and carbonaceous materials.[69] Furan-based fine chemicals and synthons for pharmaceuticals and other molecules represent the second most important outlet of furfural.[70,71] C_6 sugars and polysaccharides can be converted into hydroxy-methylfurfural following the same type of process as for furfural and its industrial implementation will be a reality very soon following recent progress in its optimization.[72,73]

Furfural and hydroxymethylfurfural are the two first-generation furan derivatives obtained directly from renewable resources and they represent the starting points of an ambitious strategy[74,75] that consists of (i) exploring their conversion into polymerizable structures, i.e., monomers for chain and step reactions simulating the well-known petroleum-derived aliphatic and aromatic counterparts, (ii) studying those polymerization processes and establishing their similarities and differences with

respect to standard systems, and (iii) characterizing the structure and properties of the ensuing furan polymers and copolymers and assessing their interest, viability, and/or competitiveness as macromolecular materials.

Some of these polymers do represent promising and sometimes better alternatives to existing fossil-based materials like, (i) the mixed furanic-aromatic polyamide which has properties comparable to those of Kevlar, (ii) polyurethanes with thermoplastic elastomeric properties, coupled with a tendency to graphitize upon pyrolysis, and (iii) the conjugated polymers and oligomers which display good electronic conductivity when doped, photo- and electroluminescence and whose dimer appended on diverse polymer chains displays an efficient photo-cross-linking ability.[75]

An additional area of polymer science and technology in which furans can provide a substantial contribution is related to the specific chemical properties of this heterocycle. One of them is the propensity and regioselectivity of the 2-substituted furan ring to undergo electrophilic substitution at its C_5 position which was exploited to prepare end-functionalized poly(isobutene) and its block copolymers by cationic polymerization in the presence of a suitable furan derivative.[3,74,75]

1.2.2.4.2 Lactic acid

One of the outstanding achievements in the realm of polymers from renewable resources is undoubtedly the rapid progress related to the research and development activities for the production of poly(lactic acid) (PLA) or polylactide.[76,77] This ongoing scenario is too familiar and well documented to require any extensive coverage here but it is important to emphasize its most important aspect which has to do with the practical relevance of this polymer. PLA has been an industrial commodity with important applications particularly in packaging and fiber technology, which has reached a global capacity exceeding 250,000 tons per year with a steadily declining price.[77] Starch is the precursor for the lactide monomers and it can be available from a variety of sources.[3] PLA is accompanied by adequate mechanical and thermal properties.[77-79] PLA represents the very paradigm of the renewable polymer of the future in that it fits perfectly within the biomass refinery concept, green chemistry postulates, and is biodegradable.

1.2.3 Animal resources

1.2.3.1 Chitin and chitosan

Chitin is undoubtedly the most abundant animal derived polysaccharide on earth.[80] Chitin is a regular linear polymer whose structure differs from cellulose by the presence of *N* -methylamide moieties instead of the hydroxyl groups at C_2. Given the susceptibility of this function to hydrolysis, chitin often bears a small fraction of monomer units in the form of primary amino groups resulting from that chemical modification.

Chitin is sparingly soluble even in very polar solvents, because of its high cohesive energy associated with strong intermolecular hydrogen bonds (NH-CO) which is also the cause of its lack

of melting because the temperature at which this phase change occurs is higher than that of the onset of its chemical degradation just like with cellulose.[3] It follows that the potential uses of chitin are strongly limited by these obstacles during their processing. The possibility of exploiting chitin is therefore dependent on its transformation into deacetylated derivatives through hydrolysis. As the amide functionality of chitin is converted into primary amino groups it progressively becomes more soluble in weak aqueous acids or polar protic solvents.[81]

The derivative of chitin in which at least 50% of amide functionality is fully hydrolyzed to amine is named as chitosan.[81] Chitosan has become one of the most attractive polymers derived from renewable resources because it possesses remarkable properties which find applications in many areas of material science and technology particularly related to biomaterials and medical aids. The interest in these polysaccharides as materials is relatively recent compared with the age-old exploitation of cellulose and starch. The insolubility of chitin in commonly available solvents is the principal reason for this delayed attention despite its abundance in both the animal and fungal kingdoms and it was only when its transformation into chitosan received close scrutiny that these precious renewable resources began to show their remarkable potential. Chitosan can readily be spun into fibers cast into films or precipitated in a variety of micromorphologies from its acidic aqueous solutions. The major applications of chitosan are in biomaterials, pharmaceuticals, cosmetics, metal ion sequestration, agriculture, and foodstuff treatment.[82,83]

1.2.3.2 Proteins

Because of their highly polar and reactive macromolecular structure proteins have attracted much attention in the last few decades as possible sources of novel polymeric materials.[84,85] A particularly interesting natural protein material is undoubtedly the spider dragline silk because of its extraordinary mechanical properties.[3] Given the obvious difficulties related to gathering viable amounts of this biopolymer much research is being devoted to its bioengineering production. Soy protein, zein, gluten, rapeseed protein, casein, and collagen are currently being investigated to prepare edible and non-edible films. These also find applications in adhesives, plastics, blends and composite materials.[86]

1.2.4 Bacterial polymers

Cellulose and poly(hydroxyalkanoate)s (PHAs) are macromolecules synthesized by bacteria and can be used as polymeric materials.[56] For reasons that are not always easy to rationalize and that are not the same for both neither of these bio-derived polymers has yet attained a commodity status on the market.

1.2.4.1 Bacterial cellulose

At regular intervals for the past two decades, bacterial cellulose has been heralded as the marvel polysaccharide by various specialists in such different domains as biomedical

applications,[56,87,88] papermaking, nanocomposites,[89] electronic and acoustic devices, and foodstuffs.[56,88,89]

1.2.4.2 Poly(hydroxyalkanoate)s

Polyhydroxyalkanoates (PHAs) represent an important group of biodegradable plastics. The simplest PHA is polyhydroxybutyrate (PHB). This polymer and its copolymer with polyhydroxyvalerate seem to be at present the only PHAs relevant for practical applications.[90]

PHB can be characterized as a rather controversial polymer. It is produced from renewable resources *via* a classical biotechnological process.[91] The polymer is completely biodegradable, highly hydrophobic and thermoplastic, with high crystallinity, high melting temperature, good resistance to organic solvents and possesses excellent mechanical strength and modulus, resembling that of polypropylene. In spite of these excellent properties especially the strength parameters the application of the polymer is limited to small volumes and for rather special purposes. High volume applications are hindered by several serious drawbacks especially pronounced brittleness, very low deformability, high susceptibility to a rapid thermal degradation, difficult processing by conventional thermoplastic technologies (mainly due to fast thermal degradation) and rather high price compared to other high volume plastics. Additional problems related to processing are connected mainly with low shear strength of the melt which needs to be addressed when considering certain applications. Its copolymer with valerate (PHBV) is much more acceptable, especially regarding improved toughness with an acceptable loss of strength and modulus.[3,56, 92,93]

However, until now the production process of PHBV has been more demanding and hence its price is even higher than that of PHB. In spite of this, PHAs are considered to be promising materials worthy of being broadly investigated and are being produced on a large scale in several regions of the world.

1.2.5 Cashew Nut Shell Liquid (CNSL)

Among vegetable oils (oleochemicals), cashew nut shell liquid is one of the major sources of naturally occurring phenols. Cashew nut shell liquid (CNSL)[94] is a by-product of the cashew industry. CNSL occurs as a greenish-yellow viscous liquid in the soft honeycomb of the shell of the cashew. Cashew tree (*Anacardium accidentale Linn*), originally from Brazil is now being grown extensively in India, Bangladesh, Tanzania, Kenya, Mozambique, tropical regains of Africa, and South-East and Far-East Asia.

1.2.5.1 Composition

The earliest work published concerning composition of CNSL was by Staedeler.[95] Since then; many researchers have investigated the composition of the oil.[96] Naturally occurring CNSL contains mainly four components: Cardanol, cardol, anacardic acid and 6-methyl cardol.

Commercial grade CNSL contains hardly any anacardic acid because of the decarboxylation

during the roasting process which converts anacardic acid to cardanol.[97,98] The components of CNSL are themselves mixtures of four constituents differing in side chain unsaturation, namely, saturated, monoene, diene and triene. CNSL is extracted by employing a variety of methods. The popular methods currently employed are, hot oil bath method, roasting method, heating by super-heated steam, and extraction of the oil by solvents. Crude CNSL is refined chemically to get it free from sulfides, nitrogenous materials and minerals.[97,98]

1.2.5.2 Chemistry

The chemical structure of CNSL is such that it can take part in a variety of reactions.[97,98] Broadly, CNSL is a phenol with an unsaturated carbon chain attached-that is of interest to chemists. While the unsaturation present in the C_{15} side chain offers chemistry as in linseed or soybean oils, on the other hand, aromatic structure and hydroxyl group allows chemists to do traditional phenolic chemistry.

There is a wide array of data published on CNSL and it's chemistry.[97,99,100] Cardanol can undergo a range of electrophilic aromatic substitution reactions such as sulfonation, nitration, halogenation, etc. leading to important precursors to fine chemicals. CNSL can be polymerized by a variety of techniques. The presence of aliphatic side-chain gives these resins pronounced hydrophobicity.[97] The unsaturation in the side-chain can be the basis for addition polymerization using free radicals or ionic initiators.[101] The polymer of CNSL is rubber-like and has low susceptibility to oxidation.

The phenolic nature of CNSL makes it suitable as a starting material for condensation polymers by reaction with formaldehyde, furfural, HMTA, etc.[97]

Pillai and co-workers have investigated the phosphorylation of cardanol and the prospective applications of the products.[102] Urethanes have been synthesized from CNSL. Acetals of CNSL have been prepared by the reaction of dimethyl acetal or polymeric acetals. Acetals of CNSL resin have advantages such as better electrical properties due to the total absence of water, ease of processing because of the non-volatile nature of the reactants and less dermatic effect on the skin.[97]

Isocyanates have been prepared from hydrogenated cardanol by reaction with SO_2Cl_2 followed by nitration, methylation and reduction. Azo dyes are made by the reaction of phenols with primary aromatic amines after diazotization of hydrogenated cardanol. By reacting CNSL with triethylene-tetramine, phenolic polyamines can be prepared. Benzotriazole derivatives were prepared from hydrogenated cardanol by diazotizing with aromatic amines followed by reduction. Styrenation of CNSL resin can be done by reacting styrene with CNSL hexamine condensate.[97]

1.2.5.3 Applications

Polymers derived from CNSL have certain outstanding properties which make them unique for many applications.[97,103-105] The most attractive aspect of CNSL is the abundant availability and low cost starting material. The polymer shows flexibility due to internal plasticization resulting from

the presence of a long side-chain. The long pentadecyl chain also imparts hydrophobic character to the material. It has low fade characteristics, which makes it desirable component in brake linings formulations. CNSL has inherent anti-microbial and anti-termite properties. It is compatible with a wide variety of polymers such as alkyds, melamines, polyesters, etc.[97,104] It's excellent solubility in number of common organic solvents makes it an ideal choice for a large number of surface-coating applications such as paints and primers, specialty coatings, varnishes, lacquers, etc.[97] The high polarity and inherent tackiness allows CNSL to be used as a material in adhesive formulation. The fire-retardant and ablative properties associated with CNSL facilitate its use in foundry industry.[97]

There have been a number of reviews on the applications of CNSL-based materials.[97,105] Considerable attention from polymer scientists throughout the world is devoted to utilize potential attributes of CNSL as a substitute for petrochemical derivatives and has found use in many areas. In **Chapter 3**, we have attempted to include most of the available reports on CNSL from chemicals, additives, monomer and polymer point of view.

The subsequent sections deal with developments in the chemistry of high performance/ high temperature polymers that have led to improvements in processability characteristics. The main focus of these discussions is on polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(etherketone)s and poly(ethersulfone)s.

1.3 Polyazomethines

Polyazomethines (PAZs) or polyimines (PI's) are a class of polymers containing CH=N linkages in the backbone. The CH=N linkage in polyazomethines is isoelectronic with C=C group in poly(*p*-phenylene vinylene)s and, therefore, finds applications in opto-electronics.[107-113]

The first polymer of this class was synthesized by Adams et al. by polycondensation reaction between terephthaldehyde and benzidine.[114] In 1938, Steinkopf and Eger reported the reaction of hydrazine with terephthaldehyde or isophthaldehyde in the molten state and obtained an insoluble and infusible product.[115] Marvel and Hill in 1950 also tried the synthesis of PAZ's by solution polycondensation of aromatic dialdehydes with *o*-phenylenediamine or hydrazine and obtained low molecular weight products due to their insolubility in the reaction medium.[116] However, PAZs became to be the subject of a systematic research beginning with D'Alelio's pioneering work as a result of the strong interest in thermally stable polymers for aircraft applications.[109,110,117,118]

The presence of nitrogen in the main chain also connects PAZs to other heteroatom containing polymers, i.e., polyaniline and polypyrrole. PAZs have attracted much attention not only as high-performance fiber and film-forming polymers with remarkable thermal stability, high strength, and high modulus,[119-121] but also as particularly promising electronic materials with

semiconducting properties,[122] and ability to form chelates.[123] Also, many of these polymers can form mesophases by heating or in solution,[124] but their high melting temperatures and low solubilities make both their characterization and processing difficult. Therefore, a great deal of efforts have been expended to try to improve processability of polyazomethines.

1.3.1 Synthesis of polyazomethines

Generally, polyazomethines have been synthesized by solid state or solution polycondensation reaction of a dialdehyde and a diamine. This reaction was first described by Schiff in 1864; hence polyazomethines or imines are often referred to as Schiff bases.[125] The introduction of imine structure into a polymer chain can be realized by two ways: (i) reaction of monomers with functional groups leading to imine group formation, in the case when the reacting groups are aldehyde and amine; (ii) reaction of monomers containing preformed imine linkage and equipped with other functional groups capable of polyreactions.

Polycondensation can be performed in the melt or in solution using a suitable solvent and catalyst. Melt polycondensation[109-111] of such monomers is hard to control and gives side reactions that lead to undesirable by-products. It was ascertained that the synthesis of PAZs by solution polycondensation using methanol, ethanol, or water, in the presence of a Lewis acid, leads to low yields because of the equilibrium installed. Therefore, other solvents such as benzene and toluene were used, which allow the removal of water formed in the polycondensation reaction by azeotropic distillation. Azeotropic distillation of water accelerates the condensation reaction and enhances the yields, but it does not significantly increase the degree of polycondensation. An explanation is that PAZs precipitate out of the solution during the polycondensation reaction because of the low solubility of the polymers having a rigid backbone chain structure in the reaction media. Better results are obtained when polar aprotic solvents, such as THF, DMAC, DMF, NMP, DMSO or HMPA or protic solvents, such as *m*-cresol or *p*-chlorophenol are used because the polymers are more soluble in these polar solvents.[109-111] Calcium chloride or lithium chloride can be added to the polycondensation system to obtain higher molecular weight polymers. These salts are used to improve the solubility of the growing macromolecular chain in the polycondensation system and to maintain it in solution until the higher polycondensation degree is obtained. Moreover, $CaCl_2$ is also used as a dehydrating agent so that the eliminated water in the reaction is absorbed; thus, the resulting equilibrium favors the formation of the polymer. Another dehydrating agent that can be employed is P_2O_5.

The polycondensation can be performed in the absence or presence of catalysts. Usually, small quantities of acids; HCl, H_2SO_4, CH_3COOH, CF_3COOH, *p*-toluene sulfonic acid, or salts, such as $ZnCl_2$ can be used, but in the last case the salt may leave traces, which could act as a dopant. The viscosity and molecular weight data reported so far suggest that the number-average molecular weights (M_n) of the most aromatic PAZs prepared by solution polycondensation are in the range of

500-2000 g/mol. Considerably better results are obtained for their synthesis in *m*-cresol at 200°C, because the polymers remain in solution over the entire course of polycondensation, in this case M_ns within the 5000-25,000 range were obtained.[109-111]

The elementary step in the polycondensation of diamines with dicarbonyl derivatives is the nucleophilic attack of the amine group on the carbonyl bond followed by dehydration of the tetrahedral intermediate. Therefore, the rate of reaction is dependent on the diamine nucleophilicity and the electrophilicity of the carbonyl compound. As a general rule, the reactivity of diamine derivatives decreases in the same order as their basicity: hydrazine > aliphatic diamine > aromatic diamine, while in the case of carbonyl compounds the order is: dialdehyde > diketone > quinone. The condensation of aliphatic diamines with aromatic dialdehydes is a highly exothermic reaction, which proceeds rapidly in solution to high conversions, while for the polycondensation of quinones more special conditions are necessary.

The chemical vapor deposition polymerization technique was used to obtain PAZs starting from terephthaldehyde and *p*-phenylenediamine. This method is very interesting because thin films for new applications can be obtained.[109]

1.3.2 Structure-property relationship in polyazomethines

A major drawback of the linear azomethine polymers is their limited solubility in most organic solvents due to their rigid chain structure, this also being the main reason for their low molecular weight.[109-111,126] Because the growing macromolecular chain comes out of solution during the polycondensation at low polymerization degrees; high molecular weight polymers cannot be obtained.

This disadvantage is common for all organic conjugated polymers. There are some general methods used to improve solubility of PAZs, such as:

a. Insertion of flexible bonds between main chain aromatic rings.[109,127,128]
b. Introduction of pendant groups, i.e., aromatic or alkyl substituents, onto the polymer chain.[109-111,129,130]

Among the above mentioned means to improve solubility of PAZs, introduction of alkyl groups or flexible spacers in the polymer backbone helps in substantial decrease in T_g of the polymer, while on the other hand improves solubility and processability *via* internal plasticization. The representative examples of monomers to obtain organo-soluble PAZs are presented in **Table 1.2**.

Table 1.2 Representative examples of monomers to obtain organo-soluble polyazomethines

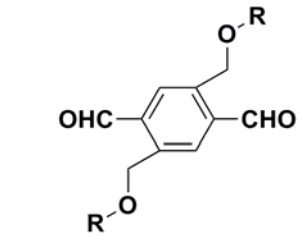
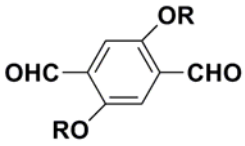
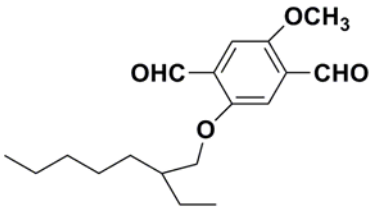
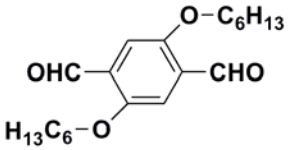
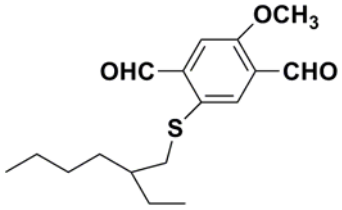
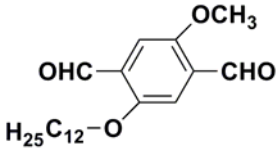
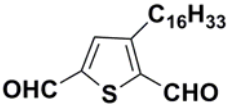
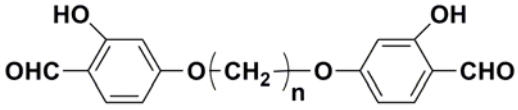
No.	Monomer	References
1.	 R = C_4H_9 , C_6H_{13} , C_8H_{17} , $C_{12}H_{25}$	131, 130
2.	 R = C_8H_{17} , $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$	133,134
3.		135
4.		136
5.		137
6.		138
7.		139
8.	 n = 2 , 6 , 10	140

Table 1.2 Continued……..

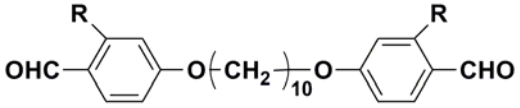
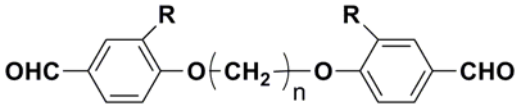
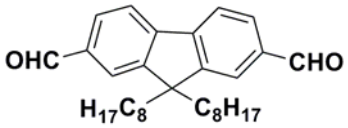
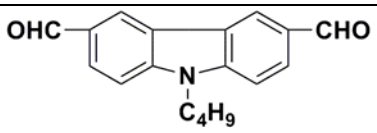
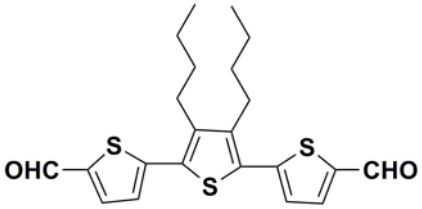
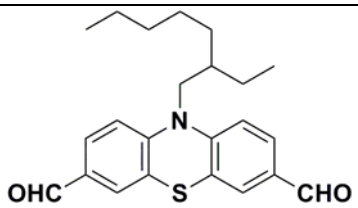
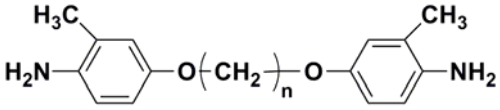
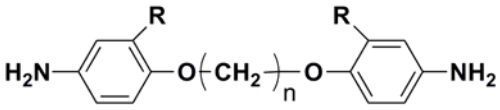
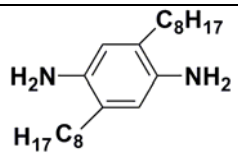
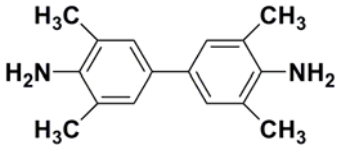
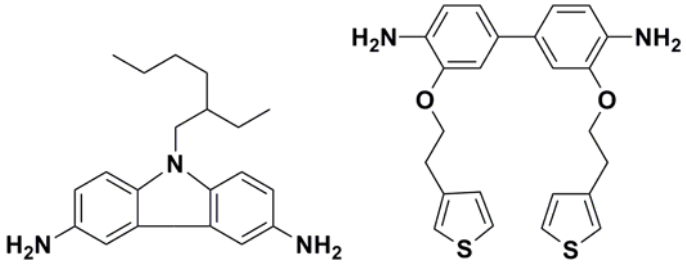
9.	 R = H or OH	141
10.	 n = 2 , 3 , 4 , 5 , 6 , 10 R = H , OCH_3 , OC_2H_5	142
11.		143
12.		133
13.		144
14.		145
14.	 n = 1-10 , 12 , 14 , 16	146
15.	 n = 6 , 12 R = H , F , Cl	147

Table 1.2 Continued……

16.		148
17.		149
18.		150

1.4 Polyamides

Polyamides are polymers with recurring amide groups (-CO-NH-) as an integral part of the main polymer chain. Polyamides occupy a prominent position among the synthetic high polymers. The first synthetic aromatic polyamide, polybenzamide, was obtained by Harbordt in 1862.[151] The first commercially produced aromatic polyamide was poly (*m*-phenyleneisophthalamide) (Nomex, Du Pont, 1967).[152,153] Some years later, efforts towards development of poly(*p*-phenylene terephthalamide) led to the commercialization of the *para* product –Kevlar (DuPont) in the early seventies.[153]

Although these products have become of great commercial importance, the fabrication of unsubstituted aromatic polyamides has in general proved to be difficult because they show tendency to decompose during, or even before melting and are insoluble in most common organic solvents.[154] There has been, therefore, an increased interest in the preparation of polyamides with different substituents or structural irregularities in order to improve their processability.

1.4.1 Synthesis of polyamides

Aromatic polyamides have been prepared by several methods.

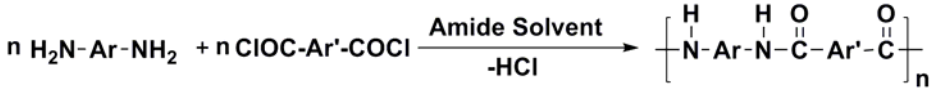
1.4.1.1 Low temperature polycondensation of diamine and diacid chloride

Low temperature polycondensation (<100°C) of diamines and diacid chlorides has been used for the preparation of high molecular weight polyamides. This method was developed by DuPont and can be carried out in solution or at the interface of two solvents.[155]

1.4.1.1.1 Solution polycondensation of diamine and diacid chloride

Solution polycondensation involves a diamine and a diacid chloride reacting in an amide

solvent such as NMP, HMPA, DMAc or tetramethylurea.



Scheme 1.1 Solution polycondensation of a diamine and a diacid chloride

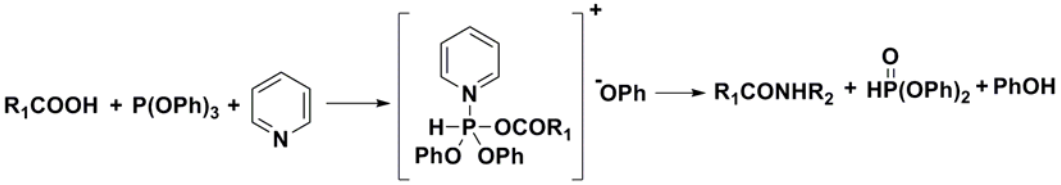
The amide solvent serves also as an acid acceptor for the hydrogen chloride produced in the reaction. Other polar aprotic solvents such as DMF and DMSO cannot be used because they react significantly with acid chlorides. The solvent should allow maximum solubility (swellability) of the polymer formed at the early stage of polycondensation, and the solvation properties of amide solvents can usually be increased by the addition of salts such as LiCl or $CaCl_2$.[156]

1.4.1.1.2 Interfacial polycondensation of diamine and diacid chloride

The so-called interfacial polycondensation method is an adaptation of the well known Schotten-Baumann reaction. In this method, two fast reacting reagents are dissolved in a pair of immiscible liquids, one of which is preferably water. The water phase generally contains the diamine and usually an inorganic base to neutralize the by-product acid. The other phase contains the acid chloride in an organic solvent such as dichloromethane, toluene or hexane. The two-phase system is stirred vigorously to obtain high molecular weight polymers. The difference between conventional step polymerization and interfacial polymerization is that in the interfacial polymerization the monomer diffusing to the interface reacts only with the end of the polymer chain resulting in high molecular weight polymer. The key factors that influence this type of polycondensation have been studied in detail by Morgan.[157] Since the temperatures needed are low, the side reactions are minimized and also the polymers, which are unstable at high temperatures, can be synthesized.

1.4.1.2 High temperature solution polycondensation of dicarboxylic acid and diamine

In the beginning of 1970's, two Japanese groups Ogata and Tanaka[158] and Yamazaki and Higashi[159] published a series of papers on the successful use of phosphorus compounds as condensing agent for the direct polycondensation of dicarboxylic acids and diamines to form polyamides. This reaction involves the formation of a complex of the acid with triphenylphosphite in NMP and pyridine, which further reacts with diamine to give the product **(Scheme 1.2)**.



Scheme 1.2 Condensation reaction involving acid and amine to form amide in the presence of triphenylphosphite

$CaCl_2$ and LiCl were used along with NMP to improve the molecular weight of polymers. The role of $CaCl_2$ and LiCl is quite complicated. They can form complexes with pyridine which are

more soluble than the salts alone and NMP with a higher content of metal salt can solubilize polyamide formed in the reaction medium more effectively leading to high molecular weight products. Several key factors can considerably influence the molecular weight of the final polymer such as: (i) concentration of monomers, (ii) ratio of triphenylphosphite to monomer, (iii) reaction temperature and time, (iv) concentration of LiCl or $CaCl_2$ and (v) solvent and amount of pyridine relative to the metal salt.

Eventually, Krigbaum et al[160] optimized the conditions successfully for synthesis of polyphenylene terephthalamide with $\eta_{inh} = 6.2$ dL/g.

1.4.1.3 Polycondensation of N-silylated diamines and diacid chlorides

While most of the efforts in the synthesis of high molecular weight polyamides have been oriented towards the activation of the diacids, there are some reports on the activation of diamine component by reacting it with trimethylsilyl chloride. Indeed, high molecular weight polyamides have been synthesized by low temperature polycondensation of an N-silylated aromatic diamine with aromatic diacid chloride.[161]

Lozano et al have reported the formation of silylated diamines *in situ* by adding trimethylchlorosilane to the diamine solution that, on addition of diacid chloride gives polyamides.[162] This method is especially useful for the preparation of polyamides from aromatic diamines having low reactivity.

1.4.1.4 Polycondensation of diisocyanates and dicarboxylic acids

Another promising route for the preparation of aromatic-aliphatic copolyimides has been developed by Simioneseu et al[163] and Onder et al[164] from a combination of aromatic diisocyanates and dicarboxylic acids. This route leads to the direct formation of polyamides with the elimination of CO_2 without the use of any condensing agents. Several polyamides and copolyimides have been prepared by this method.[165] A commercial scale preparation of aromatic polyamides from 1,3-phenylene diisocyanate and isophthalic acid in the presence of a catalyst has been reported.[166] Polyamides have also been prepared by the reaction of aromatic diisocyanates with aromatic hydrocarbons in the presence of Friedel-Crafts catalyst.[167]

1.4.1.5 Transition metal-catalyzed polycondensation of aromatic diamines, dihalides and carbon monoxide

Polyamides can also be synthesized by palladium-catalyzed carbonylative coupling of diamines and dihalides.[168,169]

1.4.2 Structure-property relationship in polyamides

Recently, there has been an increasing requirement for new processable engineering plastics having a moderately high softening temperature and solubility in organic solvents. A number of strategies were adapted to synthesize soluble/processable polyamides without significantly affecting the thermomechanical properties. Attempts have been made to increase the solubility of polyamides

by introducing flexible bonds in the polymer backbone or bulky pendant groups or alkyl chain along the main chain.[170] It has been observed that incorporation of pendant phenyl groups improved solubility, retaining thermal stability.[171,172] The incorporation of halogen atoms showed increase in T_g and it had a direct dependence on the size of the halogen.[173] Kajiyama et al[174] studied the effect of perfluoro alkyl group on the properties of polyisophthalamides. There was a decrease in T_g with increase in carbon chain length.

The representative examples of the monomers (diamines/dicarboxylic acids) having pendant bulky groups or alkyl chains for the synthesis of polyamides are given in **Table 1.3.**

Table 1.3 Representative examples of monomers containing pendant flexible/bulky groups used in the synthesis of polyamides

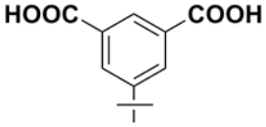
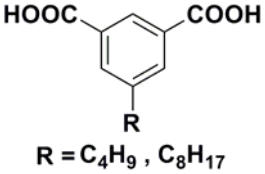
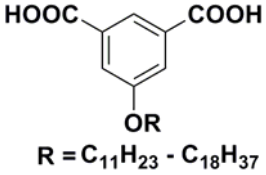
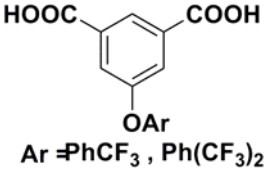
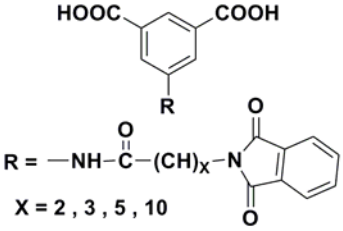
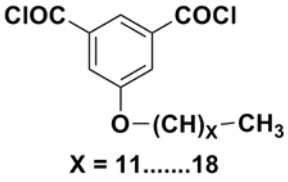
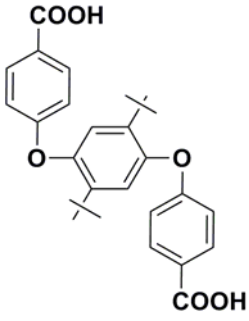
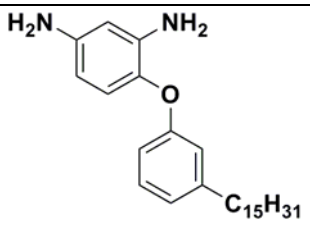
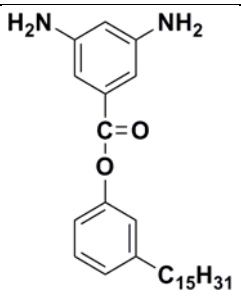
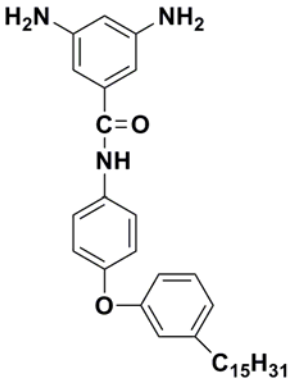
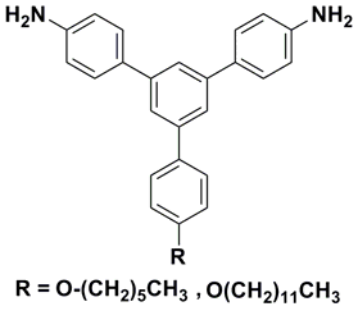
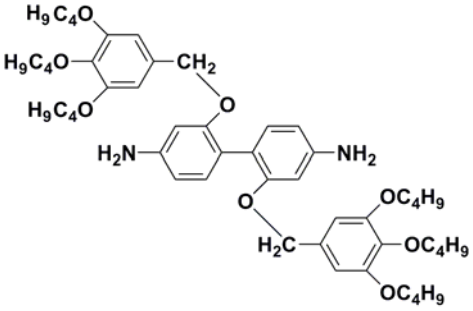
No.	Monomers	Ref	No.	Monomers	Ref
1.		175	2.		176
3.		177	4.		178
5.		179	6.		180
7.		181	8.		182

Table 1.3 Continued……..

9.		183	10.		183
11.		183	12.		184
13.					185

1.5 Poly(amideimide)s

Poly(amideimide)s are a class of polymers containing amide and heterocyclic imide unit in the polymer backbone.

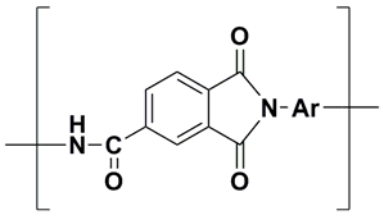


Figure 1.2 General Structure of polyamideimide

Historically, the first report concerning aromatic polyamideimide was made by DuPont in 1945. However, only in 1972 polyamideimide was successfully introduced as commercial polymeric materials (Torlon) by Amoco.[186] Since that time, an impressive variety of poly(amideimide)s have

been synthesized and reported in the literature.

Poly(amideimide)s are important, both scientifically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties, and superior chemical resistance.

1.5.1 Synthesis of poly(amideimide)s

Poly(amideimide)s can be synthesized by methods similar to those of polyimides and polyamides **(Section 1.4.1)**. They are usually synthesized through three main routes.

a) Amide-imide forming reaction,[187-189]

b) Imide forming reaction using amide containing monomers,[190]

c) Amide forming reaction using imide containing monomers.[191-194]

Apart from above mentioned routes, poly(amideimide)s can also be prepared by acid hydrazide route.[195] As very well described in a review published by Imai,[196] poly(amideimide)s can be synthesized by a polycondensation reaction involving the formation of either imide rings or amide functions. The former method usually yields rather unstable polyamic acids which have to be thermally or chemically cured to provide fully cyclized poly(amideimide)s. On the contrary, the step polymerization involving the formation of amide functions implies the use of monomers with preformed imide rings to lead to polyamideimides. Initially reported by Wrasidlo and Augl in 1969,[197] this method has been very widely used for the last thirty years mainly because it avoids handling rather unstable intermediates and the subsequent step of thermal or chemical curing according to the pioneering works in this field.[198]

The synthesis of highly pure diamine telechelic monomers with preformed imide rings being rather difficult,[199] the telechelic monomers with preformed imide rings which are the most commonly used are diacid derivatives such as anhydrides[200] or more generally dichlorides.[201] More recently, new polymerization techniques have been developed to allow a significant increase of the diamines reactivity towards less activated carbonyl groups by the use of condensing agents (triphenyl phosphite and pyridine, Higashi[202]—Yamazaki[203] method[204]) or silylating additives.[205] The former methods enable the use of diacids, thus avoiding the step of diacid derivatization prior to polycondensation. The *in-situ* synthesis of telechelic diacid chlorides from diacids with a minimal amount of thionyl choride has also been reported for the polycondensation with aromatic diamines.[206] The polycondensation with diacid chlorides usually leads to high molecular weight polymer and a very good control of the macromolecular structure, without requiring additives which could be a problem for polymer materials for membrane separation systems.

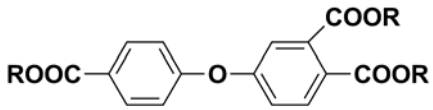
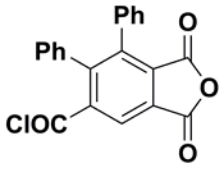
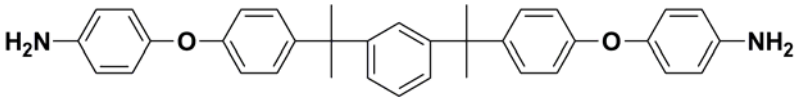
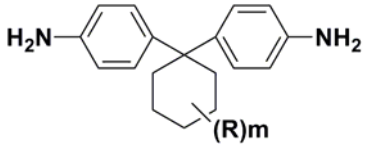
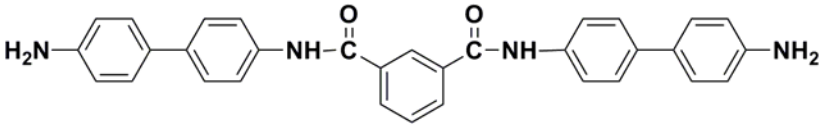
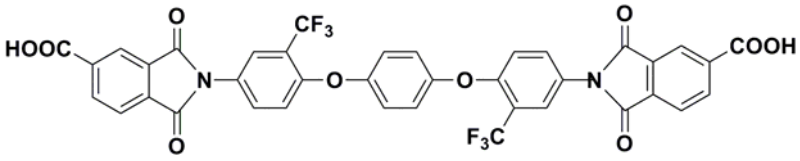
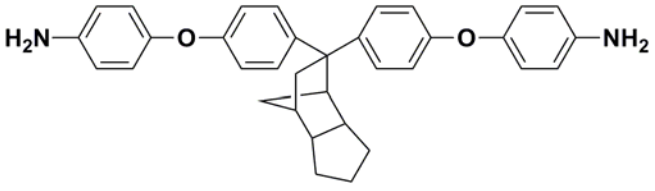
1.5.2 Structure-property relationship in poly(amideimide)s

Poly(amideimide)s, as a family, have deserved particular attention as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore, the inclusion of an amide group into the polyimide backbone increases its

processability, solubility, and moldability.[207] However, these are still difficult to process because of their high softening temperatures and poor solubility in organic solvents.[208] In order to improve their solubility, several approaches have been proposed based on the incorporation of flexible segments containing ether, ester or amide moieties in the polymer backbone without sacrificing the heat resistance.[208] To further improve processability and solubility in organic solvents of poly(amideimide)s, several approaches have been adapted.

Representative monomers which have been used for synthesis of organo-soluble poly(amideimide)s are collected in **Table 1.4.**

Table 1.4 Representative examples of monomers for synthesis of organo-soluble poly(amideimide)s

No.	Monomer	Ref
1.		209
2.		210
3.		211
4.		212
5.		213
6.		214
7.		215

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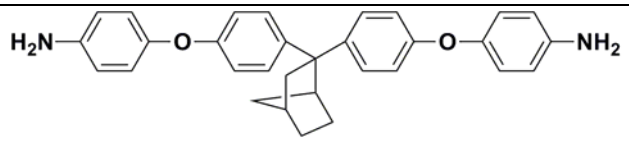
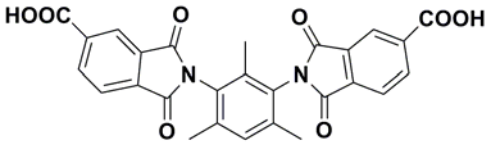
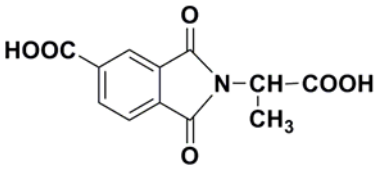
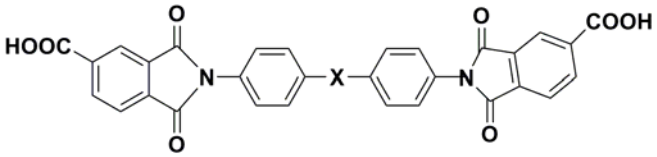
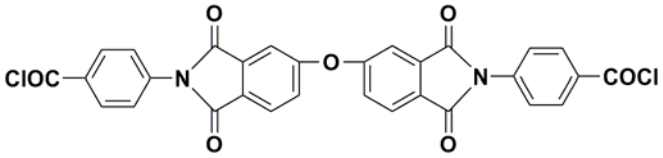
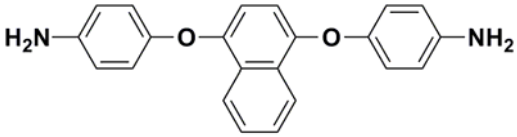
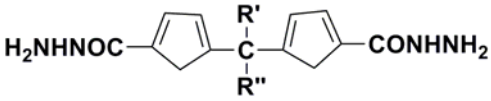
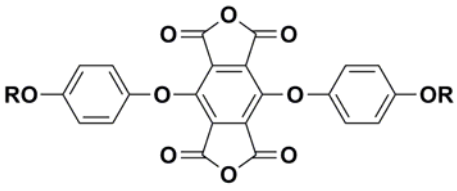
8.		216
9.		217
10.		218
11.		219
12.		220
13.		221
14.	 R'/R'' = CH_3/CH_3; CH_3/C_6H_5; CH_3/C_2H_5; CH_3/H; CH_3/C_5H_{11}; CH_3/CF_3	195
16.	 R = C_4H_9 ; C_8H_{17} ; $C_{12}H_{25}$	222

1.6 Polyhydrazides and polyoxadiazoles

Polyhydrazides have been extensively studied since they enhance dyeability of synthetic fibers, improve elasticity over other polymer types, possess fair absorption characteristics,[223] can be cyclized to give polytriazoles[224] and polyoxadiazoles[225] and provide a synthetic base for the

chelating polymers[226] since the hydrazide group (-CO-NH-NH-CO-) can make a complex with metal ions. Polyhydrazides are generally synthesized by low temperature solution polycondensation,[227] interfacial polycondensation[228] and by direct polycondensation reaction by means of di- or triphenyl phosphate.[229]

Polyoxadiazoles have been the focus of considerable attention with regard to the production of high-performance materials, particularly owing to their high thermal stability and mechanical properties along with a fruitful combination of optical and electronic properties determined by the specific structure of 1,3,4-oxadiazole ring.[230]

1.6.1 Synthesis of polyhydrazides and polyoxadiazoles

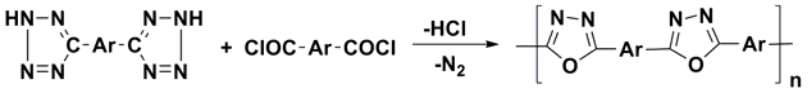
1.6.1.1 Polyhydrazides

Polyhydrazides of low molecular weight were first prepared in 1942 by the condensation of hydrazine with dicarboxylic acid.[231]

A more satisfactory procedure is to react dihydrazides of dicarboxylic acids with diacid, diester or diacid chloride monomers.[232] The high molecular weight polymers have been obtained by reacting diacid chloride with dihydrazide at low temperature in DMAC solvent[233] or by Yamazaki's phosphorylation method using dihydrazide and dicarboxylic acid using different condensing agents.[234,235]

1.6.1.2 Polyoxadiazoles

Various methods have been tried out for the synthesis of polyoxadiazoles**.** The first reported method consists of the reaction between ditetrazoles and diacid chlorides,[236] as shown in **Scheme 1.3** However, only low-molecular weight polymers were obtained which were completely insoluble in organic solvents. Further developments using tetrazole-monomers of various structures and reactivities led to polymers with improved solubility, but the molecular weight was not sufficiently high to be useful in practice.[237] Thus, this method is mostly of historical interest.



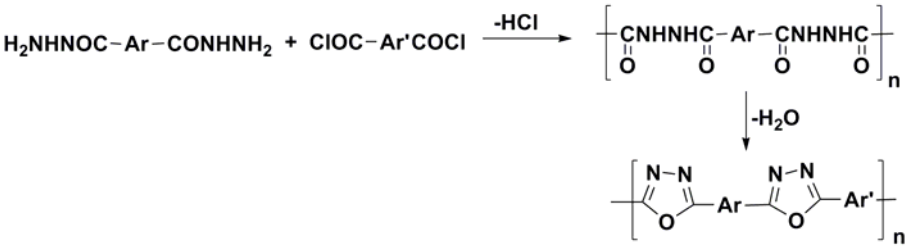
Scheme 1.3 Synthesis of polyoxadiazoles using ditetrazoles and diacid chlorides

A method reported in the mid-1960s was the polycondensation of bis(amidrazones) with diacid chlorides resulting in poly(*N*-acy1amidrazone)s that were converted into the corresponding polyoxadiazoles.[238]

The new development is the direct use of dicarboxylic acids and bis(amidrazones) in a one-step reaction which is carried out in a mixture of methanesulfonic acid and P_2O_5 as shown in **Scheme 1.4**, resulting in polyoxadiazoles,[239] However, the reduced availability of the bis(amidrazone) monomers and the low molecular weight of the resulting polymers can constitute a drawback of this procedure.

Scheme 1.4 Synthesis of polyoxadiazoles using bis(amidrazones) with diacid chlorides

A widespread route to poloxadiazoles involves the preparation of a polyhydrazide as a soluble precursor polymer by the reaction of dihydrazides of dicarboxylic acids with diacid chlorides followed by cyclization to the corresponding polyoxadiazoles by heating up to 300 ^{0}C under vacuum or by heating in dehydrating solvents, as shown in **Scheme 1.5**. This method offers the advantage of a processable intermediate polyhydrazide polymer of high molecular weight which can be cast into films or fibers. This method was first experimented with in the mid-1960s[240] and it continues to be the subject of many investigations using a wide variety of monomers and different reaction parameters.[241] Various polar aprotic solvents such as DMAC, NMP, and hexamethylphosphoramide (HMPA) have been used for the synthesis of polyhydrazides.

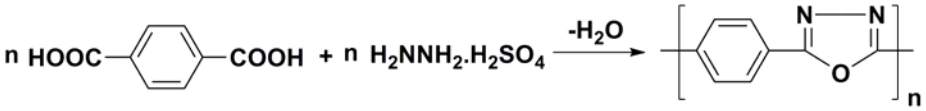


Scheme 1.5 Two step synthesis of polyoxadiazoles

The conversion of polyhydrazide films or fibers into the corresponding polyoxadiazole structures was performed by gradual heating up to 300 ^{0}C over long periods of time, i.e., up to 100 h. However, the properties of the resulting product are strongly influenced by the cyclization temperature.

The kinetics of thermal cyclodehydration of polyhydrazides has been studied and it was found that slight deviations from the expected first-order kinetics are evident after the cyclization is about 80 % complete.[224] This is reasonable in view of the fact that as the cyclization proceeds the polymer chain becomes more rigid and in the latter stages the reaction is probably diffusion limited.

Another method which is also widely used to obtain polyoxadiazoles is the one-step polycondensation of dicarboxylic acids or their derivatives (nitrile, amide, or ester) with hydrazine or hydrazine sulfate in fuming sulfuric acid (oleum)[242] or in a mixture of strong acids[243,244] as shown in **Scheme 1.6**.



Scheme 1.6 Synthesis of polyoxadiazoles using hydrazine or hydrazine sulfate

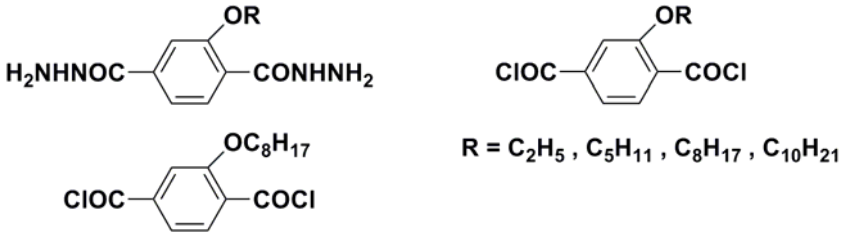
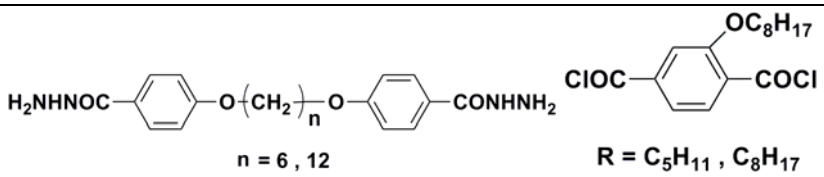
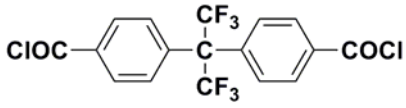
Of all the methods and variations that have been tried out over the years for the preparation

of aromatic polyoxadiazoles, two of them are useful from a practical point of view: the one-step polycondensation of dicarboxylic acids or their derivatives with hydrazine or hydrazine sulfate, and the two-step polycondensation of dihydrazides with diacid chlorides. Although the former leads to high molecular weight materials, its application is limited to monomers that are stable in strong acids. Although the molecular weight of polyoxadiazoles formed by the polyhydrazide route is not so high, the use of a wide variety of monomers is possible.

1.6.2 Stucture-property relationship in polyhydrazides and polyoxadiazoles

Aromatic polyhydrazides and polyoxadiazoles constitute a group of specialized-performance polymers that are meant to be used in small quantities but have very high values in their end-uses.[245] Since polyoxadiazoles are difficult to solubilize in organic solvents, modified polymers have been synthesized containing voluminous substituents on the arylene rings, or bulky moieties such as hexafluoroisopropylidene or diphenyl-silane units in the main chain, alkyl chain as pendants or in the polymer backbone which show improved solubility in common organic solvents and can be processed from such solutions. **Table 1.5** presents a list of representative monomers to obtain soluble and processable polyhydrazides and polyoxadiazoles.

Table 1.5 Representative examples of monomers to obtain organo-soluble polyhydrazides and polyoxadiazoles

No.	Monomers	Ref.
1.		246
		247
2.		248
3.		249

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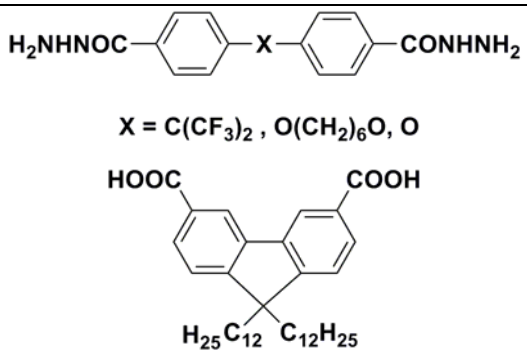
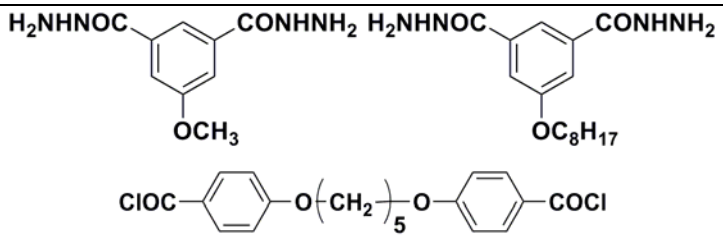
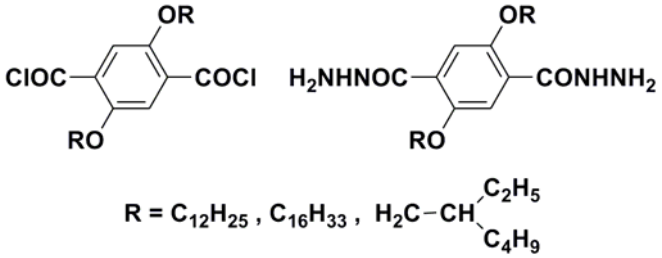
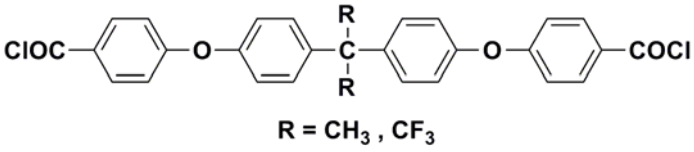
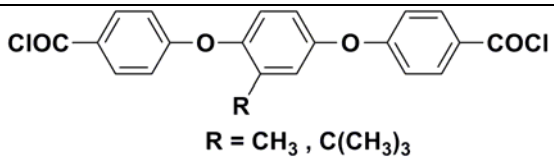
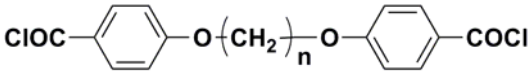
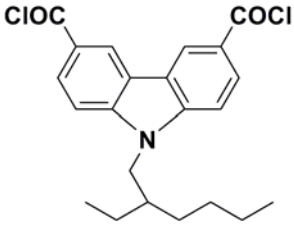
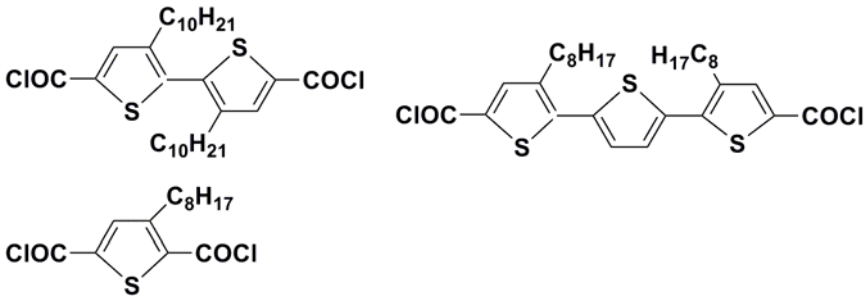
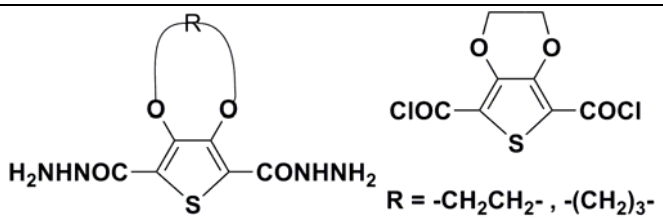
4.		250
5.		251
7.		252
8.		253
9.		254
10.		255
11.		256

Table 1.5 Continued…….

12.		257
14.		258

1.7 Polyesters

Polyesters or polyarylates are polymers with recurring ester groups (-CO-O-) as an integral part of the main polymer chain.

The reaction of aromatic dicarboxylic acids and diphenols was first noted by Conix[259] in 1957. The literature on polyarylates based on aromatic dicarboxylic acids is extensive. Before the production of the first commercial aromatic polyester, U-polymer (a polyarylate based on bisphenol A and tere/isophthalates) by Unitica in 1974, 140 different chemical compositions of polyarylates were listed.[260]

Polyesters have found applications in a wide variety of areas by virtue of their attractive electrical and mechanical properties. However, polyarylates are generally difficult to process because of their limited solubility in organic solvents and high glass transition and melting temperatures. The melt viscosity of BPA-based polyesters is noted to be high and thus their injection mouldability is considered to be a limitation. Therefore, a great deal of effort has been expended to try to improve processability of polyarylates.

1.7.1 Synthesis of polyesters

High molecular weight aromatic polyesters are prepared by two chemical routes:

1. Acid chloride route
2. Transesterification route

1.7.1.1 Acid chloride route

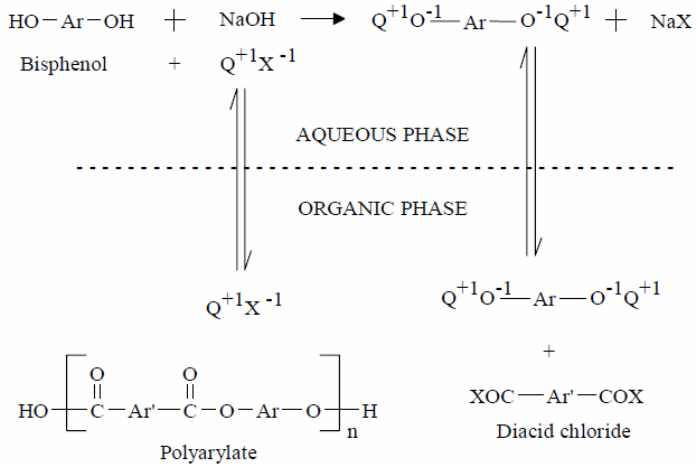
This route is generally applicable and mostly used for the synthesis of polyarylates. The diacids are converted into diacid chlorides followed by condensation with diphenols. The reaction can be performed by three different processes.

1.7.1.1.1 Interfacial polycondensation

The interfacial process for the preparation of polyarylates was first described by Eareckson[261] and Conix.[259] Basically, the interfacial polymerization involves the reaction of dialkali metal salt of a diphenol with diacid chloride(s) in systems such as water-dichloromethane or water-chlorobenzene. The acid chloride, which can be either aliphatic or aromatic, is dissolved in the water-immiscible organic phase and is reacted with the aqueous alkaline bisphenolates under high speed stirring. Aliphatic diols do not form alcoholate ions in aqueous solutions and are, therefore, not suitable monomers for the preparations of polyesters by interfacial technique.

Since reaction takes place at the interface or near the interface, factors such as stirring speed, the relative volume of organic and aqueous phases, monomer concentrations and the nature and concentration of phase transfer catalyst (PTC) exert a marked influence on reaction kinetics and on the resulting polymer yield and molecular weight.[262] PTC facilitates the transportation of phenolate ions in the organic phase and can also act as a surfactant, which increases the total interfacial area and consequently overall reaction rate.[262]

A typical phase -transfer catalyzed interfacial polycondensation is shown in **Scheme 1.7.**



Scheme 1.7 Phase-transfer catalyzed interfacial polycondensation

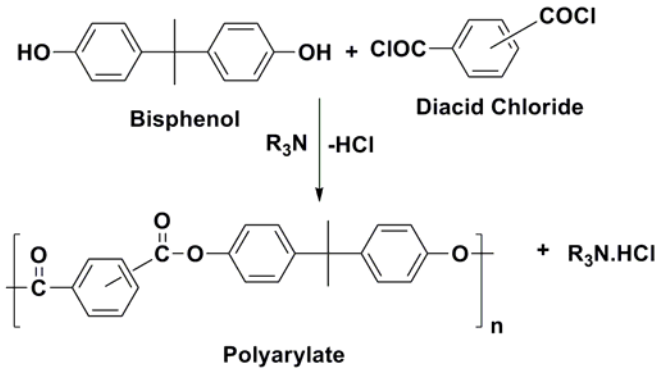
The basic function of PTC is to transfer the anions of the reacting salt into the organic medium in the form of ion pairs. These ion pairs react with chloride ions in the organic phase producing the desired product. The regenerated PTC is transferred back into the aqueous medium.[262,263] The most commonly used PTC's are benzyltriethyl-ammonium chloride, tetraethylammonium chloride, tetramethylammonium chloride, benzyltriphenyl phosphonium chloride, 15-crown-5, and 18-crown-6.[262] The choice of organic solvent is very important in interfacial polycondensation. It is advantageous that polyarylate formed during the polymerization should remain in the solution form to obtain the high molecular weight polymers. The precipitation of polymer lowers the reaction rates; hence, low molecular weight polymers are obtained.

In constrast to polyesterification carried out in homogeneous media, the maximum

molecular weight is not necessarily obtained at the equimolar ratio of reactants. The actual optimum stoichiometric ratio depends on the rate of diffusion of individual reactants to the reaction zone. The synthesis of high molecular weight polyesters has been reported for diacid chloride-bisphenol stoichiometric ratios ranging between 0.58 and 2, depending on reactants and experimental conditions.[264]

1.7.1.1.2 Low temperature solution polycondensation

Low temperature solution polycondensations are generally run at room temperature or between -10°C to +30 °C. Polyarylates are synthesized by the reaction of equivalent amounts of a diacid chloride and a dihydroxy compound in an inert solvent such as THF or DCM in the presence of a tertiary amine such as triethyl amine or pyridine, which plays a role of both reaction catalyst and HCl acceptor. This synthetic method is also termed acceptor-catalytic polyesterification.[265] **Scheme 1.8** depicts the synthesis of polyester from bisphenol-A and terephthalic acid chloride or isophthalic acid chloride.



Scheme 1.8 Solution polycondensation of bisphenol and diacid chloride

High molecular weight polyarylates are successfully synthesized in pyridine alone or in combination with a tertiary amine in an inert organic solvent.[259,265,266]

1.7.1.1.3 High temperature solution polycondensation

The polycondensation of a diacid chloride with a bisphenol without an acid acceptor is slow at room temperature. The high temperature solution polycondensation is carried out at elevated temperatures (~200^{o}C) in an inert high boiling solvent. The high boiling solvents used are nitrobenzene or o-dichlorobenzene. The o-dichlorobenzene and pyridine system is the most effective one to produce the polymer with high molecular weight.[267] Polyarylates are also prepared in good yields at 215-220^{o}C in dichloro- ethylbenzene.[268] No acid acceptor is needed because the evolved hydrogen chloride is continuously removed from the system with the aid of an inert gas. A wide variety of other solvents are useful and include chlorinated benzenes (tetrachlorobenzene), chlorinated biphenyls or diphenylethers, chlorinated naphthalenes, as well as non-chlorinated aromatics such as terphenyl, benzophenones, dibenzylbenzenes,and the like.

1.7.1.2 Transesterification route

Transesterification reactions can be carried out by reaction of,

1) Diphenyl ester of an aromatic dicarboxylic acid and bisphenol,[269]
2) Aromatic dicarboxylic acid and diacetate derivative of bisphenol,[259,270]
3) Dialkylester of dicarboxylic acid and diacetate derivative of bisphenol.[271]

1.7.1.3 Miscellaneous routes for polyester synthesis

Various routes other than those mentioned above have been used for polyester synthesis. Phenol silyl ether route demonstrated by Kricheldorf,[272] direct esterification route using activated diacid intermediate,[273] palladium-catalyzed carbonylation of aromatic dihalides with bisphenols,[274] are few of them.

1.7.2 Structure-property relationship in polyesters

Various efforts have been made to elucidate the structure-property relationship in polyarylates.[271-277] The properties of polyesters depend on the kind of substitution present at the central carbon atom between the two phenyl rings. Polyesters bearing phenyl rings or large cross planar substituents show higher thermal properties, they are soluble in common organic solvents and do not show a tendency to crystallize.[275] Also the inclusion of $-CF_3$ group into the polyester backbone improves the solubility and thermal stability of the resulting polymers.[276] Introduction of cardo "loops" groups along the polymer backbone has been shown to impart greater solubility as well as better mechanical and thermal properties.[277] Use of *meta*- substituted aromatic monomers such as substituted isophthalic acid or resorcinol results in the formation of kinks in the polymer chain, which disrupt lateral interactions. Substituted terephthalic acid with pendant functional groups also lead to polyesters with improved solubility. 2-Sulfomethylterephthalic acid and 2-phosphono-terephthalic acid have been employed in the preparation of rigid-rod polymers with enhanced solubility.[278]

Thermally stable polyarylate derived from a mixture of isophthalic acid and terephthalic acid with bisphenol A has been commercialized.[279] There are studies on different co-polyesters, in which composition of the co-polyester is varied in the diol structures rather than in the diacid chloride structures[280] to control the final properties of the polymers. Introduction of bulky pendant substituents or pendant flexible alkyl chains along the polymer backbone is one of the approaches to obtain processable/ soluble polymer. A number of monomers containing bulky pendant groups have been synthesized for the synthesis of polyesters. Representative examples of such bisphenols and diacids are presented in **Table 1.6.**

Table 1.6 Representative examples of monomers containing bulky pendant groups/ alkyl chains used in the synthesis of polyesters

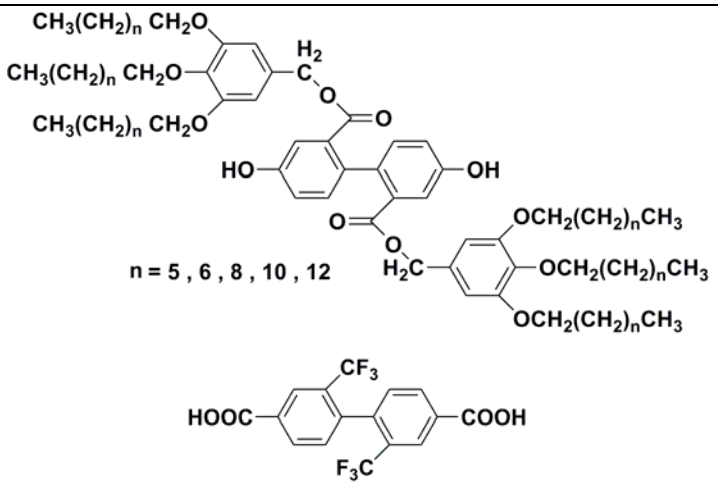
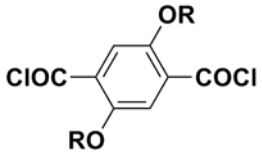
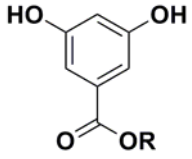
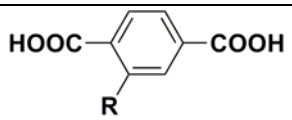
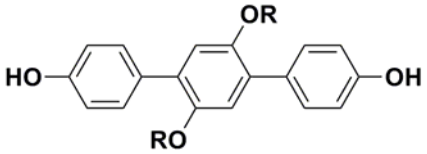
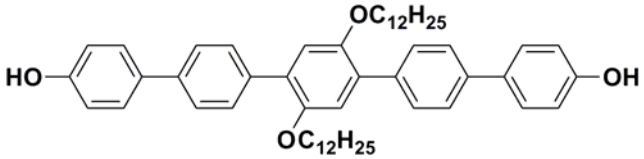
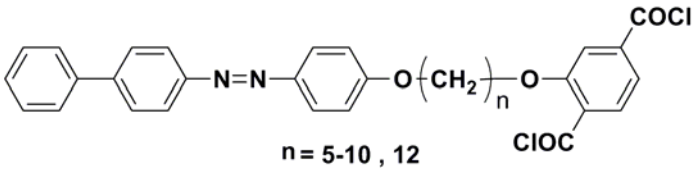
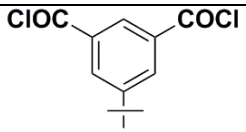
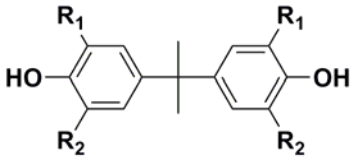
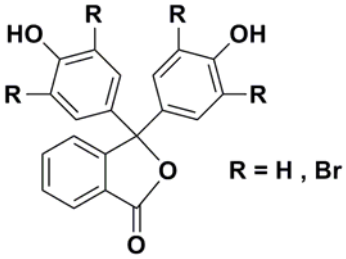
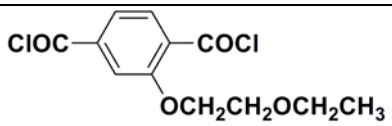
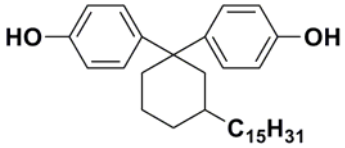
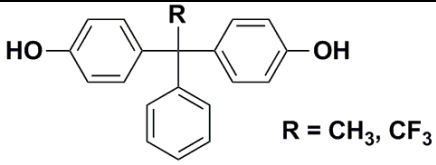
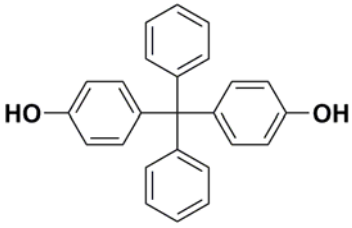
No.	Monomers	Ref.
1.		281
2.	 R = C_6H_{13} , $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$	282
3.	 R = CH_3 , C_4H_9 , C_8H_{17} , $C_{12}H_{25}$	283
4.	 R = OC_6H_5 , SC_6H_5 , $S(CH_2)_5CH_3$	284
5.	 R = $C_{12}H_{25}$, $C_{16}H_{33}$ 	285

Table 1.6 Continued…….

6.		286
7.		287
8.		288
9.		287, 289
10.		290
11.		100
12.		291
13.		292

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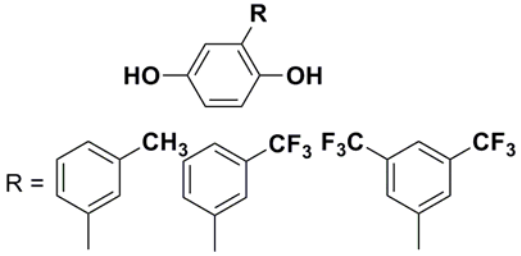
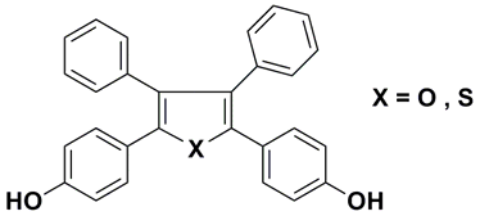
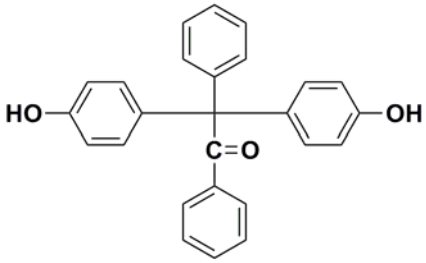
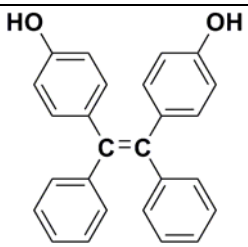
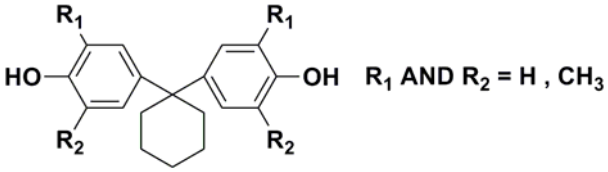
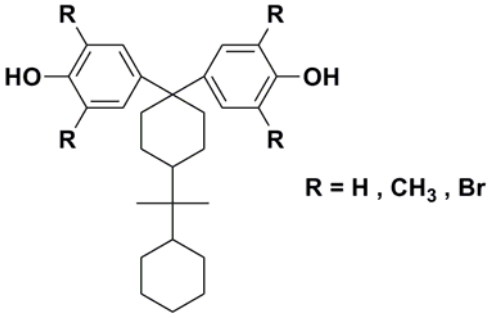
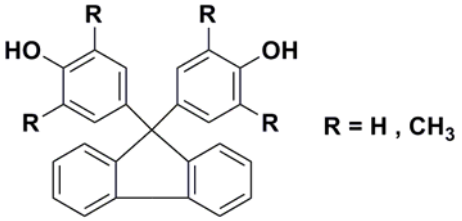
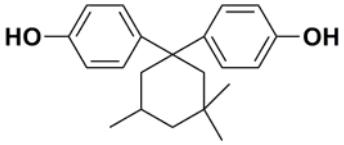
14.		293
15.		294
16.		295
17.		296
18.		297
19.		298

Table 1.6 Continued…….

20.		299
21.		300

1.8 Polyethers

Polyethers or poly(arylene ether)s,[301] are engineering thermoplastics having importance in a wide variety of applications such as structural resins, gaskets, tubing, and microelectronic components. Furthermore, light weight structural thermoplastics are often preferred relative to their metallic or ceramic counterparts. Poly(arylene ether)s (PAE) have received considerable attention as a consequence of a wide range of physical and chemical properties resulting from the variation in structure of the backbone, and were synthesized *via* nucleophilic aromatic substitution step growth or condensation polymerization of an activated dihalide with bisphenol.[302]

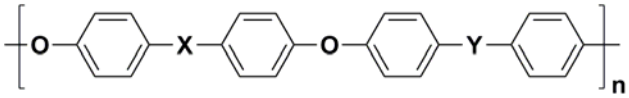


Figure 1.3 A generic representation of poly(arylene ether) backbone structure

Figure 1.3 represents a poly(arylene ether) where X is commonly a carbonyl or sulfone moiety derived from the activated dihalide and Y is a connecting unit that could be, for example, a similar functional group, isopropylidene, or a chemical bond.

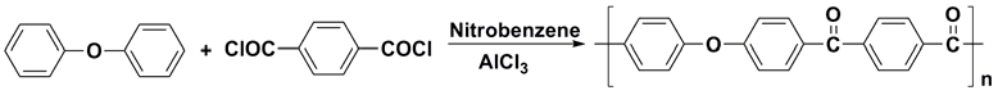
1.8.1 Synthesis of poly(arylene ether)s: [poly(ether ketone)s and poly(ether sulfone)s]

Poly(arylene ether)s have been synthesized using a variety of different methods, including nucleophilic aromatic substitution,[303] ring opening of arylene ether cyclics,[304] silyl ether displacement, electrophilic substitution[305,306] and catalytic coupling.[307]

1.8.1.1 Electrophilic route

Traditionally, poly(ether ketone)s (PEKs) and poly(ether sulfone)s have been synthesized by two types of reactions: Friedel-Crafts acylation or sulfonation polycondensation and nucleophilic aromatic substitution (SNAr) polycondensation. PEKs are generally semicrystalline polymers with limited solubility in common organic solvents. The early research in this area was focused on finding a suitable solvent system for the synthesis of PEKs by Friedel-Crafts acylation polycondensation. Bonner[308] at DuPont pioneered the synthesis of PEKs through Friedel-Crafts

acylation. He used terephthaloyl chloride and diphenyl ether in nitrobenzene solution with a catalyst such as aluminum chloride or antimony pentachloride **(Scheme 1.9)**.



Scheme 1.9 Synthesis of PEKK *via* Friedel-Craft acylation

However, only low molecular weight polymers were obtained. Goodman[309] used methylene chloride as the solvent. Polymers with moderate molecular weights were obtained. Under the same conditions, condensation of an AB monomer *p*-phenoxybenzoyl chloride afforded a high molecular weight poly(ether ketone). Iwakura et al[310] found that polyphosphoric acid can be used as an alternative solvent to condense p-phenoxybenzoic acid to form PEK with moderate success.

A breakthrough in the synthesis of PEK was made by Marks when the HF/BF_3 solvent system was found.[311] The polyacylation reaction in HF/BF_3 proceeds very rapidly. Under well controlled reaction conditions, it is possible to get high molecular PEK with more than 100 repeating units. Rose et al[312] at ICI discovered that trifluoromethanesulfonic acid can be used as the solvent as well as the catalyst for polyacylation. This method has been successfully applied to polymerize 4-(4'-phenoxy)phenoxybenzoic acid to prepare a polymer with an inherent viscosity of 1.19 dl/g **(Scheme 1.10)**.

Scheme 1.10 Polyacylation method

However, HF/BF_3 is not easy to handle and the polymerization has to be carried out on a vacuum line. Trifluromethanesulfonic acid is very expensive and neither solvent is attractive for industrial applications. There has been renewed interest in using the methylene chloride/aluminum chloride system, but the solubility problem has to be solved. Jansons et al[313] found that Lewis bases such as DMF, tetramethylene sulfone, dimethyl sulfone, butyronitrile, lithium chloride and sodium chloride could act as swelling media or as solvents for the polymer to give high molecular weight polymers. The researchers found that Lewis bases can complex with aluminum chloride. The complexes are best prepared in chlorinated hydrocarbon solvents at temperatures below 0^oC.

Analogously, poly(ether sulfone)s can be synthesized by Friedel-Crafts sulfonylation, In contrast to the acylation reaction, the preferred catalyst is ferric chloride instead of aluminum chloride. The sulfonylation can be carried out in the melt state at temperatures below 250 ^oC.

1.8.1.2 Nucleophilic route

In contrast to the electrophilic route, the nucleophilic aromatic substitution reaction involving bisphenoxide and activated dihalide is more controllable and high molecular weight polymers can be more easily obtained from bisphenols and activated dihalides. This reaction can be generalized as in **Scheme 1.11**.

EWG = CO , SO_2 , SO ,Phosphine Oxide

X = F , Cl , NO_2

Scheme 1.11 Synthesis of poly(arylene ether)s *via* nucleophilic route

Electron withdrawing groups such as sulfone, carbonyl, sulfoxide or phosphine oxide are necessary to activate the aromatic dihalides. The reactivities of aromatic halides are in the order of F>>Cl>Br. In general, with a strong electron withdrawing group such as sulfone, the leaving group can be F^- or Cl^-. In the case of weak electron-withdrawing groups, the leaving group should be F^- to get high molecular weight polymer. For the less reactive monomers, such as 4, 4'-dichlorobenzophenone, single electron transfer side reactions were observed which prevent building up of high molecular weight. [314] Percec et al[315] tried polymerization with dichloroketone monomers but the ability to achieve high molecular weight poly(ether ketone)s was not consistently demonstrated.

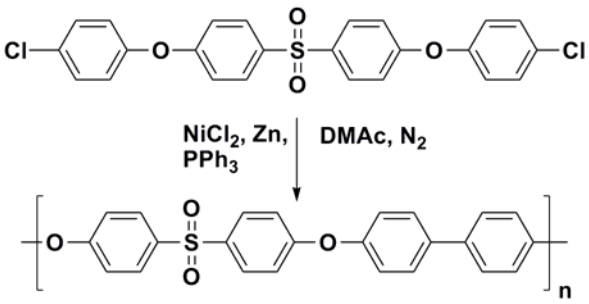
DMSO was used as the solvent in the pioneering work of Johnson et al.[316] Sodium hydroxide was the base to deprotonate the bisphenol to generate the reactive bisphenoxide. Chlorobenzene was the azeotropic solvent to remove the water from the system. Strict stoichiometry of the bisphenol and sodium hydroxide is required as excess sodium hydroxide can attack the activated dihalide or ether linkage of the polymer which will reduce the molecular weight. Another drawback of using sodium hydroxide as the base is the insolubility of the sodium phenoxide which prevents successful polymerization.

McGrath et al[317] found that alkali metal carbonates such as sodium and potassium carbonate can be substituted for sodium or potassium hydroxide as the base. Excess carbonate can be tolerated because the carbonate is a poor nucleophile.

Kricheldorf and Bier[318] invented a synthesis of poly(arylene ether)s from silylated bisphenols. The activated cesium phenoxide is generated with CsF as the catalyst. A unique feature of Krichelodorf's[318] synthesis is that the polymer is produced in the melt. The side product trimethylsilyl fluoride is a volatile compound which is removed at high temperature. Polymer is obtained in pure form without the need to remove the solvent and the salts. For example, high molecular weight PEEK was produced by this method.

1.8.1.3 Carbon-carbon coupling route

The ether sulfone group can be pre-made in the monomers and poly(ether sulfone)s then synthesized by C-C coupling reactions. This technique has been successfully applied to synthesize a number of polysulfones.[319] An example is shown in **Scheme 1.12**.



Scheme 1.12 Carbon-carbon coupling route to poly(ether sulfone)s

There are several key factors for the polymerization to be successful. The system should be free from water and oxygen, and the zinc should be of high quality.

1.8.1.4 Cyclic macromer route

Ring-opening polymerisation of macrocyclic aromatic ether ketones and ether sulfones offers a potentially valuable route to high-performance aromatic polymers,[320] and such chemistry has recently become the focus of significant research activity. Advantages of this approach in the production of composite structures, for example include the very much lower initial viscosities of macrocyclic oligomers relative to the corresponding high molecular weight polymers, the complete absence of by-products, and the fact that ring-opening polymerisations of strain-free macrocycles are largely entropy-driven and thermally neutral.[321]

1.8.2 Structure-property relationship in poly(arylene ether)s

Poly(arylene ether)s are a class of high performance polymers known for their excellent combination of chemical, physical and mechanical properties. Poly(arylene ether)s, i.e. poly(ether ketone)s and poly(ether sulfone)s are classes of high performance materials that display excellent mechanical properties, high thermal and environmental stability, solvent and hydrolytic resistance.[307a,302a] However, particularly in case of PEEKs , their highly crystalline nature and low solubility in organic solvents often restricts the use of these materials. Various structural changes have been introduced in the basic PEEK resin by several researchers to obtain different properties for different applications. Structural changes have focussed on the order and ratio of ether–ketone linkage,[322] on the ratio of *meta* and *para* phenyl substitution,[323] and the incorporation of $–CR_2$ and sulfone groups in the backbone of the polymeric chain.[324] Introduction of pendant alkyl or phenyl groups on to the poly(aryl ether ether ketone) main chain is another important structural change.[325] Ueda et al prepared PEK having two alkyl substituents per repeating unit.[326] The introduction of the bulky substituents onto the PEK backbone could suppress crystallisation to improve its solubility in contrast to non-substituted PEK, leading to novel applications of PEK derivatives.

The representative examples of monomers containing bulky side groups, cardo groups or alkyl chains used in the synthesis of poly(arylene ether)s are given in **Table 1.7 .**

Table 1.7 Representative examples of monomers containing bulky side groups, cardo groups or alkyl chains used in the synthesis of poly(arylene ether)s

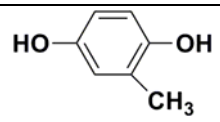
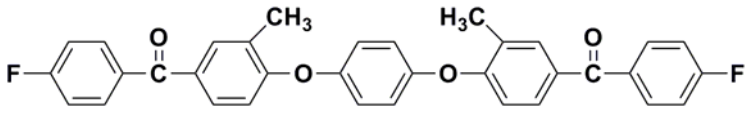
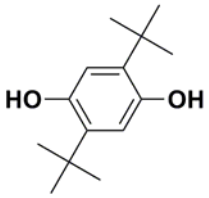
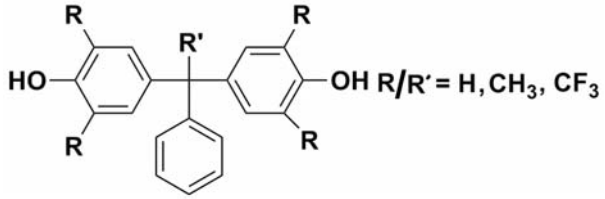
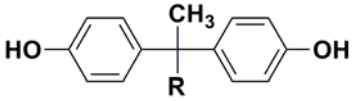
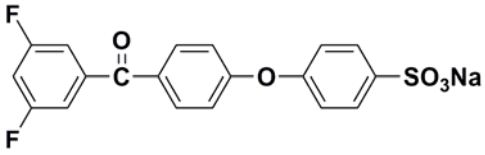
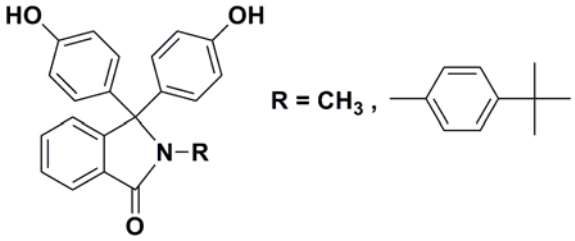
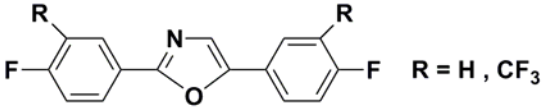
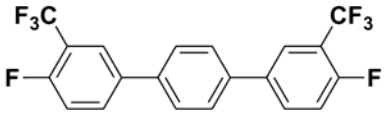
No.	Monomer	Ref.
1.		327
2.	 	328
3.		329
4.	 $R = C_{11}H_{23}$, $C_{17}H_{35}$	330
5.		331
6.		332
7.	 $R = H$, CF_3 	333

Table 1.7 Continued…….

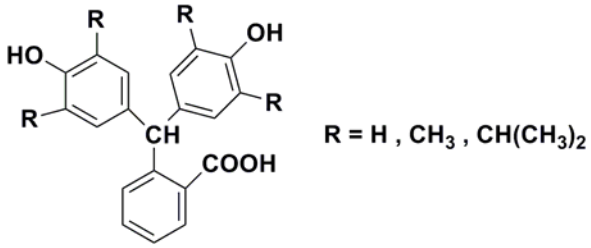
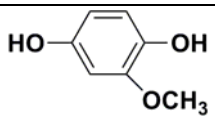
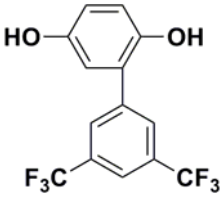
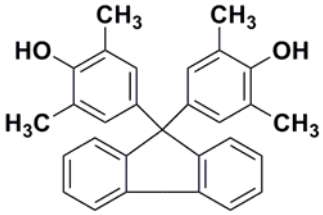
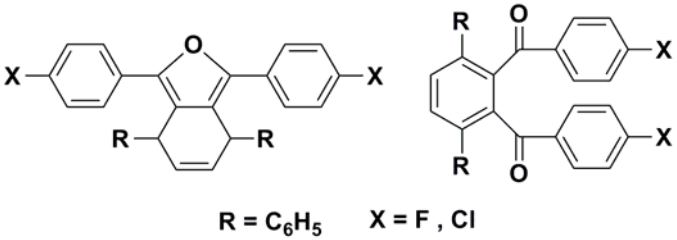
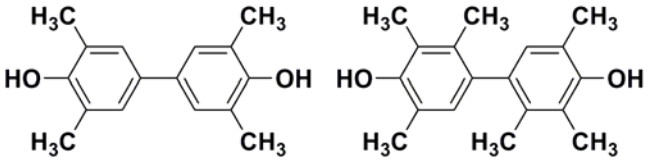
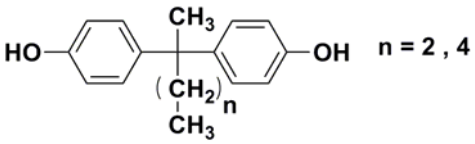
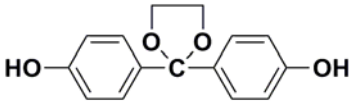
8.		334
9.		335
10.		336
11.		337
12.		338
13.		339
14.		340
15.		341

Table 1.7 Continued…….

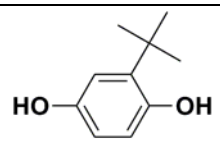
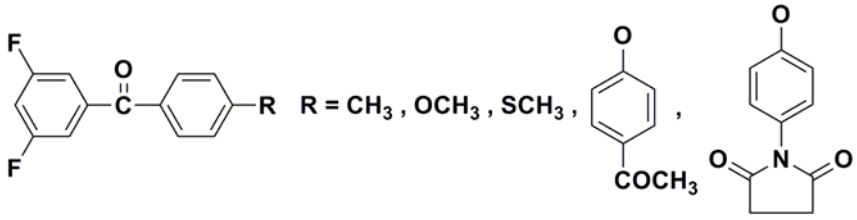
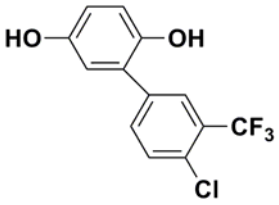
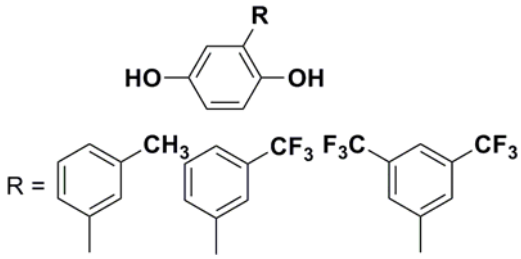
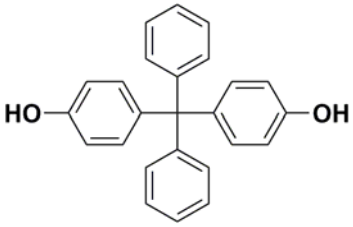
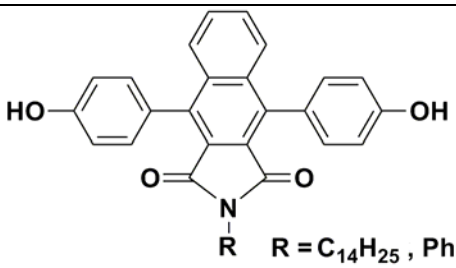
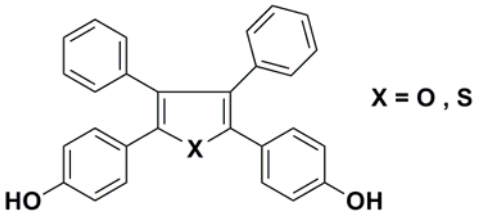
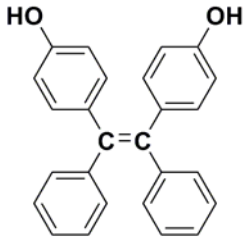
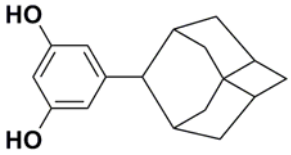
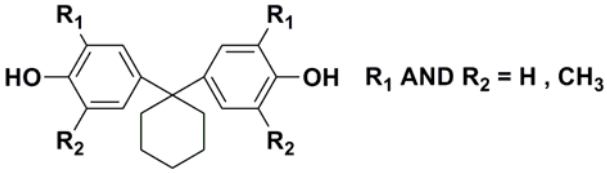
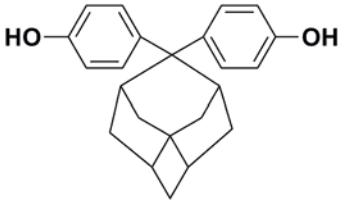
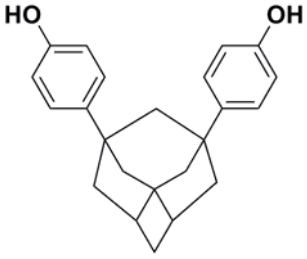
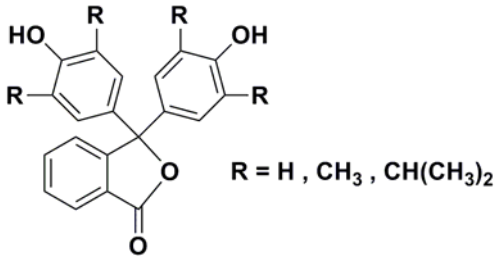
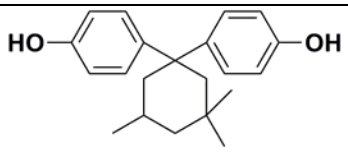
16.		342
17.		343
18.		344
19.		345
20.		346
21.		347
22.		348

Table 1.7 Continued…….

23.		349
24.		350
25.		351
26.		351
27.		352
28.		353
29.		354

1.9 Concluding Remarks

- Nature produces the vast amount of 170 million metric tons (t) of biomass per year by photosynthesis. These abundantly available renewable resource materials are currently viewed as a feedstock for the Green Chemistry of the future.
- Cardanol, an inexpensive and abundantly available renewable resource material obtained from distillation of Cashew Nut Shell Liquid, has been used for the preparation of fine chemicals. The long aliphatic chain attached to the *meta*- position of the phenolic ring of cardanol makes this chemical a unique natural source because it confers to all derivatives specific properties (good solubility, good processability, interesting physical properties and so on). The massive amount of literature on CNSL points out that the chemistry of cardanol is becoming a stimulating and fruitful area in academic and industrial research.
- High performance/ high temperature polymers have come a long way since the early efforts at DuPont. Over the years, significant improvements have been made in the processability, stability and high temperature performance of these materials. The research efforts during the last four decades to develop new monomers has enriched the chemistry of high performance polymers to such an extent that it would be difficult to find another field of macromolecular chemistry where the investigations have produced a similar variety of new species with wide range of properties. The knowledge of characteristic features of the formation of high performance/ high temperature polymers and the relation between their structure and properties has led to enormous prospects for specific design of the polymer chain and hence for imparting a set of desired properties to such polymers. While the field of high performance/ high temperature polymers can not be described as young, it still has a bright future. The research continues in many areas such as microelectronics (photoresists, interlayer dielectrics), electroactive activators and devices, optical fibre wave guides, proton exchange membranes for fuel cells, separation/ barrier materials, etc.

References:

01 Odell, J.R. Oil and Gas Resources and the Supply/ Demand Pattern Beyond 2000, Proceedings, Chemrawn III, **1984**.

02 Annon. The Economist, London, August 5th **1984**, p. 15.

03 Belgacem, M.N.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, **2008.**

04 Kamm, B.; Gruber, P. R.; Kamm, M. *Biorefineries Industrial Processes and Products*; Wiley-VCH: Weinheim, **2006**; Vols. *1* and *2*.

05 Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. *Angew. Chem.,Int. Ed.* **2005**, 44, 3358.

06 Klemm, D.; Heinze, T.; Wagenknecht, W. *Comprehensive Cellulose Chemistry*; Wiley-VCG: Weinheim, **1998**.

07 Shah, J.; Brown Jr. R.M. *Appl. Microbiol. Biotechnol.* **2005**, 66,352.

08 El Seoud, O.A.; Heinze T., *Advances in Polymer Science* **186**, Ed.: Heinze T., Springer Verlag, Berlin, Heidelberg, **2005**, pp. 103–149.

09 Mohanty, A.K.; Misra, M.; Hinrichsen, G. *Macromolecular Mater. Eng.* **2000**, 1, 276.

10 Belgacem, M.N.; Gandini, A. *Compos. Interface.* **2005**, 12, 41.

11 Sabu, T.; Pothan, L. *Cellulose Fibre Reinforced Polymer Composites,* Old City Publishing , **2007**.

12 Stevens, C.V.; Verhe, R.G. *Renewable Bioresources: Scope and Modifi cation for Non-Food Applications,* John Wiley & Sons, Ltd, Chichester, **2004**, pp. 310.

13 Rowell, R.M.; Property enhanced natural fiber composite materials based on chemical modification, in *Science and Technology of Polymers and Advanced Materials: Emerging Technologies and Business Opportunities*, (*Proceedings of the Fourth International Conference on Frontiers of Polymers and Advanced Materials* , Cairo, Egypt, 4–9 January 1997), Plenum Press, New York N.Y. **1998**, pp. 717.

14 Sakakibara, A.; Sano Y. Chemistry of lignin, in *Wood and Cellulosic Chemistry* (Eds. Hon D.N.-S. and Shiraishi N.), 2nd Edition , Marcel Dekker Inc. New York, USA, **2001**, pp. 109.

15 Sjostrom, E. *Wood Chemistry. Fundamentals and Applications,* 2nd Edition, Academic Press, San Diego, CA, USA, **1993**. p. 293.

16 Anderso,n J.W.; Hanna, T.J. *J. Nutr.* **1999**, 129**,** 1457.

17 Li, J.; Kamath, K.; Dwivedi, C. *J. Biomater. Appl.* **2001**, 15, 321.

18 Brookshier, K.A.; Tarbell, J.M. *Biorheology,* **1993**, 30, 107.

19 Brendan, R. *Rubber Compounding: Chemistry and Applications* , Marcel Dekker Inc., New York, **2004**

20 Kawahara, S.; Saito, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, 44**,** 1561.

21 Jacob, M.; Francis, B.; Varughese, K.T.; Thomas, S. *Macromol. Mater. Eng.* **2006**, 291, 1119.

22 Kolattukudy, P.E. *Science*, **1980**, 208**,** 990.

23 Kolattukudy, P.E.; Espelie, K.E.; Chemistry, biochemistry, and function of suberin and associated waxes, in *Natural products of woody plants, chemical extraneous to the lignocellulosic cell wall,* Ed.: Rowe, J., Springer, Berlin, Heidelberg, **1989.**

24 Cordeiro, N.; Belgacem, M .N.; Gandini, A.; Neto C.P. *Ind. Crops Prod.* **1999**, 10, 1.

25 Douliez, J.P.; Barrault J.; Jerome, F.; Heredia, A.; Navailles, L.; Nallet, F. *Biomacromolecules*, **2005**, 6, 30.

26 Roux, D.G. *Modern Applications of Mimosa Extract,* Leather Industries Research Institute, Grahamstown, South Africa, **1965,** pp. 34.

27 Roux, D.G.; Ferreira, D.; Hundt, H.K.L.; Malan, E. *Appl. Polymer Symp.* **1975**, 28, 335.

28 Fengel, D.; Wegener, G.; Wood, Chemistry, Ultrastructure, Reactions, Walther DeGruyter, Berlin, **1984.**

29 Pizzi, A. Wood Adhesives–Chemistry and Technology, Volume I, Ed. Pizzi, A.) Marcel Dekker, New York, 1983, Chapter 4; *J. Macromol. Sci. Chem* . Ed. **1980**, C18, 247.

30 Mitsunaga, T. in *Plant Polyphenols 2* Eds. Gross G.G., Hemingway, R.W., Yoshida, T., Kluwer Academic/Plenum Publishers, New York, pp. 555.

31 Maiti, S.; Ray, S.S.; Kundu, A.K. *Prog. Polym. Sci.* **1989**, 14**,** 297.

32 Niemo, L. Internal sizing of paper, in *Papermaking Chemistry* (Ed. Niemo L.), Tappi Press, Helsinki, **1999**.

33 Cochet, F.; Claverie, J.P.; Graillat, C.; Sauterey, F.; Guyot A. *Macromolecules*, **2004**, 37, 4081.

34 Comyn, J. *Int. J. Adhes.* **1995**, 15, 9.

35 Pekarovicova, A.; Bhide, H.; Fleming, P.D.; Pekarovic, J. *J. Coating Technol.* **2003**, 75, 65.

36 Ramani, C.C.; Puranik, P.K.; Dorle, A.K. *Int. J. Pharm.* **1996**, 137, 11.

37 Pathak, Y.V.; Dorle, A.K. *Drug Dev. Ind. Pharm.* **1986**, 12**,** 2217.

38 Ruckel, E.R.; Arlt, H.J. in *Polyterpene Resins* (Eds. Zinkel, D.F. and Russel, J.), Pulp Chemical Association, New York, **1989**, pp. 510.

39 Yang, M.C.; Perng, J.S. *J. Appl. Polym. Sci.* **2000**, 76, 2068.

40 Shin, C.Y.; Chase, G.G. *Polym. Bull.* **2005**, 55, 209.

41 Di Lorenzo, M.L. *Prog. Polym. Sci.* **2003**, 28**,** 663.

42 Galliard, T. Starch availability and utilization, in *Starch: Properties and Potential,* Ed.: Galliard, T., 1st Edition, John Wiley & Sons, New York, **1987**, Chapter 1. pp. 1.

43 Daniel, J.; Whistler, R.L.; Voragen, A.C.J.; Pilnik, W. Starch and other polysaccharides, in *Ullmann ' s Encyclopedia of Industrial Chemistry*, Eds.: Elvers, B.; Hawkins, S. and Russey, W., 5th Edition, VCH Verlagsgesellschaft mbH, Weinheim, **1994**, A25, pp. 1.

44 Herrmann, A.S.; Nickel, J.; Riedel, U. *Polym. Degrad. Stab.* **1998**, 59, 251.

45 Guner, F.S.; Yagci, Y.; Erciyes, A.T. *Prog. Polym. Sci.* **2006**, 31, 633.

46 Bailey, A.E. *Bailey's Industrial Oil and Fat Products*, Wiley, New York, **1996**.

47 Deligny, P.K.T.; Tuck, N. Alkyds and polyesters, in *Resins for Surface Coatings* (Ed. Oldring P.K.T.), Wiley, New York, **2000**, Volume II.

48 Nayak, P.L. *J. Macromol. Sci. Rev. Macromol. Chem. Phys*. **2000**, 40, 1.

49 Sharma, V.; Kundu, P.P. *Prog. Polym. Sci.* **2006**, 31**,** 983.

50 Gultekin, M.; Beker, U.; Guner, F.S.; Erciyes, A.T.; Yagsi, Y. *Macromol. Mater. Eng.* **2000**, 283, 15.

51 Marks, D.W.; Li, F.; Pacha, C.M.; Larock, R.C. *J. Appl. Polym. Sci.* **2001**, 81, 2001.

52 Eren, T.; Kusefoglu, S.H. *J. Appl. Polym. Sci.* **2005**, 97, 2264.

53 Pelletier, H.; Belgacem, N.; Gandini, A. *J. Appl. Polym. Sci.* **2006,** 99, 3218.

54 Jain, J. P.; Sokolsky, M.; N. Kumar.; Domb, A. J. *Polym. Rev.* **2008**, 48, 156.

55 Petrovic, Z. S. *Polym. Rev.* **2008**, 48, 109.

56 Gandini, A. *Macromolecules*, **2008**, 41, 9491.

57 Corma A.; Iborra S.; Velty A. *Chem. Rev.* **2007**, 107, 2411.

58 Johnson, D. T.; Taconi, K. A. *Environ. Progr.* **2007,** 26, 338.

59 Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008,** 10, 13.

60 Pagliaro, M.; Rossi, M. *The Future of Glycerol*; RSC Publishing: Cambridge, **2008.**

61 http://www.dupont.com/Plastics/en_US/Products/Sorona/sorona_ep_trademark.html

62 Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. *Angew. Chem. Int. Ed*. **2007**, 46, 4434.

63 Plasman, V.; Caulier, T.; Boulos, N. *Plastics Additives & Compounding*, March/April **2005**, 30.

64 Norn, V. Polyglycerol Esters, in *Emulsifiers in Food Technology* (Ed. Whitehurst R.J.), Blackwell, Oxford, 2004, Chapter 5, pp. 110.

65 Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008**, 10, 13.

66 Polat, T.; Linhardt, R.J. *J. Surfact. Deterg.* **2001**, 4, 415.

67 Patel, M. *J. Ind. Ecol.* **2004**, **7**, 47.

68 Varma, A.J.; Kennedy, J.F.; Galgali, P. *Carbohyd. Polym.* **2004**, 56, 429.

69 Donnely, D.M.X.; Meegan, M.J. in *Comprehensive Heterocyclic Chemistry*, Eds.: Katritzky, A.R. and Rees, C.W. Vol. 4, Pergamon, Oxford, **1984,** p. 657.

70 Bird, C.W.; Cheeseman, G.W. in *Comprehensive Heterocyclic Chemistry,* Eds.: Katritzky, A.R. and Rees, C.W. Vol. 4, Pergamon, Oxford, **1984**, Chapters 1.

71 Kirsch, S.F. *Org. Biomol. Chem*. **2006**, 4, 2076.

72 Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. *Science* **2006,** 312, 1933.

73 Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, C. *Science* **2007,** 316, 1597.

74 Gandini, A. *Adv. Polym. Sci.* **1977**, 25, 47.

75 Hou, X.L.; Yang, Z.; Wong, H.N.C. *Prog. Heterocycl. Chem.* **2003**, 15, 167.

76 Averous, L. *J. Macromol. Sci., Polym. Rev.* **2004**, C4, 231.

77 Anon. *Biofuels, Bioprod. Bioref.* **2007**, 1, 8

78 Hartmann, H. High molecular weight polylactic acid polymers, in *Biopolymers from Renewable Resources,* Ed.: Kaplan, D.L., 1st edition, Springer-Verlag, Berlin, **1998**, pp. 367.

79 Sodergard, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, 27**,** 1123.

80 Roberts, G.A.F. *Chitin Chemistry*, The Macmillan Press Ltd, London , **1992,** p. 350.

81 No, H.K.; Meyers, S.P. *J. Aquat. Food Prod. Tech.* **1995**, 4, 27.

82 Pillai, C.K.S.; Paul, W.; Sharma, C.P. *Prog. Polym. Sci.* **2009**, 34, 641.

83 Rabea, E.I.; Badawy, M.E.-T.; Stevens, C.V.; Smagghe, G. , Steurbaut, W. , *Biomacromolecules* , **2003**, 4, 1457,

84 Fukushima, D. *Advance of Science and Technology,* Korin Press, Tokyo, **1988,** p. 21.

85 Li, M.S.; Klimov, D.K.; Thirumalaib D. *Polymer*, **2004**, 45, 573.

86 Lieberman, E.R.; Gilbert, S.G. *J. Polym. Sci.* **1973**, 41, 33.

87 Dalton, L. W. *C & EN Sci. Technol.* **2004,** 82, 24.

88 Czaja, W. K.; Young, D. J.; Kawecki, M.; Brown, R. M., Jr. *Biomacromolecules,* **2007,** 8, 1.

89 Brown, E. E.; Laborie, M.-P. G. *Biomacromolecules,* **2007,** 8, 3074.

90 Braunegg, G.; Lefebvre, G.; Genser K.F. *J. Biotechnol.* **1998**, 65, 127.

91 Sudesh, K.; Abe, H.; Doi, Y. *Prog. Polym. Sci.* **2000,** 25, 1503.

92 Morawetz, H. *In Polymers: The origin and growth of a science,* John Wiley, New York, **1985**. pp. 41.

93 Braunegg, G. in *Sustainable Poly(hydroxyalkanoate) (PHA) Production Degradable Polymers: Principles and Application*, Ed.: Scott, G. 2nd Edition, Kluwer Academic Publisher, Dordrecht/Boston/London, **2002**, Chapter 8.

94 Harvey, M.T.; Caplan, C. *Ind. Eng. Chem*. **1940**, 10, 1306.

95 Staedeler, *Ann. Chem. Pharm*. **1847**, 63, 137.

96 Menon, A.R.R.; Pillai, C.K.S.; Sudha, J.D.; Mathew, A.G. *J. Sci. Ind. Res*., **1985**, 44, 324.

97 Lubi, M.C.; Thachil, E.T. *Des. Monomers Polym.* **2000**, 3, 123.

98 Tyman, J.H.P.; Wielezynski, D.; Kashani, M.A. *J. Am.Chem. Soc*. **1978**, 55, 663.

99 Shingte, R.D.; Wadgaonkar, P.P. U.S. Patent Number 6,790,993, **2004.**

100 Avadhani, C.V.; Wadgaonkar, P.P.; Sivaram, S. U.S. Patent Number 6,255,439, **2001.**

101 Antony, R.; Pillai, C.K.S.; Scariah, K.J. *J. Appl. Polym. Sci*. **1990**, 41, 1765.

102 Menon, A.R.R.; Pillai, C.K.S.; Nando, G.B. *J. Adhes. Sci. Tech*., **1995**, 9, 443.

103 Suresh, K.I.; Kishanprasad, V.S. *Ind. Eng. Chem. Res.* **2005**, 44, 4504.

104 Tullo, A. H. *Chem. Engg News*. **2008**, 86, 26.

105 Mele, G.; Vasapollo, G. *Mini-Rev in Organic Chem*. **2008**, 5, 243.

106 Lu, Y. Larock, R.C. *ChemSusChem* **2009**, 2, 136.

107 Lee, K. S.; Samoc, M. *Polym. Commun.* **1991**, 32, 361.

108 Yang, C. J.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, 32, 165.

109 Grigoras, M.; Catanescu, C.O.; Simionescu, C.I. *Rev. Roum. Chim.* **2001**, 46, 927.

110 Grigoras, M.; Catanescu, C.O. *J. Macromol. Sci. C Polym. Rev.* **2004**, C44, 1.

111 Iwan, M. A.; Sek, D. *Prog. Polym. Sci*. **2008**, 33, 289.

112 Bagheri, M.; Entezami, A. *Eur. Polym. J.* **2002**, 38, 317.

113 a) Dutta, P.K.; Jain, P.; Sen, P.; Trivedi, R.; Sen, P.K.; Dutta, J. *Eur. Polym. J.* **2003**, 39**,** 1007.
b) Suh, S.C.; Shim, S.C. *Synth. Met.* **2000**, 114, 91.

114 Adams, R.; Bullock, R. E.; Wilson, W. C. *J. Am. Chem. Soc.* **1923,** 45, 521.

115 Steinkopf, W.; Eger, N. *Liebigs. Ann. Chem.* **1938**, 533, 270.

116 Marvel, C. S.; Hill, H. W. *J. Am. Chem. Soc.* **1950**, 72, 4819.

117 D'Alelio, G. F.; Crivello, J. V.; Schoenig, R. K.; Huemmer, T. F. *J. Macromol. Sci. Chem.* **1967**, A1, 1161.

118 D'Alelio, G. F.; Strazik, W. F.; Feigl, D. M.; Schoenig, R. K. *J. Macromol. Sci. Chem.* **1968**, **A2**, 1457.

119 Millaud, B.; Strazielle, C. *Polymer* **1979**, 20, 563.

120 Preston, J. *Angew. Makromol. Chem.* **1982**, 109/110, 1.

121 Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, 20, 729.

122 Saegusa, Y.; Sekiba, K.; Nakamura, S. *J. Polym. Sci.Polym. Chem.* **1990**, 28, 3647.

123 Rudzinski, W. E.; Guthrie, S. R.; Cassidy, P. E. *J. Polym. Sci.Polym. Chem.* **1988**, 26, 1677.

124 Barbera, J.; Oriol, L.; Serrano, J. L. *Liq. Cryst.* **1992**, 12, 37.

125 Yamada, S. *Coord. Chem. Rev.* **1999**, 190–192, 537.

126 Kaya; Senol, D. *J. Appl. Polym. Sci.* **2003**, 90, 442.

127 El-Shekeil, A. G.; Khalid, M. A.; Al-Yusuf, F. A. *Macromol. Chem. Phys.* **2001**, 202, 2971.

128 Weng, J.; Sun, W.; Jiang, L.; Shen, Z. *Macromol. Rapid Commun.* **2000**, 21, 1099.

129 Kim, H.C.; Kim, J.S.; Kim, K.S.; Park, H.K.; Baek, S.; Ree, M. *J. Polym. Sci.Polym. Chem.* **2004**, 42, 825.

130 Elizbarashvili, E.; Matitaishvili, T.; Topuria, K. *J. Braz. Chem. Soc.* **2007**, 18, 1254.

131 Park, S. B.; Kim, H.; Zin, W.C.; Jung, J. C. *Polymer* **1996**, 37, 2845.

132 Park, S. B.; Kim, H.; Zin, W.C.; Jung, J. C. *Macromolecules* **1993**, 26, 1627.

133 Farcas, A.; Grigoras, M. *High. Perform. Polym.* **2001**, 13, 201.

134 Farcas, A.; Grigoras, M. *Polym. Int*. **2003**, 52, 1315.

135 Thomas, O.; Inganas, O.; Andersson, M.R. *Macromolecules* **1998**, 31, 2676.

136 Choi, M.K.; Kim, H.L.; Suh, D.H. *J. Appl. Polym. Sci*. **2006**, 101, 1228.

137 Chang, C.P.; Wang, C.C.; Chao, C.Y.; Lin, M.S. *J. Polym Res*. **2005**, 12, 1.

138 Jeffries-El, M.; Ambrassio, K.C.; Torkka, R.M. *Polym. Prerprints* **2001**, 42, 446.

139 Tsai, F.C.; Chang, C.C.; Liu, C.L.; Chen, W.C.; Jenekhe, S.A. *Macromolecules* **2005**, 38, 1958.

140 Adell, J.M.; Alonso, M.P.; Barbera, J.; Oriol, L.; Pinol, M.; Serano, J. L. *Polymer* **2003**, 44, 7829.

141 Cerrada, P.; L. Oriol, L.; Pinol, M.; Serano, J.L.; Alonso, M.P.; Pueltolas, I.; Iribarren, S.; Guerra, M. *Macromolecules* **1999**, 32, 3565.

142 Nakamura, S.; Sato, T.; Nishimoto, Y. *J. Therm. Anal. Calorim*. **2002**, 70, 733.

143 Liu, C.L.; Chen, W.C. *Macromol. Chem. Phys*. **2005**, 206, 2212

144 Wang, C.; Shieh, S.; Legoff, E.; Kanatzidis, M.G. *Macromolecules* **1996**, 29, 3147.

145 Park, L.S.; Han, Y.S.; Kim, S.D.; Hwang, J.S. *Mol. Cryst. Liq. Cryst*. **2001**, 371, 309.

146 Wojtkowski, P.W. *Macromolecules* **1987**, 20, 740.

147 Choi, E.J.; Ahn, J.C.; Chien, L.C.; Lee, C.K.; Zin, W.C.; Kim, D.C.; Shin, S.T. *Macromolecules* **2004**, 37, 71.

148 Krebs, F.C.; Jorgensen, M. *Synth. Met*. **2004**, 142, 181.

149 Meghdadi, F.; Tasch, S.; Winkler, B.; Fischer, W.; Stelzer, F.; Leising, G. *Synth. Met.* **1997**, 85, 1441.

150 Kim, H.C.; Kim, J.S.; Kim, K.S.; Park, H.K.; Baek, S.S.; Ree, M.H. *J. Polym Sci. Polym. Chem*. **2004**, 42, 825.

151 Morgan. P. W. in *Encyclopedia of Polymer Science and Engineering*, 2nd Edn., Vol. 8, Mark, H. F., Kroschwitz, J. I.(Eds.), Wiley Interscience: NewYork, **1988**, 221.

152 Reisch, M. S. *Chem. Engg. News.* **1987**, 65, 9.

153 Morgan. P. W.in *Encyclopedia of Polymer Science and Engineering*, 2nd Edn., Vol.11, Mark, H. F., Kroschwitz, J. I. (Eds.), Wiley-Interscience: NewYork, 1988, p 381

154 Vollbracht, L. in *Comprehensive Polymer Sci.*Vol.5., 1st Edn., Allen, G.; Bevinaton, J.C.; Eastmond, G. C. (Eds.), Pergamon Press: Oxford, **1989**, 375.

155 Kwole, S. L.; Morgan, P. W.; Sorenson, W. R. US Patent Number 3,63,966, 1962.

156 a) Preston, J. *Polym. Eng. Sci*. **1975**, 15**,** 199. b) Bair, T.I.; Morgan, P.W.; Killion, P.L. *Macromolecules* **1977**, 10**,** 1396.

157 Morgan, P. W. *Chemtech* **1979,** 9**,** 316.

158 a) Ogata, N.; Tanaka H. *Polym. J*. **1971**, 2**,** 672. b) Ogata, N.; Tanaka, H. *Polym. J*. **1972**, *3***,** 365.

159 Yamazaki, N.; Higashi, F. *J. Polym. Sci. Polym. Lett.* **1974**, 12**,** 185.

160 Krigbaum, W.R.; Kotek, R.; Mihara,Y.; Prestone, J. *J. Polym. Sci.Polym. Chem.* **1985**, 23**,** 1907.

161 Imai, Y.; Oishi, Y. *Prog. Polym. Sci*. **1989**, 14**,** 173.

162 Lozano, A. E.; de Abajo, J.; de la Campa, J. G. *Macromolecules* **1997**, 30, 2507.

163 Simionescu, C.; Comanita, E.; Vata, M. *Angew. Makromol. Chem*. **1975**, 46**,** 135.

164 Onder, K.; Chsn, A. T. *Polym. Eng. Sci*. **1985**, 25**,** 942.

165 Wei, Y.; Jia, X.; Jin, D.; Davis, F. A.; Tarner, W. E. *Macromol. Rapid Commun*. **1996**, 17**,** 897.

166 Mitsui Toatsi Chemical Co. *Jpn. Kokai Tokkyo Koho*. JP 63,317,510, **1988.**

167 Mulik, U. P.; Ghatge, N. D. *J. Polym. Sci. Polym. Chem.* **1980,** 18**,** 1905,

168 Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1988**, 21**,** 1908.

169 Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1989**, 22**,** 4148.

170 Mallakour, S.; Kowsari, E. *Polym. Adv. Technol*. **2005**, 16, 732.

171 Oishi, Y.; Kakimoto, M.A.; Imai.Y. *Macromolecules* **1988**, 21, 547.

172 Imai, Y.; Maldar, N.N.; Kakimoto, M.A. *J. Polym. Sci.Polym. Chem*. **1985**, 23, 1797

173 Alvarez, J. C.; Garcia, J. M.; de la Campa, J. G.; de Abajo, J. *Macromol.Chem. Phys.* **1997**, 198, 3293.

174 Kajiyama, M.; Kudo, J.; Mizumachi, H. *J. Polym. Sci. Polym. Chem.* **1999**, 37, 1135.

175 Yang, C.P.; Oishi, Y.; Kakimoto, M.A.; Imai, Y. *J. Polym. Sci. Polym. Chem.* **1989**, 27, 3895.

176 Kajiyama, M.; Kudo, J.; Mizumachi, H. *J. Polym. Sci. Polym Chem.* **1999**, 37, 1135.

177 Valiyaveettil, S.; Gans, C.; Klapper, M.; Gereke, R.; Mullen, K. *Polym. Bull.* **1995**, 34, 13.

178 Alvarez, J.C.; Garcia, J.M.; de la Campa, J.G.; de Abajo, J. *Macromol.Chem. Phys.* **1997**, 198, 3293.

179 Ge, Z.; Yang, S.; Tao, Z.; Liu, J.; Fan, L. *Polymer* **2004**, 45, 3627.

180 Ferrero, E.; Espeso, J.F.; de la Campa, J.G.; de Abajo, J.; Lozano, A.E. *J. Polym. Sci. Polym. Chem.* **2002**, 40, 3711.

181 Valiyaveettil, S.; Gans, C.; Klapper, M.; Gereke, R.; Mullen, K. *Polym. Bull.* **1995**, 34, 13.

182 Espeso J.F., Jose G., Ferrero, E., De-Abajo J. *J .Polym. Sci. Polym. Chem*. **2001,** 39**,** 475.

183 Mathew, J.S. *Ph.D. Dissertation*, University of Pune, Pune, India, 2001.

184 Spiliopoulos, I.K.; Mikroyannidis, J.A. *Macromolecules* **1998**, 31, 1236.

185 Li, Y.; Ji, T.; Zhang, J. *J. Polym. Sci. Polym Chem.* **2000,** 38, 189.

186 E. I. DuPont deNemour and Co., Inc., Brit. Pat., 570,858 **1945.**

187 Privalko, V.P.; Mudrak, C.V.; Privalko, E.G.; Usenko, A.A.; Karpova, I.L. *Macromol. Symp*. **2001**, 175, 403.

188 Tussot, C. M.; Sagnier, C.; Pham, Q.T. *Macromol. Chem. Phys*. **2001**, 202, 1071.

189 Lin, C.; Xigao, J.; Haibin, Z.; Zhiyuan, W.; Wuhan, J. *Inst. Chem. Tech*. **2000**, 22, 29.

190 Ozarslan, O.; Yilmaz, T.; Yildiz, E.; Fiedeldei, U.; Kuyulu, A.; Gungor, A. *J. Polym. Sci.Polym. Chem.* **1997**, 35, 1149.

191 Yang, C.P.; Chen, Y.P.; Woo, E.M. *Polymer* **2004**, 45, 5279.

192 Liaw, D.J.; Chen, W.H. *Polymer* **2003**, 44, 3865.

193 Lee, C.; Iyer, N. P.; Min, K.; Pak, H.; Han, H. *J. Polym. Sci. Polym. Chem.* **2004**, 42, 137.

194 Hsu, M.F. *J. Appl. Polym. Sci.* **2003**, 88, 669.

195 Abid, S.; Gharbi, R. E.; Gandhini, A. *Polymer* **2004**, 45, 6469.

196 Imai, Y. *Plast, Eng.* (N. Y.) **1996**, 36, 49.

197 Wrasidlo, W.; Augl, J. M. *J. Polym. Sci. A-1*, **1969**, 7, 321.

198 a) De Abajo, J.; Gabarda, J.P.; Fontan, J. *Angew. Makromol. Chem*. **1978**, 71, 143. b) Maiti, S.; Ray, A.; Maiti, M. *Angew. Makromol. Chem*. **1982**, 107, 87.

199 Saini, A. K.; Carl-in, C. M.; Patterson, H.H. *J. Polym. Sci. Polym. Chem*. **1992**, 30, 419.

200 Babe, S. G.; De Abajo, J.; Fontan, J. *Angew. Makromol. Chem*. **1971**, 19, 121.

201 Reinecke, H.; De La Campa, J. G.; De Abajo, J. *J. Appl. Polym .Sci*. **1996**, 61, 923.

202 Higashi, F.; Hoshio, A.; Kiyogishe, J. *J. Polym. Sci*. **1983**, 21, 3241.

203 Yamazaki, N.; Iguchi, T.; Higashi, F. *Chem. Lett.* **1977**, 19, 185.

204 Kim, H. K.; Moon, I. K.; Lee, H. J.; Han, S. G.; Won, Y. H. *Polymer* **1998**, 39, 1719.

205 Oishi, Y.; Kakimoto, M.; Imai, Y. *J. Polym. Sci. Polym. Chem*. **1991**, 29, 1925.

206 Hong, Y. T.; Jin, M. Y.; Suh, D. H.; Lee, J. H.; Choi, K. Y. *Angew. Makromol. Chem*. **1997**, 248, 105.

207 Dezern, J.F. *Proc. Am. Chem. Soc.* **1990**, 63, 361.

208 M.K. Ghosh and K.L. Mittal, *Polyimides: fundamentals and applications*, Marcel Dekker, New York, **1996**.

209 Maglio, G.; Palumbo, R.; Schioppa, A.; Tesauro, D. *Polymer* **1997**, 38, 5849.

210 Lin, C.; Xigao, J.; Haibin, Z.; Zhiyuan, W.; Wuhan, J. *Inst. Chem. Tech*. **2000**, 22, 29.

211 Tamai, S.; Ohkawa, Y.; Yamaguchi, A. *Polymer* **1997**, 38, 4079.

212 Yi, M.H.; Huang, W.; Choi, K.Y. *Angew. Makromol. Chem*. **1998**, 258, 5.

213 Negi, Y. S.; Suzuki, Y.I.; Kawamura, I.; Kakimoto, M.A.; Imai, Y. *High Perfom. Polym*. **1998**, 10, 45.

214 Yang, C.P.; Chen, Y.P.; Woo, E.M. *Polymer* **2004**, 45, 5279.

215 Liaw, D.J.; Liaw, B.Y.; Kang, E.T. *Macromol. Chem. Phys*. **1999**, 200, 2402.

216 Liaw, D.J.; Chen, W.H. *Polymer* **2003**, 44, 3865.

217 Lee, C.; Iyer, N.P.; Min, K.; Pak, H.; Han, H. *J. Polym. Sci. Polym. Chem.* **2004**, 42, 137.

218 Mallakpour, S.E.; Hajipour, A.R.; Habibi, S. *J. Appl. Polym. Sci.* **2001**, 80, 1312.

219 Jonquieres, A.; Vicherat, A.; Lochon, P. *J. Polym. Sci. Polym. Chem*. **1999**, 37, 2873.

220 Yang, C.P.; Chen, R.S.; Hung, K.S.; Woo, E.M. *Polym. Int*. **2002**, 51, 406.

221 Chen, H.A.; Yang, C.P. *J. Appl. Polym. Sci*. **2000**, 77, 217.

222 Choi, K.H.; Lee, K.H.; Jung, J.C. *J. Polym. Sci. Polym. Chem*. **2001**, 39, 3818.

223 Frazer, A. H.; Wallenberger, F. T. *J. Polym. Sci. Polym. Chem.* **1964**, 2**,** 1171.

224 Frazer, A. H.; Sarasohn, I.M. ().*J. Polym. Sci. Polym. Chem.* **1966**, 4**,** 1649.

225 Srinivasan, M.; Jayalakshmi, G. *Chem. Ind*. **1985**, 339.

226 Frazer, A. H.; Reed, T. A. *J. Polym. Sci. C* **1967,** 19**,** 89.

227 Preston, J.; Black, W.B.; Hofferbert, W. L. *J. Macromol. Sci. Chem. A* **1973**, **7,** 45.

228 Afli, A.; Gharbi, S.; Gharbi, R.El; Bigot, Y.L.; Gandini, A. *Eur.Polymer J.,* **2002**, 38**,** 667.

229 Higashi, F.; Ishikawa, M. *J. Polym. Sci. Chem. Ed,* **1980**, 18**,** 2905.

230 Nanyan, M.J.; Kroschwitz, J.I. (eds) *Encyclopedia of polymer science and engineering* 2nd edition. John Wiley & Sons Inc., New York 1982.

231 a) Moldenhaur, O.; Back, H. US Pat. 2,349,979 **1944**. b) Beaman, RG. US Pat. 3,040,003 **1962**.

232 Vndenberg, E.J.; Overberger, C.G. *J. Polym. Sci.* **1963**, 141, 176.

233 Frazer, H.; Wallenberger, F.T. *J. Polym. Sci*. 1964, 2, 1147.

234 Ubale, V.P.; Sagar, A.D.; Maldar, N.N.; Birajdar, M.V. *J. Appl. Polym. Sci*. **2001**, 79, 566.

235 Shaikh, V.A.E.; Ubale, V.P.; Maldar, N.N.; Lonikar, S.V.; Rajan, C.R.; Ponrathnam, S. *J. Appl. Polym. Sci*. **2006**, 100, 73.

236 Abshire, C.J.; Marvel, C.S. *Makromol. Chem*. **1961**, 44–46, 388.

237 Bruma, M.G.; Neamtu, I.; Sava, J. *Macromol. Sci. Chem*. **1985**, 22, 833.

238 Saga, M.; Shono, T. *J. Polym. Sci.* **1966**, 4 B, 869.

239 Ueda, M.; Oda, M. *Polym. J. (Tokyo)* **1989**, 21, 193.

240 Frazer, A.H.; Wallenberger, F.T. *J. Polym. Sci. A* **1964**, 2, 1181.

241 Sava, I.; Schulz, B.; Zhu, S.; Bruma, M. *High Perform. Polym.* **1995**, **7**, 493.

242 Iwakura, Y.; Uno, K.; Hara, S. *J. Polym. Sci. A* **1965**, **3**, 45.

243 Hensema, E.R.; Boom, J.P.; Mulder, M.H.V.; Smolders, C.A. *J. Polym. Sci. Polym. Chem.* **1994**, 32, 513.

244 Schulz, B.; Leibnitz, B. *Acta Polym.* **1992**, 43, 343.

245 Schulz, B.; Bruma, M.; Brehmer,L. *Adv. Mater*. **1997**, 9, 601.

246 Gillo, M.; Ianelli, P.; Laurienzo, P.; Malinconico, M.; Roviello, A.; Mormile, P.; Petti, L. *Chem. Mater*. **2002**, 14, 1539.

247 Capitani, D.; Laurienzo, P.; Malinconico, M.; Proietti, N.; Roviello, A. *J. Polym Sci. Polym. Chem*. **2003**, 41, 3916.

248 Shigen, Z.; Schulz, B.; Bruma, M.; Brehmer, L. *Polym. Adv. Technol*. **1996**, 7, 879.

249 Carl, J.; Thaemlitz, P.; Cassidy, E. *Polymer* **1992**, 33, 206.

250 Yang, N.C.; Parl, Y.H.; Suh, D.H *J. Polym Sci. Polym. Chem*. 2003, 41, 674.

251 Nasr, M.A.M.; Kaseem, A.A.; Madkour, A.E.; Mohamed, Z.M.; Ali, A. *React. Funct. Polym*. **2003**, 65, 219.

252 a) Janietz, S.; Anlauf, S. *Macromol. Chem.. Phys*. **2002**, 203, 427. b) Janietz, S.; Anlauf, S.; Wedel, A. *Synth. Met*. **2001**, 122, 11. c) Hensema, E.R.; Sena, M.E.R.; Mulder, M.H.V.; Smolders, C.A. *J. Polym Sci. Polym. Chem*. **1994**, 32, 527.

253 Hsiao, S.H.; Yu, C.H. *J. Polym Sci. Polym. Chem*. **1998**, 36, 1847.

254 Hsiao, S.H.; Dai, L.R.; Le, M.H. *J. Polym Sci. Polym. Chem*. **1999**, 37, 1169.

255 Avitabile, G.; Gentile, G.; Laurienzo, P.; Malinconico, M.; Martuscelli, E.; Riva, F.; Volpe, M.G. *J. Polym Sci. Polym Phys*. **1999**, 37, 1687.

256 Meng, H.; Chen, Z.K.; Chang, W. *J. Phys. Chem. B*. **1999**, 103, 6429.

257 Huang, W.; Meng, H.; Yu, W.L.; Pei, J.; Chan, Z.K.; Lei, Y.H. *Macromolecules* **1999**, 32, 118.

258 Ojha, U.P.; Krishnamoorthy, K.; Anil Kumar, *Synth. Met*. **2003**, 132, 279.

259 Conix, A. J. *Ind. Chim. Belg*. **1957**, 22, 1457.

260 Korshak, V. V. *The Chemical Structure and Thermal Characterization of Polymers*, Israel Program for Scientific Translations, Keter, London, **1971**.

261 a) Eareckson, W.H. *J. Polym. Sci. Polym. Chem*. **1959,** 40, 399. b) Vinogradova, S.V.; Vasnev, V.A.; Valetskii, P.M. *Russ. Chem. Rev*. **1994**, 63, 833. c) Villegas-Coss, I.; Ruiz-Trivino, F.A.; Hernandez-Loez, S. *J. Polym. Sci. Polym. Phys*. **2006**, 44, 256. d) Bucio, E.; Lara-Estevez, J.C.I.; Ruiz-Trivino, F.A; Acosta-Huerta, A. *Polym. Bull*. **2006**, 56, 163.

262 Temin, S.C. in *Interfacial Syntheis, Vol II: Polymer Applications and Technology*, Millich, F.; Carraher, C.E.J. (Eds.), Marcel Dekker, New York, **1977**.

263 Starks, C.M. *J. Am. Chem. Soc*. **1971**, 93, 195.

264 Borissov, G.; Sivriev, H. *Makromol. Chem*. **1972**, 158, 215.

265 Vasnev, V.A; Vinogradova, S.V. *Russ. Chem. Rev*. **1979**, 48, 16.

266 Bucio, E.; Fitch, J.W.; Venumbaka, S.R.; Cassidy, P.E. *Polymer* **2005**, 46, 3971.

267 Jeong, H.J.; Iwasaki, K.M.; Kakimoto, M.A.; Imai, Y. *Polym. J*. **1994,** 26, 379.

268 Korkshak, V.V.; Vinogradova, S.V. and Lebedeva, A.S., *Vysokomol. Soedin. Ser.A*, **1959**, 1, 1482.

269 a) Blaschke, F.; Ludwing,W. US 3,395,119, **1968**. b) Schnell, H.; Boilert, V.; Fritz,G. US 3,335,167, **197**1. c) Inata, H.; Kawase, S.; Shima, T. US 3,972,852, **1974**. d) Kosanovich, G.M.; Salee, G. US 4,465,819, **1984**.

270 a) Chung, T. S. *Polym. Eng. Sci*. **1986**, 26, 901. b) Riecke, E. E.; Hamb, F. L. *J. Polym. Sci. Polym. Chem*. **1977,** 15, 593.

271 a) Bier, G. *Polymer* **1974**, 15, 527 b) Mahajan, S. S.; Idage, B. B.; Chavan, N. N.; Sivaram, S. *J. Appl. Polym. Sci*. **1996**, 61, 2297.

272 a) Kricheldorf, H. R.; Schwarz, G. *Polym. Bull*. **1979**, 1, 383. b) Kricheldorf, H. R.; Zang, Q. Z.; Schwarz, G. *Polymer* **1982**, 23, 1821. c) Kricheldorf, H. R. and Schwarz, G. *Makromol. Chem*. **1983**, 184, 475.

273 a) Higashi, F. *Polym. Appl. (Jpn.)* **1984**, 33, 171. b) Kitayama, S.; Sanui, K.; Ogata, N. *J. Polym. Sci. Polym. Chem*. **1984,** 22, 2705. c) Higashi, F.; Akiyama, N.; Koyama, T. *J. Polym. Sci. Polym. Chem*. **1983**, 21, 3233. d) Higashi, F.; Hoshio, A.; Kiyoshige, J. *J. Polym. Sci. Polym. Chem*. **1983**, 21, 3241. e) Liaw, D. J. *J. Polym. Sci. Polym. Chem*. **1995,** 33, 605. f) Matsukawa, K.; Inoue, H. *J. Polym. Sci. Polym. Lett*. **1990,** 28, 13.

274 a) Yoneyama, M.; Kakimoto, M.A.; Imai, Y. *Macromolecules* **1989**, 22, 2293. b) Jun, C.L.; Park, N. J.; *Pollimo* **1995,** 19, 676.

275 Morgan P.W. *Macromolecules* **1970**, 3, 536.

276 Hsiao, S.H.; Chiang, H.W. *Eur. Polym. J.* **2004,** 40, 1691.

277 Krigbaum, W.R.; Asrar, J.; Tariumi, H.; Ciferri, A.; Preston, J. *J. Polym. Sci.Polym. Lett.* **1982,** 20, 109.

278 Branion, S.; Vladimir B. *Synth. Comm.* **2006**, 36, 2121.

279 Robson, L.M.; Tibbit J.M., *History of polyarylates* in Seymour R.B., Krishenbaum, G.S. editors, *High Performance Polymers: Their Origin and Developments*. Amsterdam: Elsevier: **1986**, 95.

280 a) Jo, B.W.; Lenz, R.W. Jin J.I. *Makromol. Chem. Rapid Commun*. **1982**, 3, 23. b) Zhou, Q. F. *Ph.D. Thesis*, University of Massachusetts, **1983**.

281 a) Wang, D.H.; Stephen Z.D.; Cheng; Harris, F.W. *Polymer* **2008**, 49, 3020. b) Adam, A.; Spiess, H.W. *Makromol. Chem. Rapid Commun*. **1990**, 11, 249.

282 Ahn, Y.H.; Chang, J.H. *Polym. Adv. Technol*. **2008**, 19, 1479.

283 Lee, S.W.; Lee, M. *J. Polym. Sci. Polym. Chem*. **2004**, 42, 1322.

284 Centore, R.; Roviello, A.; Sirign, A. *Macromol. Chem. Phys*. **1994**, 195, 3009.

285 Kakali, F.; Kallitis, J.; Pakula, T.; Wegner, G. *Macromolecules* **1998**, 31, 6190.

286 Lee, J.W.; Jin, J.J.; Jo, B.W.; Kim, J.S.; Zin, W.C.; Kang, Y.S. *Acta. Polym*. **1999**, 50, 399.

287 Pixton, M.R.; Paul, D.R. *J. Polym. Sci. Polym. Phys.* **1995**, 33, 1135.

288 Kharul, U.K.; Kulkarni, S.S. *Bull. Mater. Sci.* **1994**, 17, 1071.

289 Pixton, M.R.; Paul, D.R. *J. Polym. Sci. Polym. Phys.* **1995**, 33, 1353.

290 Chen, Y.; Wombacher, R.; Wendroff, J.H.; Greiner, A. *Polymer* **2003**, 44, 5513.

291 a) Hsiao, S.H.; Chiang, H.W. *Eur. Polym. J.* **2004**, 40, 1691. b) Korshak, V.V. *The Chemical Structure and Thermal Characterization of Polymers*, Israel Program for Scientific Translations, Keter, London, **1971**.

292 Liaw, D.J.; Liaw, B.Y.; Hsu, J.J.; Cheng, Y.C. *J Polym Sci. Polym. Chem.* **2000**, 38, 4451.

293 Liu, B.; Dong, Y.; Hu, W.; Chen, C.; Wang, G.; Wu, Z. *Polym. Prepr.* **2000**, 41, 1268.

294 a) Jeong, H.J.; Iwasaki, K.; Kakimoto, M.; Imai, Y. *J. Makromol. Sci. Pure Appl. Chem*. **1994**, A31, 1975. b) Jeong, H.J.; Kakimoto, M.; Imai, Y. *J. Polym. Sci. Polym. Chem* **1991**, 29, 1293.

295 Watanabe, S.; Murayama,H.; Murata, M.; Tanabe,M.; Imai,Y. *J. Polym. Sci. Polym .Chem.* **1998**, 36, 2229.

296 Watanabe, S.; Imai,Y.; Kobayashi S. *J. Polym. Sci. Polym. Chem.* **1994**, 32, 909.

297 Rao, M.V.; Rojivadiya, A.J.; Parsania, P.H.; Parekh, H.H. *J. Macroml. Sci. Chem*. **1990**, A27, 53.

298 Shingate, R. D. *Ph. D. Dissertation*, The University of Pune, **2006**.

299 Morgan P. W. US 3,546,165, **1970**.

300 Jager, J.; Hendriks, A. J. *J. Appl. Polym. Sci*. **1995**, 58, 1465.

301 Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers,* Gordon and Breach: Basel, Switzerland, **1995**, pp 45.

302 a) Stainland, P.A.; Alleb, G.; Berington J.C. Eds. *Comprensive Polymer Science*, Pergamon Press, New York, **1989**. b) Labadie, J.W.; Hedric, J.L.; Ueda, M; Eds. *Step Growth Polymers for High Performance Materials, New Synthetic Method*, ACS Symposium Series 624, American Chemical Society, Washington, **1996**.

303 a) Johnson, R.N.; Farnham, A.G. *J. Polym. Sci. Polym. Chem. Ed.* **1967**, 5, 2415. b) Farnham, A.G.; Robeson, L.M.; McGrath, J.E. *J. Appl. Polym. Sci. Symp*. **1975**, 26, 373. c) Mandal, B.K.; Maiti, S. *Eur. Polym. J*. **1986**, 22**,** 447. d) Maiti, S.; Mandal, B.K. *J. Polym. Mater.* **1992**, 9, 9.

304 a) Colquhoun, H.M.; Dudman, C.C.; Thinass, M.; O'Mahoney, C.A.; Williams, D.J. *J. Chem. Soc. Chem. Comm.* **1990**, 3, 336. b) Xie, D.; Gibson, H.W. *Macromol. Chem.* **1996**, 197, 2133. c) Chen, M.; Gibson, H.W. *Mocromolecules* **1996**, 29, 5502.

305 Kricheldorf, H.R.; Delius, U.; Tonnes, K.U. *New Polym. Mater.* **1988**, 1, 127.

306 a) Rose, J.B. *NATO ASI Ser. Ser. C* **1987**, 215, 207. b) Chang, I.Y. *Sci. Adv. Matl. Proc. Eng. Ser.* **1988**, 33, 194.

307 a) Cotter, R.J. *Engineering Thermoplastics, A Handbook of Poly(arylene ether)s*, Gordon and Breach, Postfach, Switzerland, **1995**. b) Colon, I.; Kwiatkowski, G.T. *J. Polym. Sci.Part A-1* **1990**, 28, 367.

308 Bonner, W. H. US 3,065,205 **1962**.

309 Goodman, I.; McIntyre J. E.; Russell, W. GB 971,227 **1964**.

310 Iwakura Y.; Uno, K.; Takiguchi, T. *J. Polymer Sci. Part A-1* **1968**, 6, 3345.

311 Marks, B. M. US 3,441,538 **1964**.

312 Rose J. B. EP 63,874 **1982**.

313 Jansons, V.; Dahl, K. *Macromol. Chem., Macromol. Symp*. **1991**, 51, 87.

314 a) Percec, V.; Clough, R.S.; Grigoras, M.; Rinaldi, P.L.; Litman, V.E., *Macromolecules* **1993**, 26, 3650. b) Percec, V.; Clough R.S.; Rinaldi, P.L.; Litman, V.E. *Macromolecules* **1991**, 24, 5889.

315 Percec, V.; Grigoras, M.; Clough, R.S. Fanjul, J. *J. Polym. Sci. Poly. Chem*. **1995**, 33, 331.

316 Johnson, R.N.; Farnham, A.G.; Clendinning, R.A.; Hale, W.F. Merriam, C.N. J. Polym. Sci. **1967**, 5, 2375.

317 Mohanty, D.K.; Sachdeva, Y.; Hedrick, J.L.; Wolfe, J.F.; McGrath, J.E. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr*. **1984**, 25, 19.

318 Kricheldorf, H. R.; Bier, G. Polymer **1984**, 25, 1151

319 Wang, S.; McGrath, J.E. *Synthesis of Poly(Arylene Ether)s* in Synthetic Methods in Step-Growth Polymers, Rogers, M.E.; Long, T.E. (Eds.); John Wiley & Sons. Inc., New Jersey, **2003**, 327.

320 Brunelle, D. J.; Shannon, T. G. *Macromolecules* **1991**, 24, 3035.

321 Chen, M. *A Ph D Dissertation* Virginia Polytechnic Institute and State University, **1997**.

322 Hergenrother, P.M.; Jensen, B.J.; Havens, S.J. *Polymer* **1988**, 29, 358.

323 Gardner, K.H.; Hsiao, B.S.; Matheson, R.R.; Wood, A.A. *Polymer* **1992**, 33, 2483.

324 Staniland, P.A.; Wilde, C.J.; Bottino, F.A.; Di Pasquale, G.; Pollicino, A.; Recca, A. *Polymer* **1992**, 33, 1976.

325 Risse, W.; Sogah, D.Y. *Macromolecules* **1990**, 23, 4029.

326 Ueda, M. J.; Sugiyama; Yokota, H. *Polym. Prep. Jpn.* **1992**, 41, 362.

327 Rao, V.L.; Sabeena, P.U.; Saxena, A.; Gopalkrishnan, C.; Krishnan, K.; Ravindran, P.V.; Ninan, K.N. *Eur. Polym. J*. **2004**, 40, 2465.

328 Taguchi, Y.; Uyama, H.; Kobayashi, S. *J. Polym. Sci. polym. Chem*. **1996**, 34, 561.

329 Ge, X.C.; Xu, Y.; Xiao, M.; Meng, Y.Z.; A.S. Hay. *Eur. Polym. J*. **2006**, 42, 1206.

330 Granewald, S.; Cassidy, P.E. Witch, J.F.; Arbaugh, J.; Herbold, H.; Jurele, D. *High Perform. Polym*. **2001**, 13, S117.

331 Pang, J.; Zhang, H.; Li, X.; Jiang, Z. *Macromolecules* **2007**, 40, 9435.

332 Chen, G.; Zhang, X.; Zhang, S.; Chen, T.; Wu, Y. *J. Appl. Polym. Sci*. **2007**, 106, 2808.

333 Maier, G.; Banerjee, S.; HauBmann, J.; Sezi, R. *High Perform. Polym*. **2001**, 13, S107.

334 Liu, D.; Wang, Z. *Polymer* **2008**, 49, 4960.

335 Zhang, S.; Fu, L.; Lu, J.; Yang, D.; Gao, Z.; Jia, H.; Zhang, Y.; Wu, Z. *Macromol. Chem. Phys*. **2000**, 201, 649.

336 Liu, B.; Hu, W.; Chen, C.; Jiang, Z.; Zhang, W.; Wu, Z.; Matsumoto, T. *Polymer* **2004**, 45, 3241.

337 Shang, H.; Li, X.; Xiao, M.; Meng, Y. *Polymer* **2006**, 47, 3807.

338 Sing, R.; Hay, A.S. *Macromolecules* **1992**, 25, 1017.

339 Keitoku, F.; Kakimoto, M.A.; Imai, Y. *J. Polym. Sci. Polym. Chem*. **1994**, 32, 317.

340 Hoffmann, U.; Klapper, M.; Mullen, K. *Polym. Bull*. 1993, 30, 481.

341 Kelsey, D.R.; Robeson, L.M.; Clendinning, R.A. *Macromolecules* **1987**, 20, 1204.

342 Risse, W.; Sogah, D.Y. *Macromolecules* **1990**, 23, 4029.

343 Kricheldorf, H.R.; Delius, U. *Makromol. Chem*. **1989**, 190, 1277.

344 Liu, B.; Hu, W.; Jin Y.; Chen, C.; Jiang, Z.; Wu, Z.; Matsumoto, T.; Matsumura, A. *Macromol Chem. Phys*. **2004**, 205, 1677.

345 a) Liu, B.; Hu, W.; Rao, X.; Wang, G.; Jiang, Z.; Wu, Z.; Matsumoto, T. *Polym. Bull.* **2004**, 52, 235. b) Liu, B.; Wang, G.; Hu, W.; Jin, Y.; Chen, C.; Jiang, Z.; Zhang, W.; Wu, Z.; Wei, Y. *J. Polym. Sci. Polym. Chem*. **2002**, 40, 3392.

346 Wang, L.; Meng, Y. Z.; Wang, S. J.; Hay, A. S. *J. Polym. Sci.Polym. Chem.* **2004**, 42, 1779.

347 Strukelj, M.; Hay, A. H. *Macromlecules* **1991**, 24, 6870.

348 Jeong, H.J.; Iwasaki, K.; Kakimoto, M.; Imai, Y. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, A31, 1975.

349 Watambe, S.; Kobayashi, A.; Kakimoto, M.; Imai.; Y. *J. Polym. Sci. Polym. Chem.* **1994**, 32, 909.

350 Mathias L. J.; Lewis, C. M.; Wiegel, K. N. *Macromolecules* **1997**, 30, 5970.

351 Aitken .C.L.; Koros, W.J.; Paul, D. R. *Macromolecules* **1992**, 25, 3424.

352 Pixton, M. R.; Paul, D. R. *Polymer* **1995**, 36, 3165.

353 a) Liu, Z. *Thermochim. Acta*. **1991**, 183, 73. b) Wang, Z.; Chen, T.; Xu, J. *Macromolecules* **2000**, 33, 5672.

354 a) Reuter, K.; Weymans, G.; Freitag, D.; Dehin, R.; Meier, E.; Muller, G. EP 0362603 A1, **1990**.
b) Reuter, K.; Weymans, G.; Freitag, D.; Dehin, R.; Meier, E.; Muller, G. EP 0364741 B1, **1990.**

Chapter 2

Scope and Objectives

In our daily lives, we are inevitably constantly confronted with the polymer materials. On the one hand, we ourselves largely consist of polymers (biopolymers such as DNA) in addition to water and on the other hand, our daily lives are no longer conceivable without polymer materials. To date, most of the monomers that are used to prepare polymers are derived from petroleum sources. The utilization of fossil fuels in the manufacture of plastics accounts for about 7% of worldwide oil and gas.[1,2] These fossil resources particularly, petrol and natural gas, will arguably be depleted within one or three generations. Due to the depletion of petroleum resources and their escalating prices, polymer chemists have turned their attention to obtain the monomers and polymers from renewable resource materials.[3-6] The use of renewable raw materials can significantly contribute to a sustainable development usually interpreted as ''acting responsibly to meet the needs of the present without compromising the ability of future generations to meet their own needs''.[7] In ages of depleting fossil oil reserves, it is obvious that the utilization of renewable raw materials wherever and whenever possible is one necessary step towards a sustainable development.

Plant-derived fats and oils bear a large potential as substituents of currently used petrochemicals. The fine chemicals, monomers and polymers can be derived from these resources.[8-11] The synthesis of monomers as well as polymers from renewable resources derived fats and oils has already found some industrial applications and recent developments in this field offer promising new opportunities.[9-11,12] Some of the most widely applied renewable raw materials in the chemical industry for non-fuel applications include plant oils, polysaccharides (mainly cellulose and starch), sugars, wood, and others.[13-15] The use of oleochemical derivatives is dominated by applications in the field of surfactants and emulsifiers. The main field for the oleochemical industry is the preparation of soaps which are based on fatty acids or triglycerides, and other types of surfactants.[16] These other surfactants are mostly based on fatty alcohols and have a wide range of applications in detergents or as emulsifiers. There is also a remarkable amount of highly specialized uses for example in lubricants and as additives to modify the characteristics of polymers. Besides this, some products have been developed on the basis of oleochemical building blocks in the polymer backbone. Starting with oleic acid, the difunctional azelaic acid (C-9) is produced by ozonolysis for application in high-value polyesters and polyamides.[16] Pyrolysis of castor oil or ricinoleic acid is the commercial route to sebacic acid (C-10).[16] Castor oil itself is used as a polyol for the production of polyurethanes.[16] Similar polyols with modified viscosity and application characteristics are made by epoxidation and ring-opening reactions of unsaturated fatty acid derivatives.[16] Glycerol is also an intermediate in the synthesis of a large number of compounds used in industry.[17-19] The spectacular rise in glycerol production associated with the booming biodiesel industry, and its consequent drop in price, has accelerated considerable scientific and technological research aimed at multiplying its uses.

The use of oleochemical products as a part of the polymer backbone is a minor application field for oleochemical products because of the lack of di- or multifunctionality in most oils. However, some oleochemical derivatives overcome this limitation by having special application properties which allow them to find a market in the polymer field.[16]

Among oleochemicals, Cashew Nut Shell Liquid (CNSL) constitutes a major contribution to the renewable raw materials. CNSL, obtained as a by-product of cashew processing industry, is unique in that it contains phenolic moiety with an unsaturated 15- carbon side chain. It's extraction, chemistry and composition have been well documented.[20] Cardanol-a distilled product of CNSL consists of one *meta*-alkyl phenol and three *meta*-alkenyl phenols with alkenyl chains differing in their degree of unsaturation. The dual phenolic/ alkenyl nature of CNSL makes it an ideal natural raw material for the synthesis of water-resistant resins and polymers. Considerable attention from polymer scientists throughout the world is devoted to utilize its potential attributes as a substitute for petrochemical derivatives and has found use in phenolic resins in break lining, surface coatings and other miscellaneous applications.[20-24] Of late, it has been used in the preparation of many specialty materials such as liquid crystalline polyesters, cross-linkable polyphenols, polyurethanes and a range of other speciality polymers and additives.[20,22,23] In spite of the massive literature accumulated on the applications of CNSL, many areas remain which have yet to utilize this attractive raw material. The use of CNSL in the field of step-growth polymers has not been fully exploited. Thus, design and synthesis of difunctional condensation monomers for high performance polymers could be an attractive proposition.

One of the approaches to improve solubility and processability of high temperature/ high performance polymers is the attachment of flexible chains as pendant groups.[25-28] It is interesting to note that the peculiar structure of the main chain of such polymers is not altered by the attachment of flexible side chains. It is reported that the use of monomers bearing pendant flexible groups greatly reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. In general, such pendant groups not only bring about improved solubility but also help lower the melting and glass transition temperatures.[29,30]

Thus, our synthetic research effort was directed towards designing monomers with features that disturb structural regularity and chain packing hence imparting improved processability characteristics to the polymers. The goal of the present research was to utilize an opportunity provided by the nature, a phenolic moiety with flexible pentadecenyl chain. The combination of phenolic character and flexible chain of cashew nut shell liquid offers a wide variety of possibilities for the synthetic chemist. The approach involved making use of 3-pentadecyl phenol, which in turn is obtained from cashew nut shell liquid. Taking into account these features of 3-pentadecyl phenol, various difunctional monomers such as aromatic dibromide, diacid, diacylhydrazide, diamines, diisocyanate, and bisphenols were designed and synthesized. Design criteria for monomers

containing ether moiety was selected for the following reasons: i) it is well known that aromatic ether linkages inserted in the polymer main chains provide them with a significantly lower energy of internal rotation; ii) the presence of flexible pentadecyl chain on only one phenyl ring offers asymmetry to the polymer backbone leading to constitutional isomerism, which could impart interesting properties to the polymers derived. The second set of monomers, i.e. bisphenols was designed in such a way that presence of pendant pentadecyl chain would reduce strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect and consecutively aid in improved solubility and processability.

Another important aspect in designing of monomers was presence of flexible linear pentadecyl chain. The existence of long alkyl chain along the polymer backbone offers a great improvement in the polymer processability. In general, such long alkyl chains not only bring about improved solubility but also help lower the melting and glass transition temperatures.[29,30] This phenomenon is known as internal plasticization. Plasticization normally involves the incorporation of a low molecular weight plasticizer which improves polymer flow and processability. In internal plasticization, the plasticizer is chemically attached to or incorporated in the polymer backbone.[31]

The second objective of this research was to investigate the effect of incorporation of pendant pentadecyl chain on the properties of polymers, such as solubility, thermal transitions and heat resistance. For this study, polymers such as polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(etherketone)s and poly(ethersulfone)s were synthesized and characterized, thus, permitting the establishment of a reliable structure-property relationship. Based on these objectives, the following specific problems were chosen for the present work**.**

1. Design and synthesis of difunctional monomers *viz* dibromide, diacid, diacylhydrazide, diamines and diisocyanate containing flexibilizing ether linkage and pendant pentadecyl chain starting from CNSL.
2. Synthesis of a bisphenol containing pendant pentadecyl chain utilizing CNSL as a starting material.
3. Synthesis of a bisphenol containing cyclohexylidene moiety with flexible pentadecyl chain starting from CNSL.
4. Synthesis of polyazomethines, polyamides, poly(amideimide)s, polyhydrazides and polyoxadiazoles containing ether moiety and pendant pentadecyl chains.
5. Synthesis of aromatic polyesters, poly(ether ketone)s and poly(ether sulfone)s based on bisphenols containing pentadecyl chains.
6. To study the effect of the incorporation of pentadecyl chains on polymer properties such as solubility and thermal behavior.

References:

1. Okada, M. *Prog. Polym. Sci*. **2002**, 27, 87.

2. Weisz, P.B. Phys. Today, **2004**, 7, 47.

3. Ragauskas, A. J.; Wiliams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, L. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006,** 311, 484.

4. Lichtenthaler, F. W.; Peters, S. *C. R. Chem.* **2004,** 7, 65.

5. Lorenz, P.; Zinke, H. *Trends Biotechnol.* **2005,** 23, 570.

6. Kamm, B.; Kamm, M. *Appl. Microbiol. Biotechnol.* **2004,** 64, 137.

7. http://www.un.org/esa/sustdev; Report of the United Nations Conference on Environment and Development, Rio de Janeiro, **1992**.

8. Gunera, F. S.; Yagci, Y.; Erciyes, A. T. *Prog. Polym. Sci*. **2006**, 31, 633.

9. Gandini, A. *Macromolecules*, **2008**, *41*, 9491.

10. Sharma, V.; Kundu, P. P. *Prog. Polym. Sci.* **2006,** 31, 983.

11. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. *Chem. Soc. Rev.* **2007,** 36, 1788.

12. Vemula, P.; John G. *Acc.Chem. Res.* **2008**, 41 769.

13. Eissen, M.; Metzger, J.O.; Schmidt, E.; Schneidewind, U. *Angew. Chem., Int. Ed*. **2002**, 41, 414.

14. Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev*. **2006**, 106, 4044.

15. Metzger, J. O. *Angew. Chem., Int. Ed*., **2006**, 45, 5045.

16. Heidbreder, A.; Höfer, R.; Grützmacher, R.; Westfechtel, A.; Blewett. C.W. *Fett/Lipid* **1999**, S. 418.

17. Johnson, D. T.; Taconi, K. A. *Environ. Progr*. **2007,** 26, 338.

18. Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008,** 10, 13.

19. Pagliaro, M.; Rossi, M. *The Future of Glycerol*; RSC Publishing: Cambridge, **2008.**

20. Lubi, M.C.; Thachil, E.T. *Des. Monomers and Polym.* **2000**, 3, 123.

21. Suresh, K.I.; Kishanprasad, V.S. *Ind. Eng. Chem. Res*. **2005**, 44, 4504.

22. Tullo, A.H. *Chem. Engg News*. **2008**, 86, 26.

23. Mele, G.; Vasapollo, G. *Mini-Rev in Org. Chem*. **2008**, 5, 243.

24. Gedam, P.H.; Sampathkumaran, P.S. *Prog. Org. Coatings*. **1996**, 14, 114.

25. Kim, D. H.; Jung, J. C. *Polym. Bull*. **2003**, *50*, 311.

26. Jung, J. C.; Lee, K. H.; Sohn, B. S.; Lee, S. W.; Ree, M. *Macromol. Symp*. **2001**, 164, 227.

27. Ho, K.; Choi, H.; Lee, K.H.; Jung, J.C. *J. Polym. Sci. Polym. Chem*. **2001**, *39*, 3818.

28. Wang, H. *Ph.D. Dissertation;* UMI No. 9925168, The University of Akron, USA, **1999.**

29. Sathav, J. R.; Harris, F. W. *Polymer* **1995**, *36*, 4911.

30. Wang, H.; Shen, Z.; Cheng, S.Z.D.; Harris, F.W. *Polym. Prepr*. **1999**, *40*, 88.

31 Braun, D.; Cherdron, H.; Rehahn, M.; Ritter, H.; Voit, B. *Polymer Synthesis: Theory and Practice: Fundamentals, Methods, Experiments*, Springer-Verlag Berlin Heidelberg, **2005**, 359

Chapter 3

Synthesis and Characterization of Condensation Monomers

3.1 Introduction

Cashew nut shell liquid (CNSL)-a by-product of the cashew processing industry- is abundantly available worldwide (1,25,000 tpa).[1] CNSL is a product of cashew tree, *Anacardium occidentale*[2] and occurs as a greenish-yellow viscous liquid in the soft honeycomb of the shell of the cashew nut. Cashew nut consists of an ivory colored kernel covered by a thin brown membrane (testa) and enclosed by an outer porous shell-the mesocarp- with a honeycomb structure, where CNSL is stored **(Figure 3.1)**.

Figure 3.1 (a) Cross section of cashew nut (b) Cashew fruit (c) Cashew nut shell liquid

CNSL is available in many parts of the world, such as, Brazil, India, Bangladesh, Tanzania, Kenya, tropical regions of Africa and South-East and Far-East Asia. Traditionally, a number of methods are employed to extract the oil from the nuts. Hot oil bath method where raw nuts are passed through a bath of hot CNSL at 180-200°C and roasting method are commonly used ones. Reports are also available on using steam distillation, solvent extraction, supercritical extraction using a mixture of CO_2 and isopropyl alcohol for extraction of CNSL.[1]

Industrial grade CNSL is reddish brown in color. CNSL constitutes about 20-25% of the weight of cashew. Crude CNSL represents one of the major and cheapest sources of naturally occurring non-iso-prenoid phenolic lipids such as; anacardic acid, cardol, cardanol and 2-methyl cardol[1] **(Figure 3.2)**.

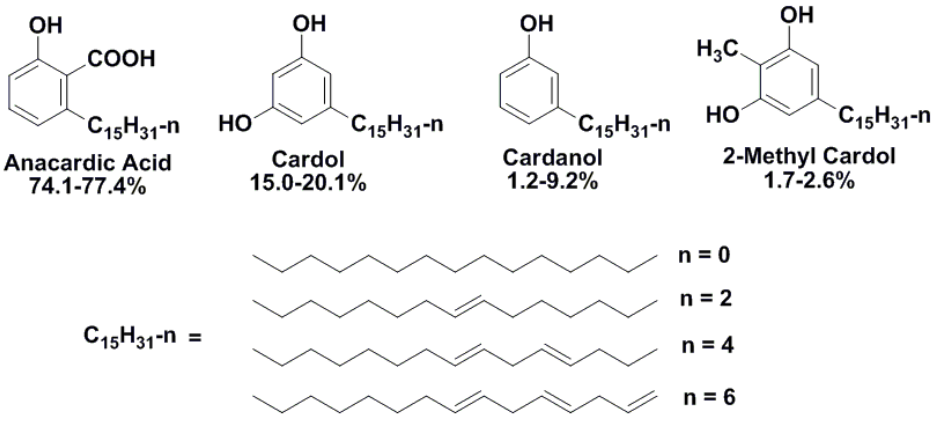


Figure 3.2 Constituents of Cashew Nut Shell Liquid (CNSL)

Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during roasting process, which converts anacardic acid to cardanol. Unsaturated 15- carbon chain and phenolic moiety in CNSL has offered a variety of possibilities for the synthetic chemist. Many reactions of CNSL such as, hydrogenation, polymerization, sulfonation, nitration, halogenation, etherification, esterification, epoxidation, phosphorylation, etc. have been documented in various patents and published reports.[1,3-5]

Considerable attention from polymer scientists throughout the world is devoted to utilize potential attributes of CNSL as a substitute for petrochemical derivatives and has found use in phenolic resins in break lining, surface coatings, adhesives, foundry resins, laminates, rubber compounding, additives, etc. Of late, CNSL has been used in the preparation of many specialty materials such as liquid crystalline polyesters, nanotubes, cross-linkable polyphenols, polyurethanes and a range of other specialty polymers and additives.[1,3] The number of chemicals that have been synthesized starting from CNSL is too large to be catalogued here. Nevertheless, representative value-added chemicals synthesized from CNSL are presented in **Table 3.1**.

Considering special structural features of cardanol and need for finding better opportunities for an appropriate utilization of this material, new strategies can be developed to design specialty/ high performance polymers from cardanol.

One of the most important criteria that determines the final properties of a polymer is the structure of monomers and by selecting suitable monomers properties of a polymer could be tailored.[6-8] Therefore, in the synthesis of polymer the first step constitutes the synthesis of desired monomers, which can give rise to polymers with expected / targeted properties.

In the area of high performance polymers such as polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyazomethines, polyetherketones and polyesters, etc., a large number of difunctional monomers have been synthesized in the past three decades with a view to overcome the traditional processing problems caused by the limited solubility and poor processability of these polymers. Efforts devoted to incorporating the structural features that improve processability have led to an outstanding enrichment of the chemistry of high performance polymers, and have allowed the opening of new investigations and application areas for these polymers.[9,10]

CNSL has special structural features like phenolic moiety with an unsaturated 15- carbon side chain. Hydrogenated cardanol- a long chain alkyl phenol with an aliphatic chain in the *meta* position- represents a versatile and easily available precursor to various derivatives. Taking these attractive aspects into consideration, a variety of new monomers *viz.*, dihalide, diacid, diacylhydrazide, diamines, diisocyanate and bisphenols were designed and synthesized starting from cashew nut shell liquid-a cheap and commercially available raw material.

Table 3.1 CNSL-based chemicals

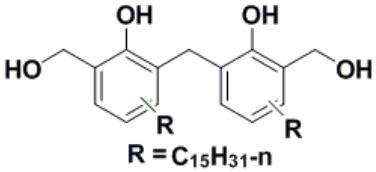
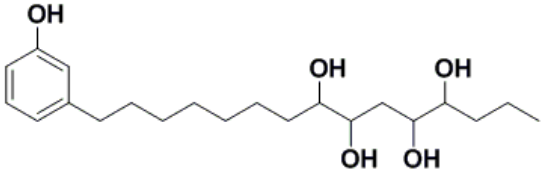
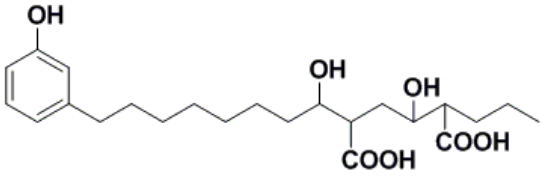
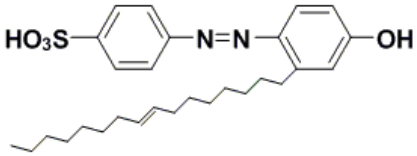
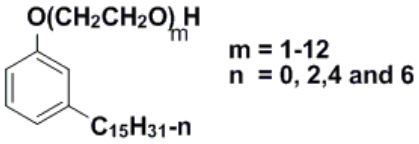
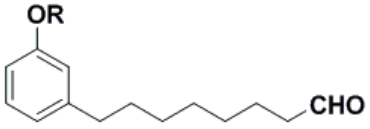
Sr. No.	CNSL-based Chemicals	Applications	Ref
1	  	• Foundry binder • Novolac resins	11, 12
2	 	Polyol for polyurethane	13
3.		Anionic surfactant for polypyrrole nanospheres	14,15, 16
4.		Surfactant composition	17
6.		Quaternary ammonium salts as phase transfer catalyst	18

Table 3.1 Continued…….

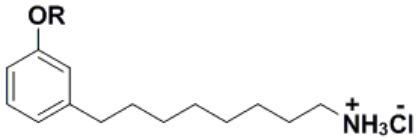
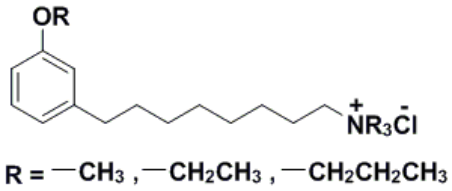
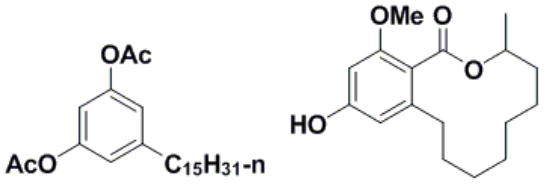
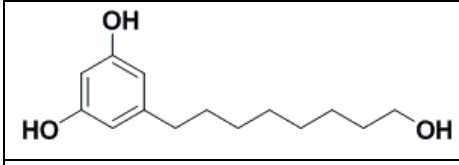
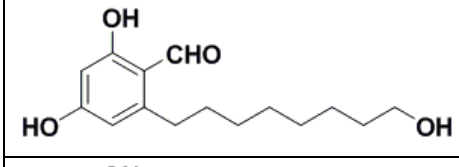
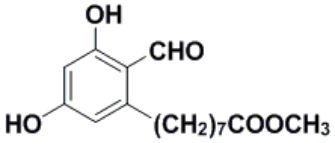
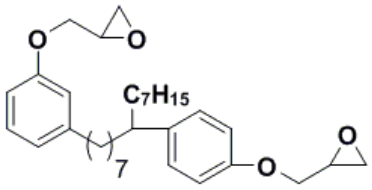
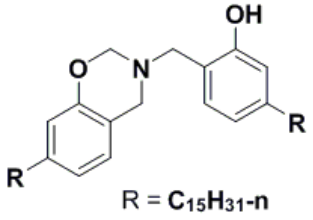
	  		
7.	    	Conversion of cardols (6-alkenyl resorcinols) into lasiodiplodin, a naturally occurring 12-membered orsellinic acid type macrolide, which exhibits plant growth regulating and antileukemic properties	19
13.	 	Lipophilic epoxy modifier for viscosifiers in drilling fluids	20
14.	 	Polybenzoxazines	21

Table 3.1 Continued…….

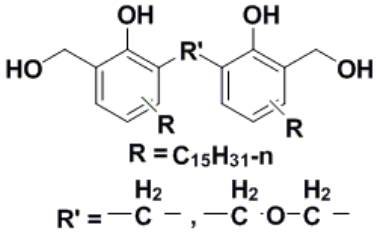
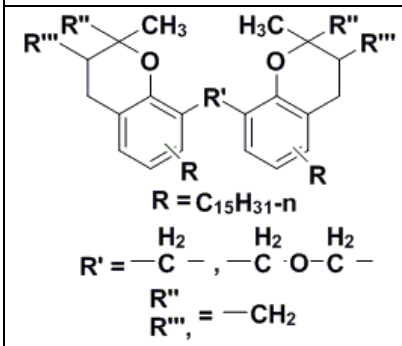
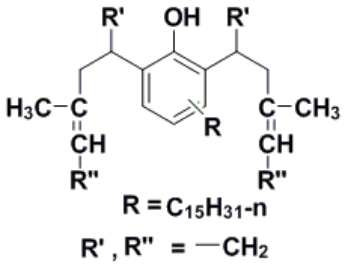
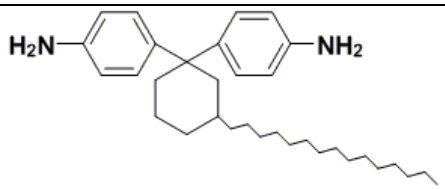
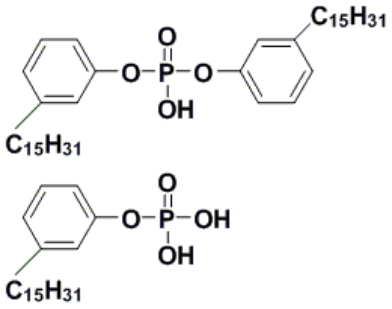
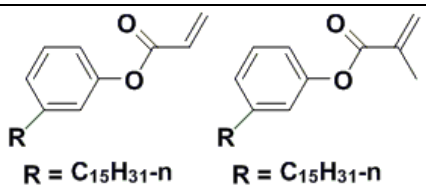
15	  	Resin to modify the properties of elastomers isobutylene isoprene rubber (IIR) and natural rubber (NR).	22
16		Monomer for synthesis of polyimides	4
17		• Polyaniline-clay composite as a novel intercalating agent cum dopant. • Flame retardation of polyethylene	23, 24
18		• Molecularly imprinted polymers • Polycardanyl acrylate	25, 26, 27, 28, 29, 30

Table 3.1 Continued…….

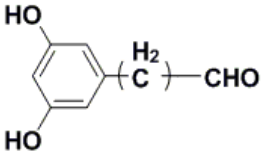
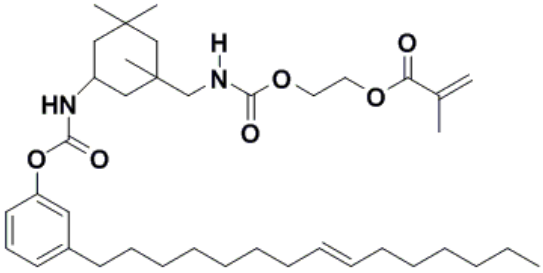
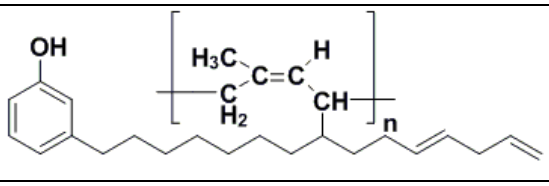
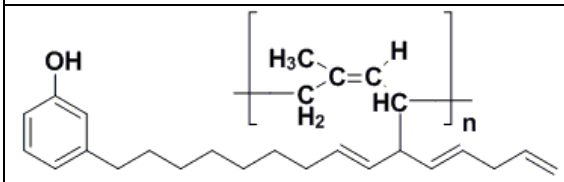
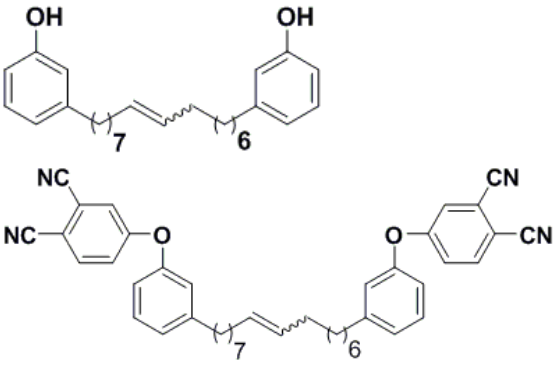
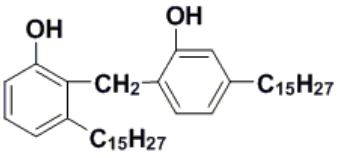
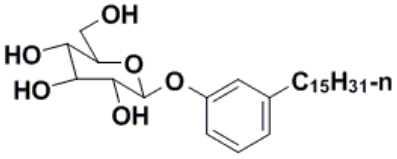
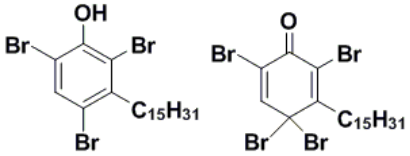
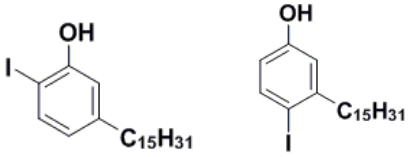
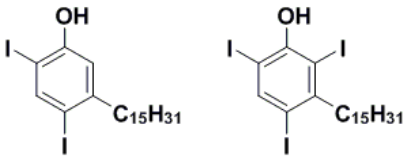
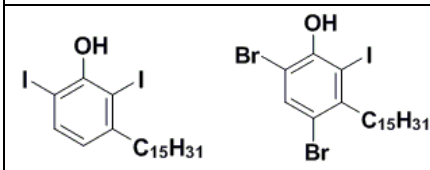
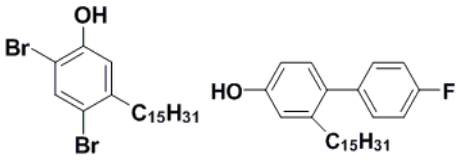
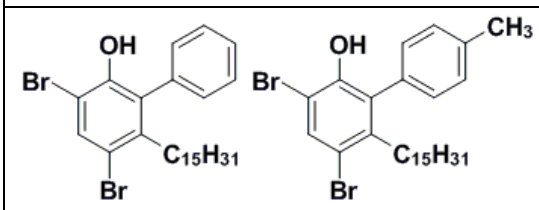
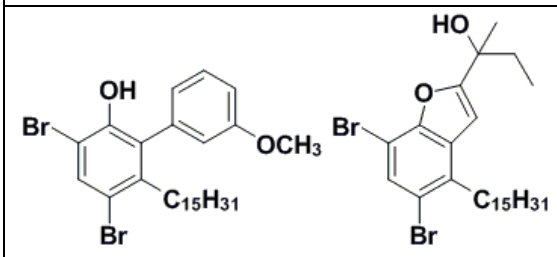
19		Used as a dietary supplements with health-promoting and disease-preventive properties	31
20		Telechelic urethane acrylate UV-curable pre-polymeric material	32
21	 	Cardanol-grafted natural rubber	33
22		Biscardanol derivatives	34
23		Monomer for novolac-type resins	35
24		Development of soft nanomaterials from bio-based amphiphiles	36

Table 3.1 Continued…….

25		Brominating agent	37
26		Cardanol derivatives	38
			
			
			
			
			

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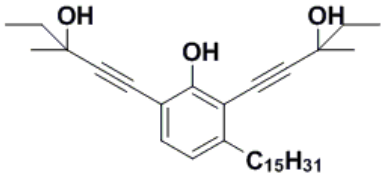
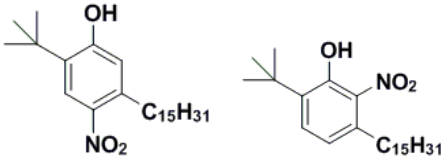
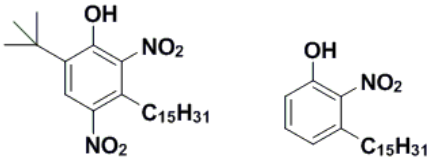
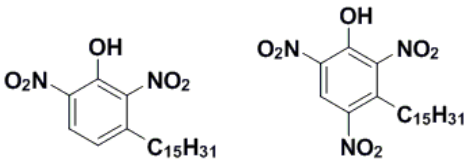
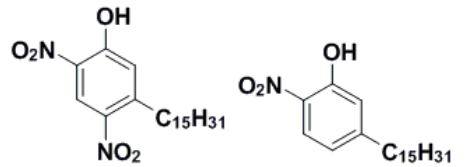
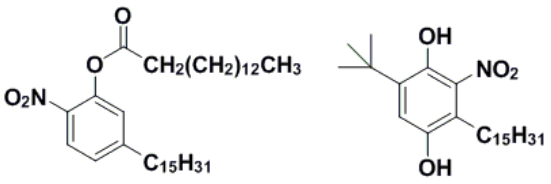
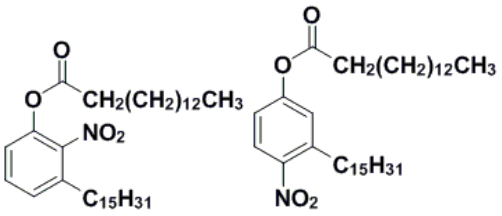
			
27		Cardanol derivatives	39, 40, 41
			
			
			
			
			
			

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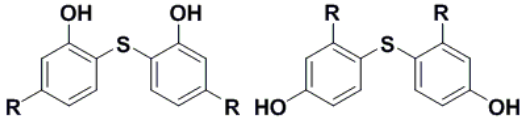
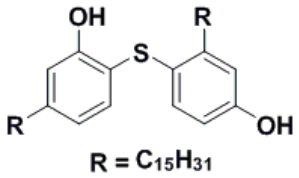
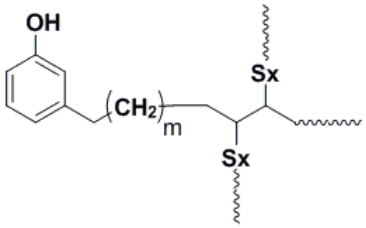
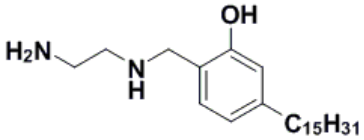
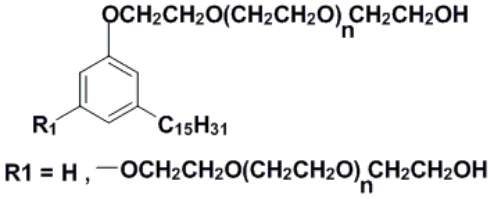
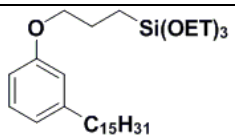
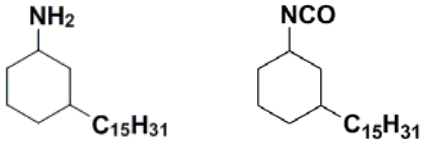
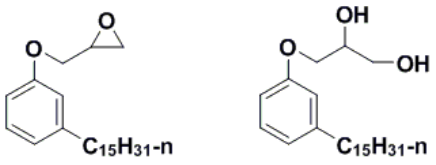
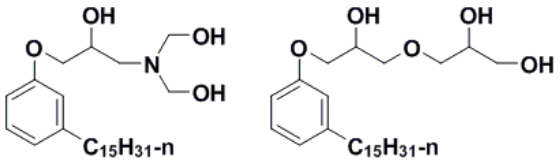
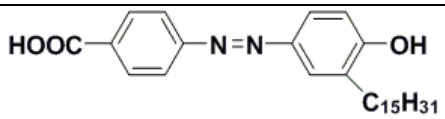
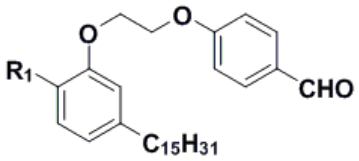
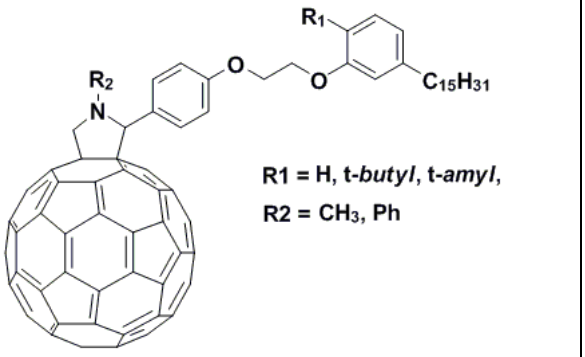
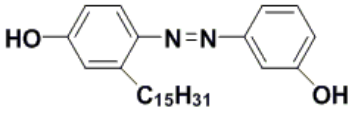
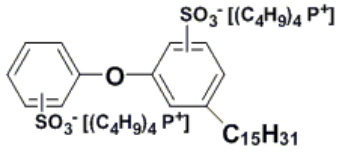
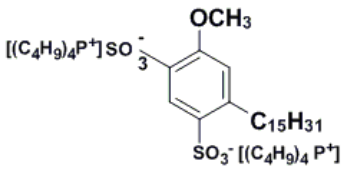
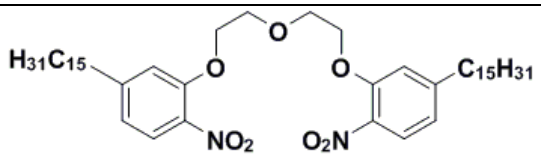
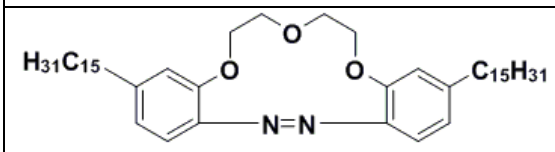
28	 	Thiobisphenols	42
29		Cardanol polysulfide	43
30		Curing agent	44
31		Use in pigment dispersions	45
32		Hydrosilylation products for grafting self-assembled monolayers onto silicon surfaces	46
33		• Hydrophobically modified poly(acrylic) acid using 3-pentadecyl cyclohexyl amine • α,ω-hydroxy-poly(ethylene oxide) end-capped with 1-isocyanato-3-pentadecyl cyclohexane	47, 144
34		Monomers for: • Polyether • Polyurethanes	48, 49

Table 3.1 Continued…….

			
35		Monomer for polyesters	50, 51, 52, 53
36			54
			
37		Monomer for polyurethane	55
38		Antistatic agents for polycarbonates	56
			
39		Chromogenic azocrown ethers	57
			

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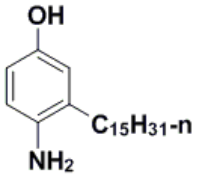
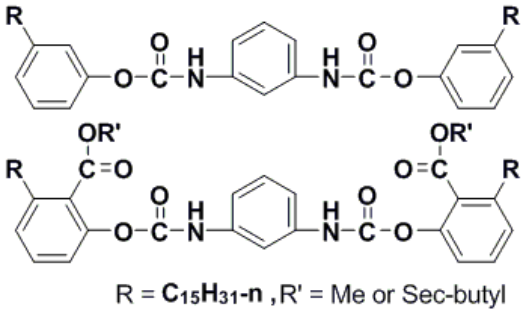
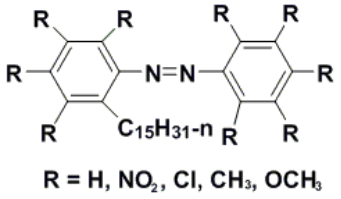
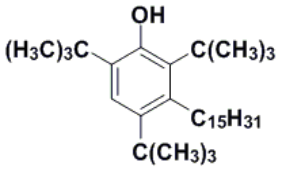
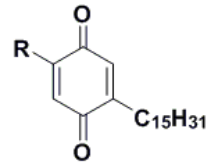
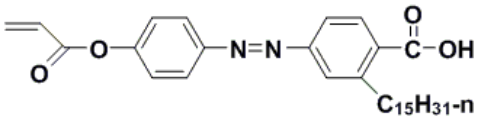
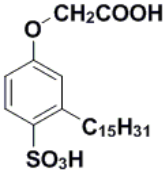
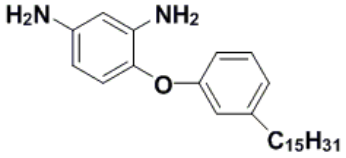
40			58
41		Blocked isocyanates	59
42		Petroleum marker dyes	60
43		Antioxidant for gasoline stabilisation	61
44			62
45		Liquid crystalline polymer with crosslinked network structures	51, 63
46		Dopant (Polyaniline)	64
47		Monomer for : • Polyimides for liquid crystal devices. • Polyamides	65

Table 3.1 Continued…….

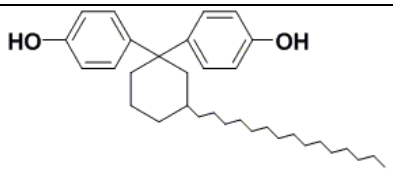
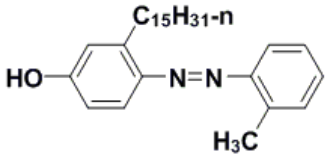
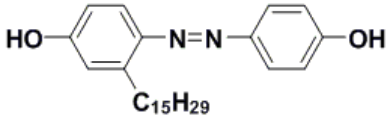
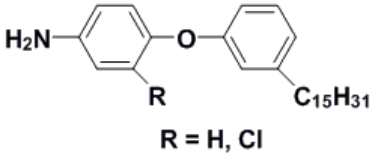
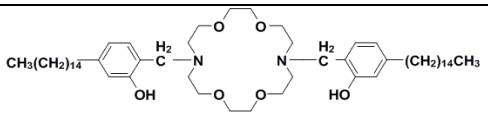
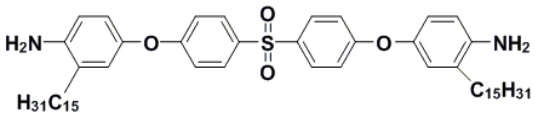
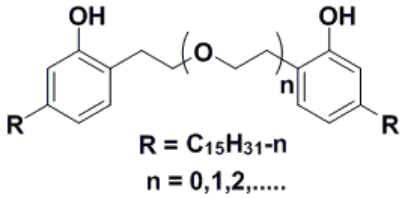
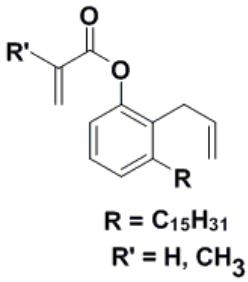
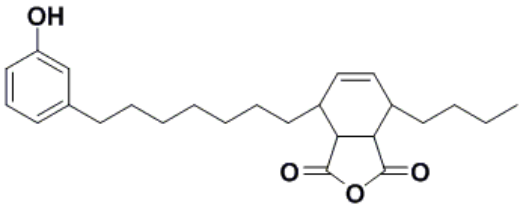
48		Monomer for polycarbonates	5
49		Resins	66
50		Monomer for: • Polyesters • Polyurethanes	67, 68, 69
51		Reagene for end-capping polyimides	70
52		Monomer for potential membrane-forming amphiphiles	71
53		Monomer for polyamides	72
54		Monomer for polyurethanes	73
55		UV-curable compositions and adhesive formulations	74
56		Polyfunctional compounds	75

Table 3.1 Continued…….

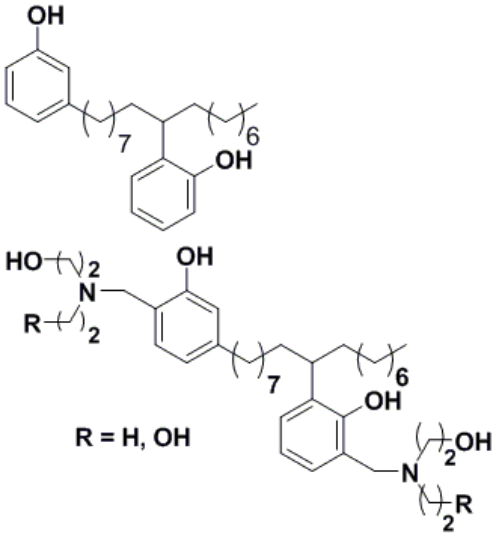
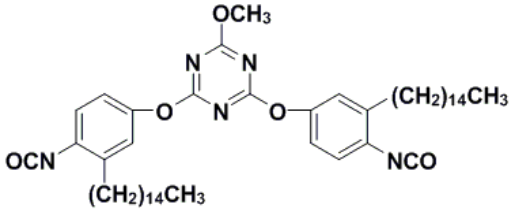
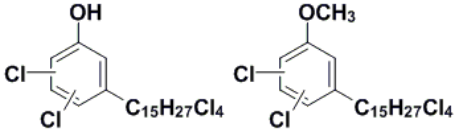
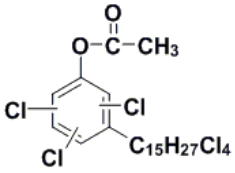
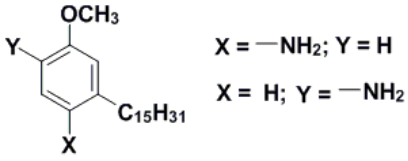
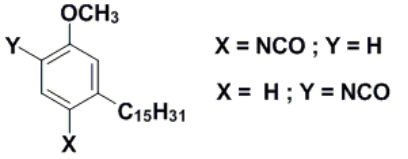
57		Mannich Bases	76
58		Diisocyanates	77
59	 	Plasticiser extenders for PVC	78
60	 	Isocyanates	40, 41

Table 3.1 Continued…….

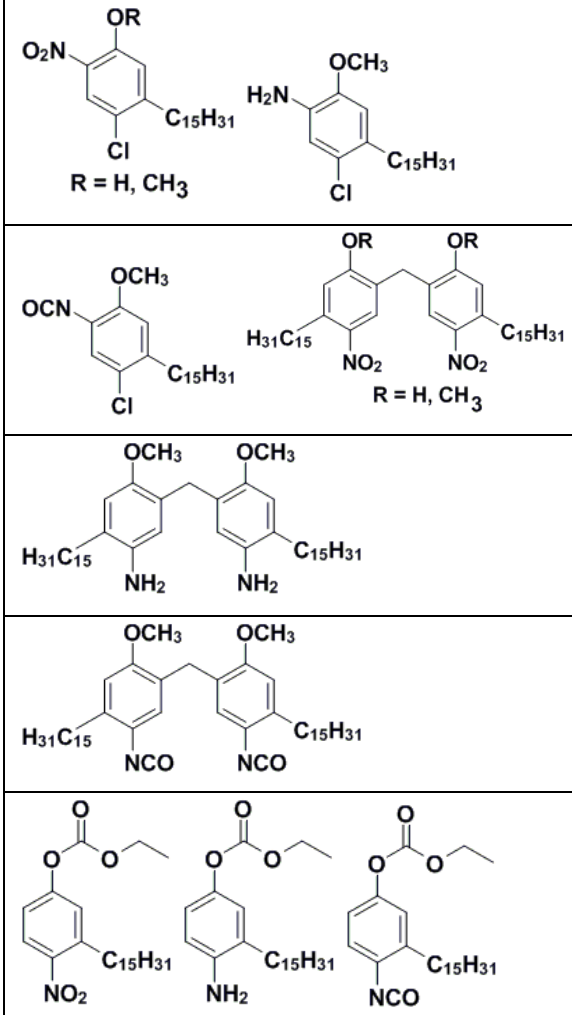
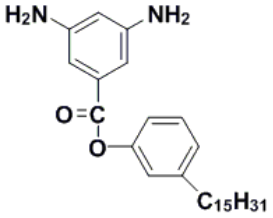
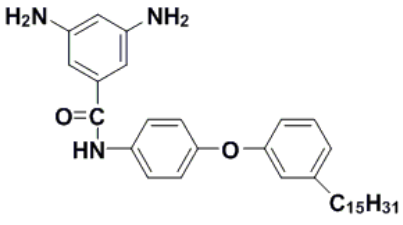
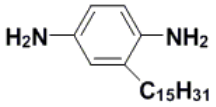
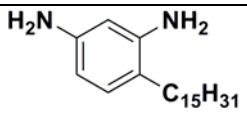
61		Cardanol derivatives	79
62		Monomer for • Polyamides • Polyimides	65
63		Monomer for • Polyamides • Polyimides	65
64		Monomer for polyimides	141

Table 3.1 Continued…….

65.		Monomer for polyimides	143

3.2 Experimental

3.2.1 Materials

3-Pentadecyl phenol, bromobenzene, copper powder, copper cyanide, palladium-on-carbon, ruthenium-on-carbon, 3-mercaptopropionic acid (3-MPA) and calcium hydride (Aldrich Chemicals) were used as received. Sulfanilic acid (Fluka), bromine, ammonia solution, copper sulfate, hydrochloric acid, sulfuric acid, pyridine, triethyl amine, ethanol, acetic acid, 1-chloro-4-nitrobenzene, ammonium acetate, aluminium chloride, phenol, sodium nitrite and sodium dithionite (Merck, India and E-Merck Germany) were used as received. Potassium hydroxide, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate, potassium carbonate, magnesium metal, acetyl chloride and methanesulfonyl chloride (Loba Chemie) were used as received. Hydrazine hydrate (99%) (S.D. Fine., India) was used as received. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[80]

Pyridiniumchlorochromate (PCC) was prepared according to the procedure reported in the literature.[81]

3.2.2 Measurements

Melting points were determined by open capillary method and are uncorrected.

FT-IR spectra were recorded on a Perkin-Elmer 599B spectrophotometer in chloroform or as KBr Pellets.

NMR spectra were recorded on a Bruker 200, 400 or 500 MHz spectrometer at resonance frequencies of 200, 400 or 500 MHz for ^{1}H and 50, 100 or 125 MHz for ^{13}C measurements using $CDCl_3$ or DMSO-d_6 as a solvent.

3.3 Preparations

3.3.1 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

3.3.1.1 Conversion of cardanol to 3-pentadecyl phenol

Cardanol (500 g, 1.64 mol) was dissolved in isopropanol (2 litres) and was hydrogenated in the presence of 5% Pd/C (1.5 g) catalyst at 70°C in a Parr autoclave under 600 psi hydrogen pressure. When no more hydrogen absorption was noticed, the hydrogenation was stopped. The reaction mixture was filtered to remove Pd/C. The solvent was evaporated to obtain crude product. Pure 3-pentadecyl phenol was obtained after recrystallization from hexane (40-60°C).

Yield: 480 g (95 %); M.P: 50-51°C (Lit.[119] m.p.: 50-51°C).

3.3.1.2 Synthesis of 1-pentadecyl-3-phenoxy benzene

Into a 1000 mL two necked round bottom flask fitted with a Dean and Stark assembly with a reflux condenser were taken 3-pentadecyl phenol (100.0 g, 0.33 mol), potassium hydroxide (22.06 g, 0.39 mol) N,N-dimethylacetamide (300 mL) and toluene (150 mL). The reaction mixture was refluxed for 7 h and the by-product water formed was removed from the reaction mixture azeotropically. After completion of the reaction, the solvent was distilled off and the dark sticky product was dried under reduced pressure. The compound obtained was potassium salt of 3-pentadecyl phenol.

Into a 1000 mL round bottom flask containing potassium salt of 3-pentadecyl phenol (111.0 g, 0.32 mol) was added bromobenzene (50.88 g, 0.32 mol), followed by Cu powder (2.22 g, 2 wt %) and DMAC (150 mL). The reaction mixture was heated at 150 ^{o}C for 6 h. After completion of the reaction, the obtained dark colored reaction mixture was poured into water (500 mL); the Cu salts were removed by filtration; The filtrate was extracted with ethyl acetate (2 x 300 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 1-pentadecyl-3-phenoxy benzene. Pure 1-pentadecyl-3-phenoxy benzene was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 70 g (57 %); M.P. 32 ^{o}C

3.3.1.3 Synthesis of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene

Into a 500 mL three necked round bottom flask equipped with a stirrer, a condenser, a dropping funnel and a thermometer containing a solution of 1-pentadecyl-3-phenoxy benzene (25.0 g, 66 mmol) in dichloromethane (150 mL) was added dropwise bromine (22.08 g, 0.14 mol) protecting from light. The top of the condenser was equipped with a trap to absorb the HBr released during the reaction. Bromine was added at a temperature between -5^{o} to 0^{o}C over a period of 15 minutes. After completion of the addition, the reaction mixture was stirred at the same temperature for 1 h and then refluxed overnight. After completion of reaction, excess bromine and HBr were neutralized with aqueous 10% NH_3 (100 mL). Two phases formed in the reaction mixture were separated, and the organic layer was washed with water (2 x 300 mL). After drying of dichloromethane solution over sodium sulfate and distillation, crude 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was obtained. Pure 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 30 g. (84%); M.P. 43 ^{o}C

3.3.1.4 Synthesis of 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile

Into a 250 mL three-necked round bottom flask containing 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene (10.0 g, 18 mmol) was added copper cyanide (6.65 g, 74 mmol) followed by $CuSO_4$ (0.10 g) and DMF (50 mL). The reaction mixture was refluxed overnight. After completion of the reaction, the obtained brown colored solution was poured into concentrated hydrochloric acid

(50 mL); and the solution was extracted with ethyl acetate (2 x 200 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile. Pure 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 6.7 g (83%); M.P. 64 ^{o}C

3.3.1.5 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

Into a 250 mL single necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were added 4-(4'-cyanophenoxy)-2-pentadecylbenzonitrile (5.0 g, 11 mmol), potassium hydroxide (7.81 g, 140 mmol), triethylene glycol (75 mL) and water (10 mL). The reaction mixture was refluxed for 72 h. Next, the temperature of the reaction mixture was lowered to 120 ^{o}C and water (50 mL) was added and the reaction mixture was heated at 100^{o}C for additional 48 h. After completion of the reaction time, the reaction mixture was diluted with water (50 mL) and poured into excess concentrated hydrochloric acid. Crude 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid precipitated as a grey solid which was filtered and thoroughly washed with water. The obtained solid was dissolved in aqueous potassium hydroxide solution and was precipitated by addition of concentrated hydrochloric acid (pH 2). The solid was filtered up and washed repeatedly with water and dried. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid was purified by column chromatography (eluent: pet ether: ethyl acetate 80:20, v/v).

Yield: 3.7 g (68%); M.P. 130 ^{o}C

3.3.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

3.3.2.1 Synthesis of methyl 4-(4'-methoxycarbonyl) phenoxy)-2-pentadecylbenzoate

Into a 250 mL two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid (14.0 g, 29.9 mmol) and 3 drops of DMF. Thionyl chloride (100 mL) was added dropwise over a period of 30 minutes and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (25 mL). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice to get 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecylbenzoyl chloride.

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a reflux condenser and two dropping funnels was placed 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecyl benzoyl chloride (15.10 g, 29.9 mmol). Pyridine (4.73 g, 59.8 mmol) and methanol (75 mL) were added dropwise to the reaction mixture over a period of 10 minutes and the reaction mixture was refluxed for 5 h. Excess methanol was removed by distillation under reduced pressure. The obtained brown colored solution was extracted with ethyl acetate (2 x 200 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over

sodium sulfate. Solvent evaporation yielded crude methyl 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate. Pure 4-(4'-methoxy carbonyl)phenoxy)-2-pentadecyl benzoate was obtained as a viscous liquid after silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 12.6 g (85%, based on 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid)

3.3.2.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

Into a 250 mL two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed methyl 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate (11.5 g, 23.1 mmol) and ethanol (100 mL). Hydrazine hydrate (99%) (23.21 g, 464 mmol) was added dropwise to the reaction mixture over a period of 15 minutes and reaction mixture was refluxed overnight. The solid that separated out was filtered and dried. Crude 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide was purified by crystallization from ethanol.

Yield: 9.77 g (85%); M.P. 62 ^{o}C

3.3.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

3.3.3.1 Synthesis of 4-amino-3-pentadecyl phenol

Into a 500 mL three necked round bottom flask equipped with a reflux condenser, a thermowell, and a magnetic stirrer were placed 3-pentadecyl phenol (30.4 g, 0.10 mol), potassium hydroxide (28.0 g, 0.50 mol), and ethyl alcohol (200 mL). The reaction mixture was stirred and to the reaction mixture was added diazonium chloride prepared from sulphanilic acid dihydrate (21.0 g, 0.10 mol) at –5 ^{o}C. The resulting red dye solution was stirred for 2 h and then heated at 75 ^{o}C on a water bath. At this temperature, a saturated solution of sodium dithionite (53.0 g, 0.30 mol) was added to the dye solution over a period of 10 min and the reaction mixture was stirred for 30 min (color of reaction mixture changed from dark red to orange). To the reaction mixture was then added acetic acid (18.0 g, 0.30 mol) dissolved in water (20 mL) and was refluxed for 1 h (color changed to pale tan). The reaction mixture was poured into water (2 L), the product was filtered and dried under reduced pressure at 50 ^{o}C for 2 h. The crude product was purified by recrystallisation using toluene.

Yield: 25.0 g (79%); M.P. 104^{o}C (lit.[65a] M.P. 105-106 ^{o}C).

3.3.3.2 Synthesis of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine

Into a 500 mL three necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirrer were placed 4-amino-3-pentadecyl phenol (20.0 g, 62 mmol), 1-chloro-4-nitrobenzene (9.87 g, 62 mmol), potassium carbonate (9.53 g, 68 mmol) and DMF (100 mL). The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. After completion of the reaction time, reaction mixture was cooled to room temperature and poured into water. The precipitated product was filtered, dried and recrystallised from ethyl alcohol.

Yield: 18.9 g (90%); M.P. 67^{o}C

3.3.3.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

Into a 250 mL three necked round bottom flask equipped with a dropping funnel and a reflux condenser were placed 4-(4'-nitrophenoxy)-2-pentadcylbenzenamine (10.0 g, 22 mmol), palladium-on-charcoal (3 wt%) and ethyl alcohol (100 mL). To the reaction mixture, hydrazine hydrate (34.13 g, 0.68 mol) was added dropwise over a period of 15 min at 80 ^{o}C. After the addition was complete, the reaction mixture was refluxed for 3 h. The reaction mixture was filtered to remove palladium-on-charcoal. The product precipitated on cooling was isolated by filtration and was recrystallised twice from ethanol.

Yield: 8.38 g (90%); M.P. 81^{o}C

3.3.4 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

3.3.4.1 Synthesis of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine

Into a 500 mL three necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirrer were charged 4-amino-3-pentadecyl phenol (7.0 g, 21.9 mmol), 1-chloro-2-nitrobenzene (3.45 g, 21.9 mmol), potassium carbonate (3.33 g, 24.1 mmol) and N,N-dimethylformamide (75 mL). The reaction mixture was refluxed for 3 h under dry nitrogen gas stream. The reaction mixture was then cooled to room temperature and poured into water. The precipitated viscous product was filtered, dried and purified by column chromatography (Eluent: pet ether).

Yield: 7.7 g (80%)

3.3.4.2 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

Into a 250 mL three necked round bottom flask equipped with a dropping funnel and a reflux condenser were charged 4-(2-nitrophenoxy)-2'-pentadcylbenzenamine (5.0 g, 11.3 mmol), palladium-on-charcoal (3 wt%) and ethyl alcohol (70 mL). To the reaction mixture, hydrazine hydrate (17.06 g, 0.3 mol) was added dropwise over a period of 15 min at 80 ^{o}C. After the addition was complete, the reaction mixture was refluxed for 3 h. The reaction mixture was filtered to remove palladium-on-charcoal. The product precipitated on cooling was isolated by filtration and was recrystallised twice from ethanol.

Yield 3.96 g (85%); M.P. 70^{o}C

3.3.5 Synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

Into a 250 mL three necked round bottom flask equipped with a stirrer, a reflux condenser, a pressure equalizing dropping funnel and a nitrogen inlet were placed 4-(4'-aminophenoxy)-2-pentadecylbenzenamine (1.0 g, 2.40 mmol) and dry toluene (50 mL). The reaction mixture was flushed with nitrogen gas and the solution was stirred at 0 ^{o}C. In another 100 mL single-necked flask, bis(trichloromethyl) carbonate (triphosgene) (4.38 g, 14.7 mmol) was weighed and dissolved in dry toluene (50 mL). The solution of triphosgene was transferred to the dropping funnel under

nitrogen atmosphere and was slowly added to the solution containing 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with constant stirring over a period of 15 minutes at 0 ^{o}C. After completion of the addition, the reaction mixture was stirred at room temperature for 2 h and then refluxed for 6 h. Finally, excess phosgene was removed by flushing the stream of nitrogen through the solution and toluene was distilled off under reduced pressure to yield 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene.

Yield: 0.84 g (75%)

3.3.6 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

3.3.6.1 Synthesis of 1-methane sulfonyloxy-3-pentadecyl benzene

Into a 250 mL two necked round bottom flask equipped with an addition funnel and an air condenser were added 3-pentadecylphenol (5.0 g, 16.4 mmol), triethyl amine (1.8 g, 18 mol) and dichloromethane (50 mL). To the reaction mixture, methanesulfonyl chloride (2.06 g, 18 mol) was added dropwise at 0 ^{o}C. After complete addition of methanesulfonyl chloride, the reaction mixture was stirred for 2 days. After completion of the reaction, the reaction mixture was extracted with dichloromethane (2 x 100 mL). The organic layer was washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL). The organic layer was dried over sodium sulfate and filtered. The evaporation of solvent afforded 1-methane sulfonyloxy-3-pentadecyl benzene.

Yield: 4 g (95.4%); M.P. 58^{o}C

3.3.6.2 Synthesis of pentadecyl benzene

Into a 250 mL two necked round bottom flask were taken 1-methane sulfonyloxy-3-pentadecyl benzene (5 g, 13.6 mmol), palladium on charcoal (0.5 g), magnesium metal (0.39 g, 16.3 mmol), ammonium acetate (14.7 g, 191 mmol) and methanol (50 mL) and the reaction mixture was degassed by three vaccum/N_2 cycles. The reaction mixture was stirred under nitrogen atmosphere at room temperature. After completion of the reaction, the reaction mixture was filtered and the filtrate was extracted with dichloromethane (500 mL). The organic layer was washed with saturated aqueous sodium chloride solution (2 x 100 mL), followed by water (3 x 100 mL). The organic layer was dried over sodium sulfate and filtered. The evaporation of solvent afforded pentadecyl benzene as a yellow liquid. The purification was done by column chromatography (eluent: pet ether).

Yield: 2.3 g (62 %)

3.3.6.3 Synthesis of 4-acetyl pentadecyl benzene

Into a 500 mL three necked round bottom flask fitted with a magnetic stirrer, a reflux condenser and a dropping funnel were charged aluminium chloride (5.82 g, 43.67 mmol) and dichloromethane (100 mL). Acetyl chloride (3.42 g, 43.67 mmol) was added to the vigorously stirred reaction mixture over a period of 15 minutes at 0^{o}C. Pentadecyl benzene (10 g, 34.66 mmol) was added over a period of 30 minutes; the reaction mixture was stirred at 0 ^{o}C for 2 h and then

allowed to attain room temperature. The reaction mixture was poured into ice and extracted with dichloromethane (3 x 100 mL). The dichloromethane solution was washed with 1 N hydrochloric acid (2 x 30 mL) and water (3 x 50 mL), dried over sodium sulfate and the solvent was evaporated to obtain 4-acetyl pentadecyl benzene as a faint yellow solid. Pure compound was obtained after column chromatography. (eluent: pet ether)

Yield: 10 g (87%); M.P. 34^{o}C

3.3.6.4 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

Into a 250 mL three necked round bottom flask fitted with a magnetic stirrer and a gas dip tube were charged 4-acetyl pentadecyl benzene (5.0 g, 15.15 mmol), phenol (8.54 g, 90.90 mmol) and 3-mercaptopropionic acid (0.13 mL). The reaction mixture was stirred at room temperature for 15 minutes, after which anhydrous hydrogen chloride gas was bubbled into the reaction mixture for 4 days at 50 ^{o}C, where upon the reaction mixture solidified. The reaction mixture was dissolved in ethyl acetate (500 mL), washed with aqueous sodium bicarbonate solution (3 x 100 mL) and water (3 x 100 mL). The organic layer was separated and dried over sodium sulfate. The vacuum stripping of solvent afforded a pink solid, which was purified by column chromatography (eluent: pet ether: ethyl acetate, 80:20 v/v) to obtain 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane in the pure form.

Yield: 4 g (52%); M.P. 114 ^{o}C

3.3.7 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

3.3.7.1 Synthesis of 3-pentadecylcyclohexanol

3-Pentadecylphenol (80 g, 0.26 mol) dissolved in isopropanol (300 mL) was hydrogenated using 5% Ru/C (2.4 g) as the catalyst in a Parr reactor at 125 ^{o}C and at hydrogen pressure of 1000 psi. After the completion of the reaction, the catalyst was filtered off and isopropanol was distilled off to obtain 3-pentadecyl cyclohexanol.

Yield: 79.90 g (98%); M.P. 46-49°C (Lit.[142] m.p. 45-48°C)

3.3.7.2 Synthesis of 3-pentadecylcyclohexanone

Into a 1 liter round bottom flask equipped with a mechanical stirrer was added a finely ground mixture of pyridinium chlorochromate (97 g, 0.45 mol) and silica gel (97 g, 100-200 mesh). To this mixture, dichloromethane (600 mL) was added, the suspension was stirred and 3-pentadecylcyclohexanol (50 g, 0.22 mol) was added in small portions at room temperature. The reaction mixture darkened (30 min) and the stirring was continued for 4 h. The reaction mixture was filtered through a short column of Celite and silica gel. The filtrate was concentrated under reduced pressure to obtain crude 3-pentadecylcyclohexanone. The crude 3-pentadecylcyclohexanone was dissolved in ethyl acetate (300 mL) and washed with saturated aqueous sodium chloride (2 × 200 mL) followed by washing with water (2 × 200 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and ethyl acetate was removed on a rotary evaporator. The residue obtained

was recrystallized from methanol.

Yield: 46.68 g (94%); M.P. 44°C (Lit.[142] m.p. 43°C)

3.3.7.3 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

Into a 250 mL three necked round bottom flask fitted with a magnetic stirrer bar, a HCl dip tube and a reflux condenser connected to a scrubber were placed 3-pentadecylcyclohexanone (20 g, 0.06 mol), phenol (36.62 g, 0.38 mol) and 3-mercaptopropionic acid (0.1 mL). Dry HCl was bubbled into the reaction mixture at room temperature. The reaction mixture became solid at the end of 1 h. The reaction mixture was dissolved in ethyl acetate (600 mL) and neutralized by washing with aqueous sodium bicarbonate solution (3 × 200 mL) followed by washing with water (2 × 200 mL). The organic layer was dried over sodium sulfate, filtered and ethyl acetate was distilled off. The excess phenol was removed by washing with hexane. The product was crystallized twice from a mixture of hexane and toluene (9:1, v/v).

Yield: 21.72 g (70%); M.P. 104°C (Lit.[142] m.p. 104°C)

3.4 Results and discussion

One of the approaches to improve solubility and processability of high temperature/ high performance polymers is the attachment of flexible chains as pendant groups. It is reported that the use of monomers bearing pendant flexible groups greatly reduces strong intermolecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. In general, such pendant groups not only bring about improved solubility but also help lower the melting and glass transition temperatures. Thus, our synthetic research effort was directed towards designing monomers with features that disturb structural regularity and chain packing hence imparting improved processability characteristics to the polymers. The approach involved making use of 3-pentadecyl phenol, which in turn is obtained from cashew nut shell liquid. A range of difunctional monomers such as aromatic dibromide, diacid, diacylhydrazide, diamines, diisocyanate, and bisphenols were designed and synthesized.

The following difunctional monomers were synthesized starting from CNSL:

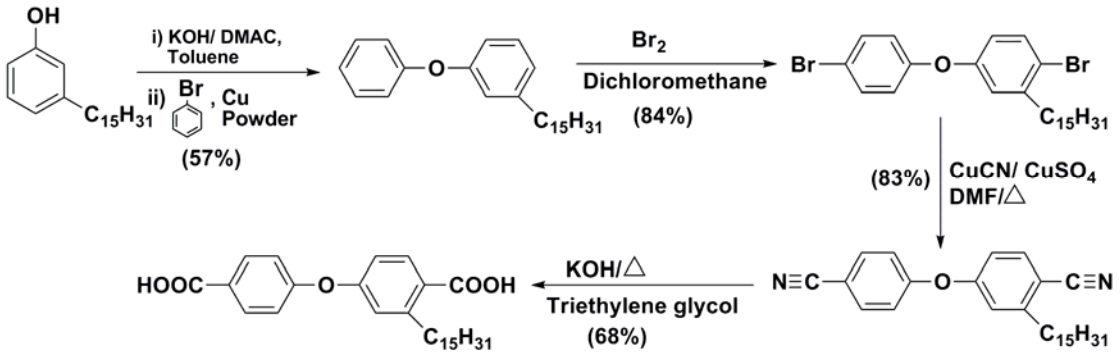
a. 1-Bromo-4-(4’-bromophenoxy)-2-pentadecyl benzene,
b. 4-(4’-Carboxyphenoxy)-2-pentadecylbenzoic acid,
c. 4-[4’-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide,
d. 4-(4’-Aminophenoxy)-2-pentadecylbenzenamine,
e. 4-(2’-Aminophenoxy)-2-pentadecylbenzenamine,
f. 1-Isocyanato-4-(4’-isocyanatophenoxy)-2-pentadecylbenzene,
g. 1,1,1-[Bis(4-hydroxyphenyl)-4’-pentadecylphenyl] ethane, and
h. 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane.

3.4.1 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

Aromatic dicarboxylic acids are an important class of monomers for the preparation of industrially useful polyesters, polyamides, polyhydrazides, poly(amideimide)s, polyimides, etc. There are several routes available to synthesize carboxylic acids. The oxidation of alkyl benzenes, oxidation of ketones or aldehydes, hydrolysis of esters, hydrolysis of nitriles, using carbon monoxide as a co-reagent, etc. are some of the routes generally adapted for synthesis of carboxylic acids.

The starting material used for the synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was 3-pentadecyl phenol, which was obtained from side chain hydrogenation of cardanol.

Scheme 3.1 depicts route for the synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid.



Scheme 3.1 Synthesis of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

A new dicarboxylic acid monomer containing pendant alkyl chain, *viz***,** 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was designed and synthesized starting from 3-pentadecyl phenol making use of simple organic transformations like Ullmann etherification, electrophilic aromatic substitution such as bromination, cyanation followed by alkaline hydrolysis.

In the first step, 1-pentadecyl-3-phenoxy benzene was prepared by reaction of 3-pentadecyl phenol with bromobenzene in the presence of potassium hydroxide and Cu as a catalyst under classical Ullmann etherification reaction conditions. Typical Ullmann etherification reaction uses Cu-powder/ Cu salts as catalyst.[82] There are several other reagents available for Ullmann etherification reaction such as use of Pd $(DBA)_2$/dppf,[83a] $Pd(OAc)_2$/aryldialkyl phosphines as a ligand,[83b] $(CuOTf)_2.PhH/EtOAc/Cs_2CO_3$/ArCOOH,[83c] CuI/ N,N-dimethyl glycine, HCl salt/Cs_2CO_3, [83d] CuCl/Cs_2CO_3/2,2,6,6- tetramethylheptane-3,5-dione,[83e] phosphazene P_4-*t*-Bu base/CuBr,[83f] CuI/K_2CO_3/Raney Ni-Al alloy,[83g] etc. In the present study, Cu-powder was used as the catalyst.

The product obtained was purified using column chromatography and was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 1-pentadecyl-3-phenoxy benzene displayed absorption band at 1267 cm^{-1} corresponding to –C-O-C- stretching. **(Figure 3.3)**

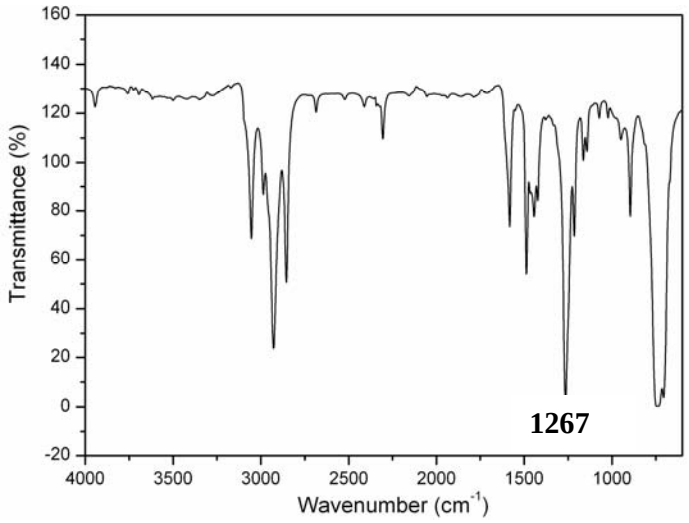


Figure 3.3 FTIR spectrum of 1-pentadecyl-3-phenoxy benzene

^{1}H-NMR spectrum of 1-pentadecyl-3-phenoxy benzene is shown in **Figure 3.4.**

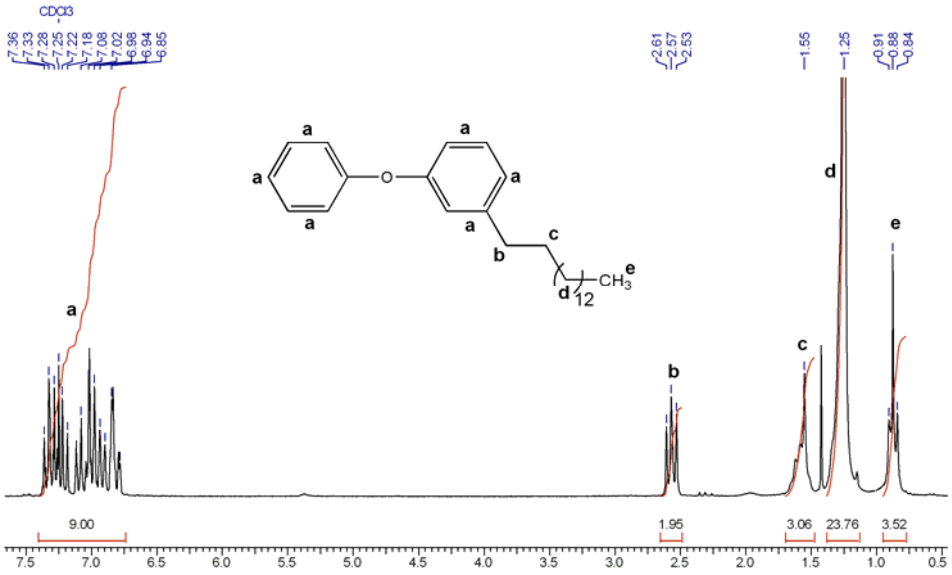


Figure 3.4 ^{1}H-NMR spectrum 1-pentadecyl-3-phenoxy benzene in $CDCl_3$

A multiplet in the region 6.80-7.38 δ ppm corresponds to aromatic protons. A triplet at 2.57 δ ppm is assigned to benzylic –CH_2. A triplet at 1.55 and a multiplet in the range 1.22-1.27 δ ppm corresponds to the methylene protons of the pendant alkyl chain. The –CH_3 protons of pentadecyl chain appeared as a triplet at 0.88 δ ppm.

^{13}C-NMR spectrum of 1-pentadecyl-3-phenoxy benzene with assignments is presented in **Figure 3.5.**

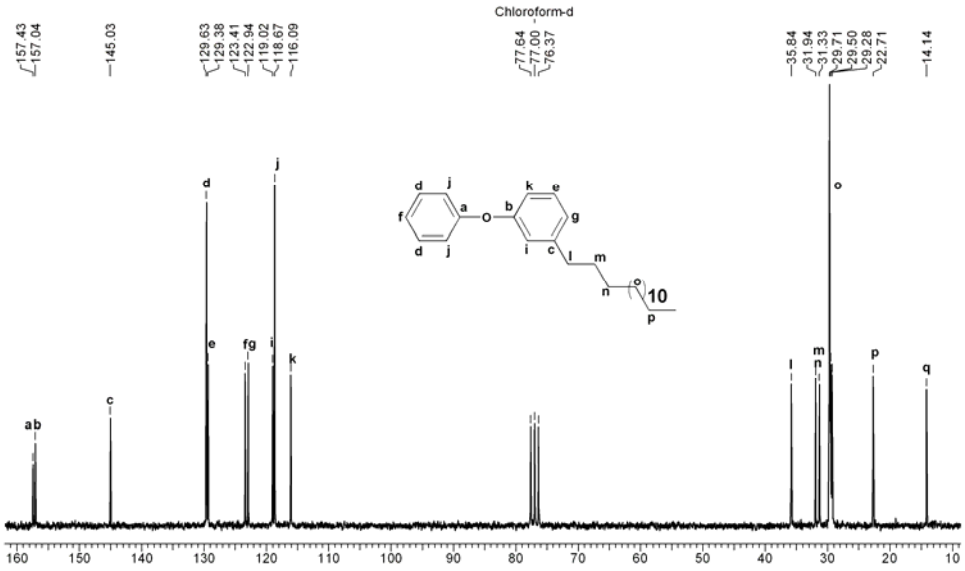


Figure 3.5 ^{13}C-NMR spectrum 1-pentadecyl-3-phenoxy benzene in $CDCl_3$

In the second step, 1-pentadecyl-3-phenoxy benzene was selectively brominated at *para* position to obtain 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene. Various methods of bromination of diphenyl ether have been described in the literature.[84] Preferred brominating agents include, e.g., Br_2, or bromine may be generated *in-situ* e.g., by employing HBr together with an oxidizing agent such as H_2O_2 or $NaBrO_3$ or the like known oxidizing agents. The reaction can be carried out in a solvent or without solvent but the presence or absence of a solvent may affect the selectivity of the bromination. When a solvent is employed, it is preferred to employ such a solvent which is unreactive under the reaction conditions such as halocarbons e.g., dichloromethane, carbon tetrachloride, and 1,2-dichloroethane.

The formation of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

In the FTIR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene **(Figure 3.6)** the band at 796 cm^{-1} is assigned to C-Br stretching.

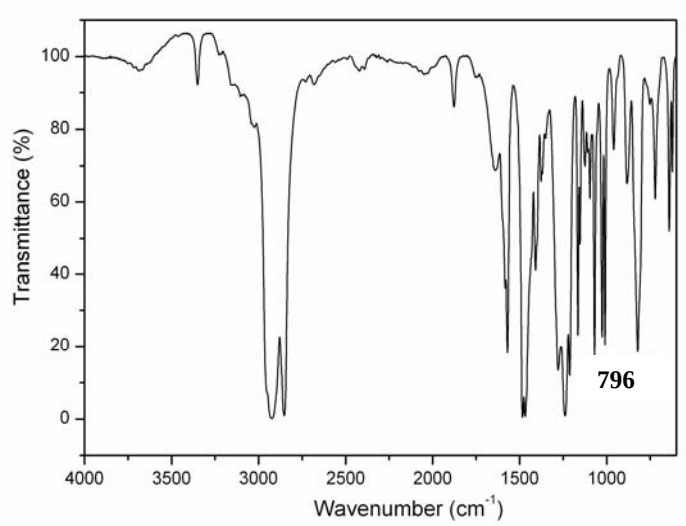


Figure 3.6 FTIR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene

In ^{1}H-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene, **(Figure 3.7)** aromatic protons *ortho* to bromine atom on both aromatic rings exhibited a multiplet in the range 7.38-7.49 δ ppm, while two aromatic protons 'b' *ortho* to ether linkage and one proton *ortho* to pentadecyl chain, displayed a multiplet in the range 6.85-6.90 δ ppm. A proton *meta* to bromine atom on pentadecyl-substituted aromatic ring appeared at 6.69 δ ppm as doublet of doublet. Due to the electron withdrawing nature of bromine atom, the benzylic $-CH_2$ in pentadecyl chain shifted to 2.66 δ ppm. The methylene protons β to aromatic ring exhibited a triplet 1.58 δ ppm and a multiplet in the range 1.23-1.27 δ ppm could be assigned to methylene protons in the pendant alkyl chain. The $-CH_3$ protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

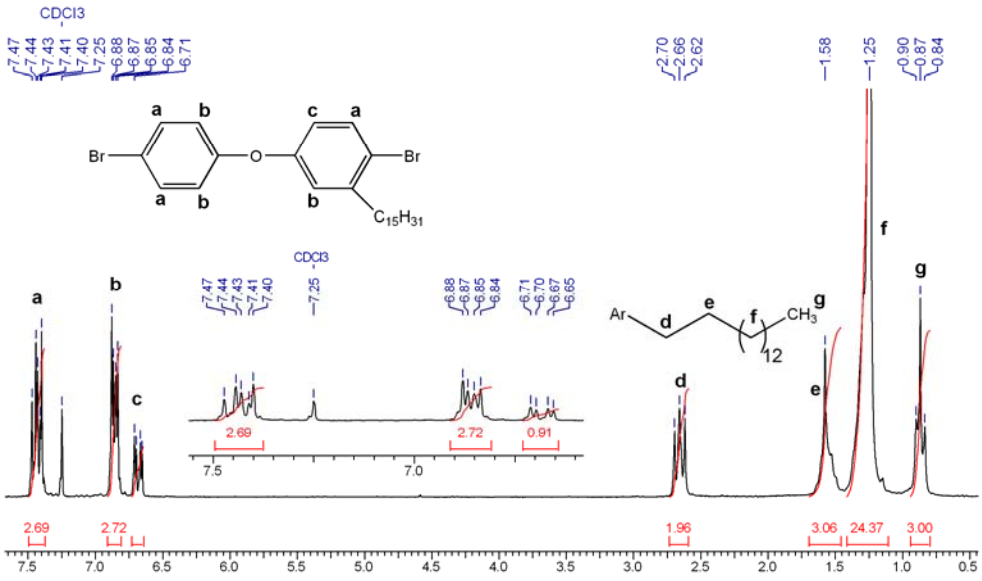


Figure 3.7 ^{1}H-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene in $CDCl_3$

^{13}C-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene with assignments is presented in **Figure 3.8.** Carbons 'a' and 'b' appeared as two signals at 156.23 and 155.93 δ ppm due to the asymmentric nature of the monomer. Carbon bearing pentadecyl chain and unsubstituted carbons both *ortho* to bromine appeared at 143.96 and 133.67 δ ppm, respectively. The peak at 132.71 and 120.30 δ ppm refers to carbons *ortho* and *meta* to bromine on unsubstituted ring, respectively. Carbons bearing bromine atom appeared at 118.30 and 115.86 ppm. Aliphatic carbons were observed in the upfield region and their assignments are shown in **Figure 3.8**.

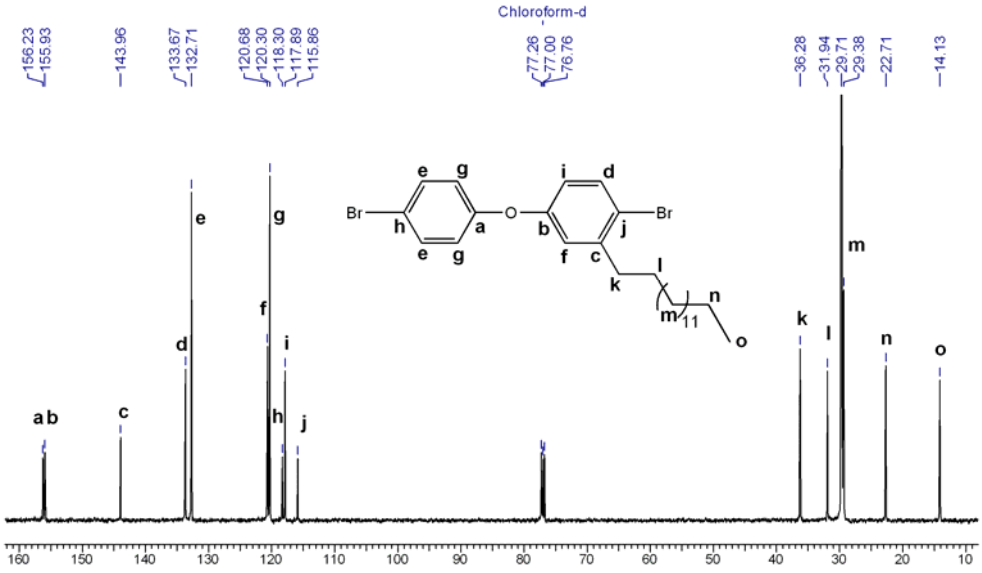


Figure 3.8 ^{13}C-NMR spectrum of 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene in $CDCl_3$

In the third step, 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene was treated with copper cyanide in the presence of copper sulfate in N,N-dimethyl formamide as a solvent to obtain 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile. A variety of methods for the preparation of aryl nitriles have been developed,[85] The direct cyanation of aryl halides by copper(I) cyanide is known as Rosenmund–von Braun reaction.[86] Recently, several palladium- or nickel-catalyzed aryl cyanation approaches were reported.[87] However, many of these methods require special reagents such as expensive and toxic phosphines as ligands, etc.[87,88] Rosenmund–von Braun reaction remains one of most practicable approaches for the synthesis of aryl nitriles because of its cost efficiency and easy operation.[89]

4-(4'-Cyanophenoxy)-2-pentadecyl benzonitrile was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile **(Fig. 3.9)** exhibited the characteristic stretching band for the -CN at 2225 cm^{-1}.

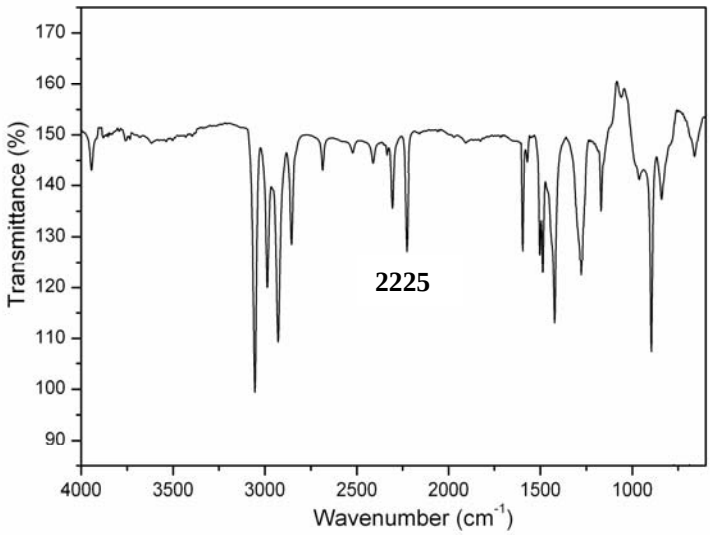


Figure 3.9 FTIR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile

^{1}H NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile is reproduced in **Figure 3.10**, It was observed that after substitution of Br with –CN group, the peaks shifted to downfield, due to more electron-withdrawing nature of -CN. The protons *ortho* to –CN group appeared in the range 7.57-7.71 δ ppm as a multiplet. Two protons *meta* to –CN group on unsubstituted ring appeared as a doublet at 7.07 δ ppm. Two protons *meta* to –CN group on pentadecyl-substituted ring showed a multiplet in the range 6.86-6.98 δ ppm. The benzylic –CH_2 in pentadecyl chain appeared as a triplet at 2.80 δ ppm due to electron-withdrawing nature of –CN group. The methylene protons β to aromatic ring appeared as a triplet at 1.64 δ ppm and a multiplet in the region 1.22-1.26 δ ppm could be attributed to remaining methylene protons. The terminal –CH_3 showed a triplet at 0.86 δ ppm.

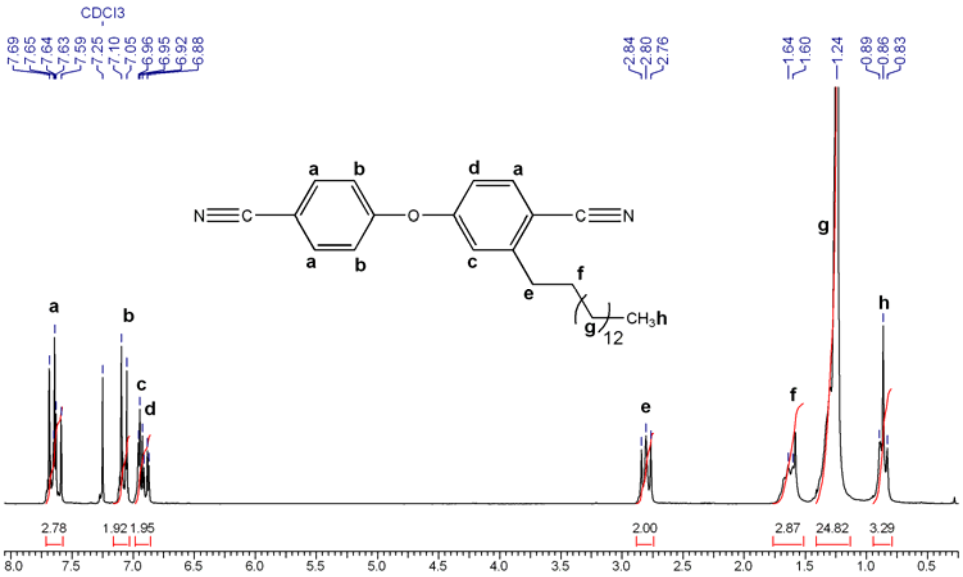


Figure 3.10 ^{1}H-NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile in $CDCl_3$

^{13}C-NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile is presented in **Figure 3.11**, along with assignments.

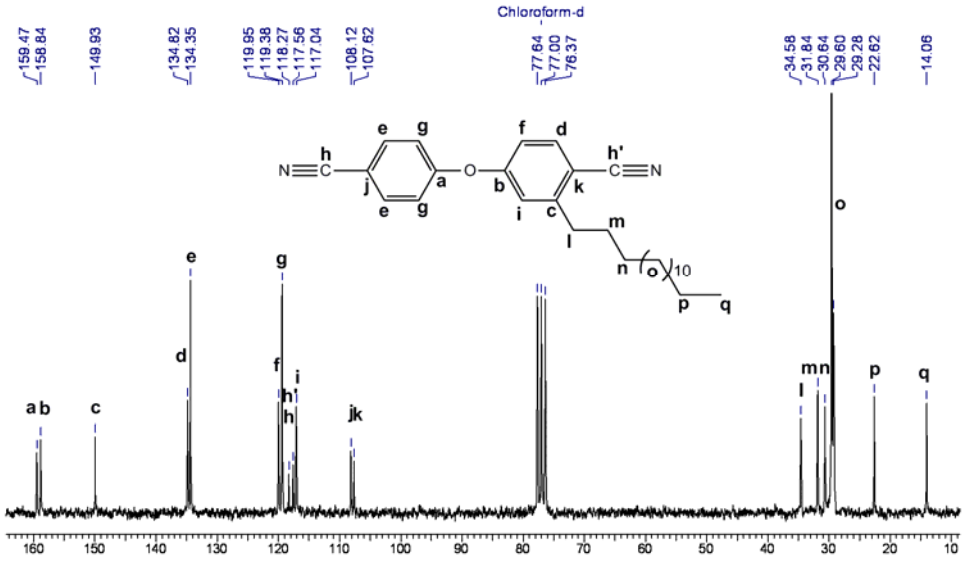


Figure 3.11 ^{13}C-NMR spectrum of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile in $CDCl_3$

In the final step, 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was hydrolyzed under alkaline conditions to yield 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid. Nitriles can be hydrolyzed using both strong acidic or alkaline conditions. **(Figure 3.12)**

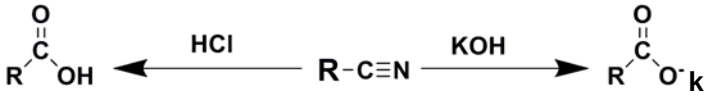


Figure 3.12 Hydrolysis of nitrile

The hydrolysis of nitriles proceeds in the distinct steps under acid or alkali treatment to achieve carboxamides [$RC(=O)NH_2$] and then carboxylic acids [RCOOH]. The hydrolysis of nitriles is generally considered to be one of the best methods for the preparation of carboxylic acids. There are various methods available for hydrolysis of nitriles. To name a few, the Mathew's reaction, a 'dry' hydrolysis procedure of nitriles,[90] alkaline or acid hydrolysis, metal-mediated and metal-catalyzed hydrolysis of nitriles,[91] biocatalysis[92] are some of the methods adapted for nitrile hydrolysis.

The hydrolysis reaction of 4-(4'-cyanophenoxy)-2-pentadecyl benzonitrile was carried out in triethylene glycol/water in the presence of KOH.

4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 3.13, depicts FTIR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid. FTIR spectrum exhibited absorption bands at 1689 cm^{-1} and 1244 cm^{-1} corresponding to C=O stretching and C-O-C stretching, respectively.

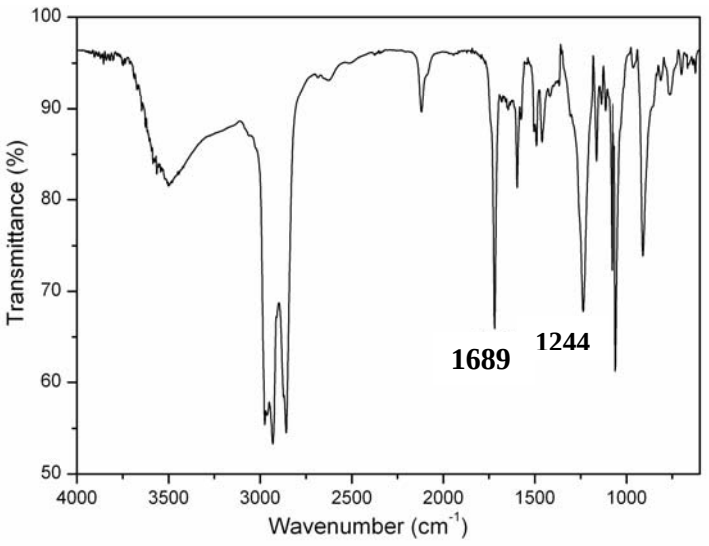


Figure 3.13 FTIR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid

^{1}H NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid along with assignments is presented in **Figure 3.14.**

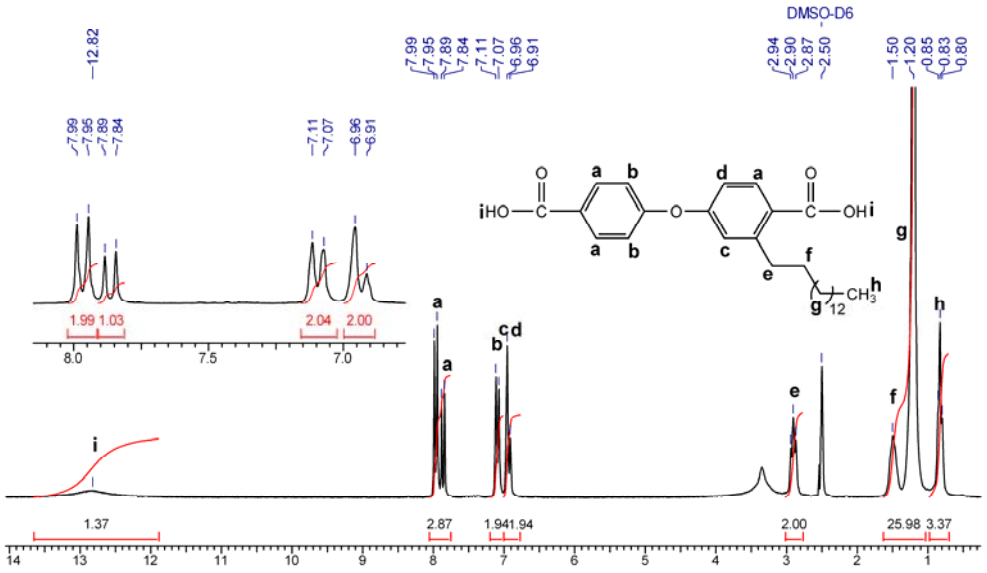


Figure 3.14 ^{1}H-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid in DMSO-d_6

Two hydroxyl protons of carboxyl groups appeared as a broad peak at 12.82 δ ppm confirming the formation of carboxylic acid. Three aromatic protons *ortho* to carboxyl group appeared as two doublets at 7.97 and 7.87 δ ppm, while rest of the aromatic protons appeared as a multiplet in the region 6.89-7.13 δ ppm. The benzylic –CH_2 appeared as a triplet at 2.90 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.50 δ ppm. The other methylene protons exhibited a multiplet over the range 1.18-1.22 δ ppm.The terminal –CH_3 showed a triplet at 0.83 δ ppm.

In ^{13}C-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid, **(Figure 3.15)**

carbonyl carbons of the carboxyl group resonated at 188.09 and 188.14 δ ppm. Carbons adjacent to carboxylic moiety appeared as two signals at 126.11 and 126.30 δ ppm. Spectral data corresponding to other carbon atoms was in good agreement with the proposed structure.

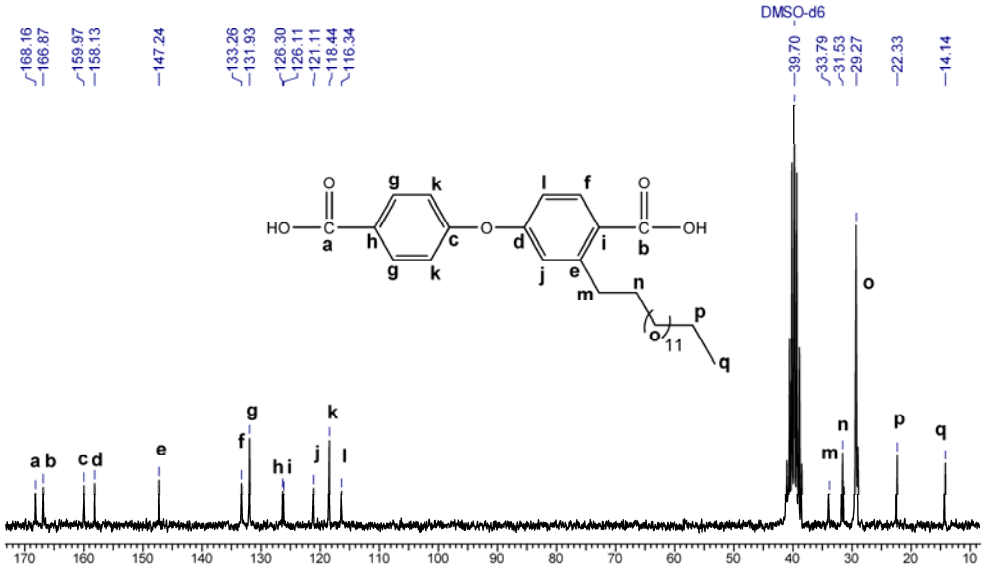
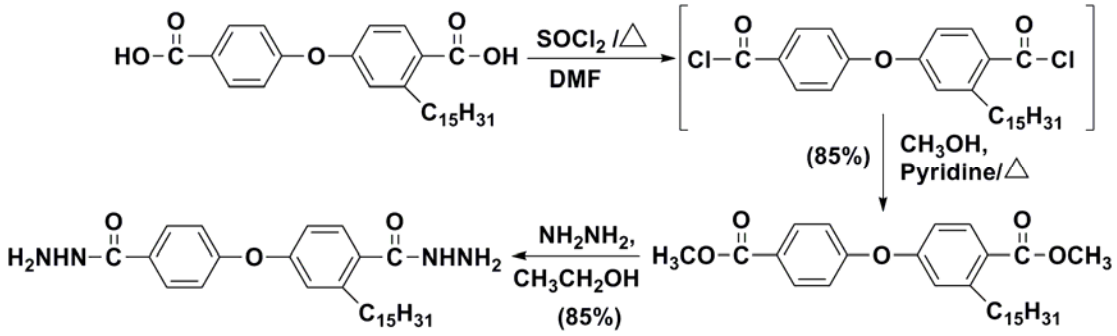


Figure 3.15 ^{13}C-NMR spectrum of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid in DMSO-d_6

3.4.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide

Scheme 3.2, outlines route for the synthesis of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide.



Scheme 3.2 Synthesis of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

The synthesis of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide involved three steps. In the first step, 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid was treated with thionyl chloride in the presence of DMF to yield 4-[4'-(chlorocarbonyl)phenoxy]-2-pentadecylbenzoyl chloride, which was converted into diester *viz,* 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate. The obtained diester after hydrazinolysis with hydrazine hydrate gave the desired diacyl hydrazide *viz*, 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide.

In the first step, the diacid was treated with thionyl chloride to obtain 4-[4'-(chlorocarbonyl) phenoxy]-2-pentadecylbenzoyl chloride. It was not isolated but directly transformed into diester.

The obtained diester is a viscous liquid and it was purified by column chromatography.

The diester viz, 4-(4'-methoxy carbonyl)phenoxy)-2-pentadecyl benzoate was characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopy.

In the FTIR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate **(Figure 3.16)** a band at 1720 cm^{-1} was observed which corresponds to the carbonyl of the ester group.

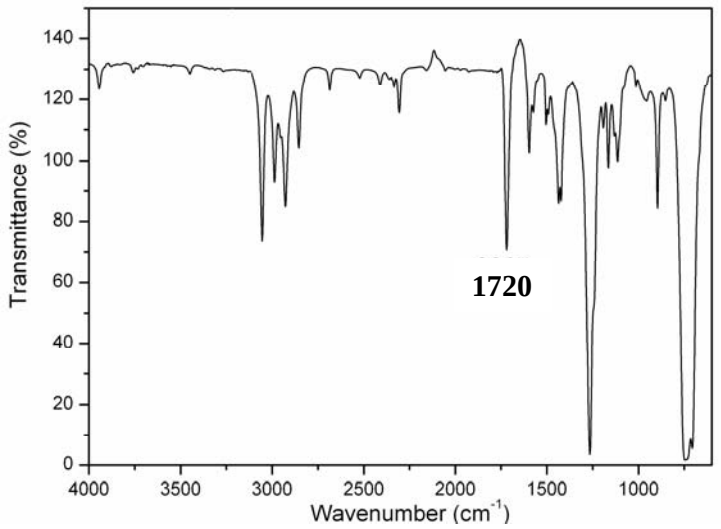


Figure 3.16 FTIR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate

^{1}H-NMR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate is shown in **Figure 3.17**.

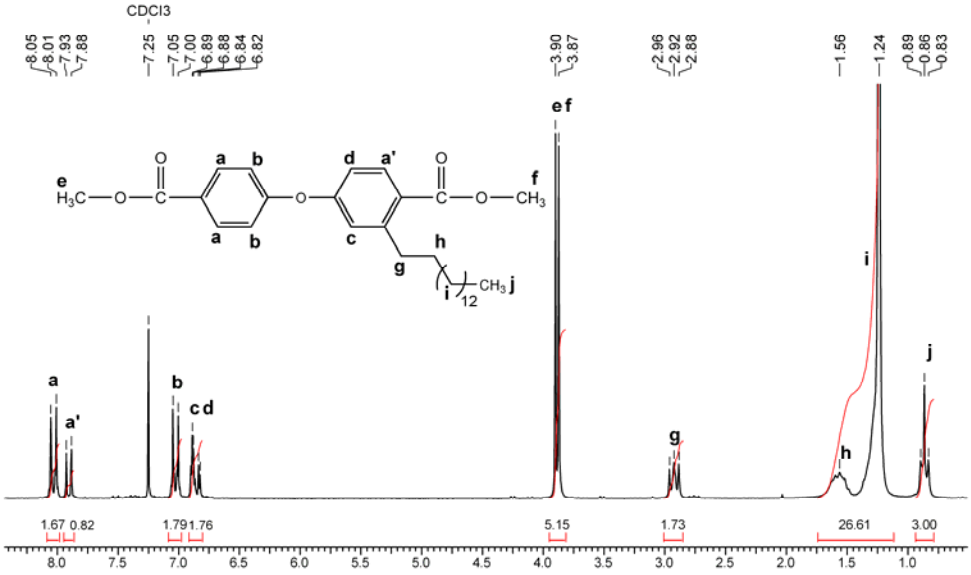


Figure 3.17 ^{1}H-NMR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate in $CDCl_3$

The protons *ortho* to ester group appeared as two doublets at 8.03 and 7.90 δ ppm. The protons *meta* to ester group appeared as a doublet at 7.03 δ ppm and a multiplet in the range 6.80-6.91 δ ppm. Methyl protons of methyl ester exhibited two singlets at 3.87 and 3.90 δ ppm. The benzylic $-CH_2$ appeared as a triplet at 2.92 δ ppm while remaining methylene protons appeared as a

triplet at 1.56 δ ppm and a multiplet in the range 1.22-1.26 δ ppm. Terminal $–CH_3$ appeared as a triplet at 0.86 δ ppm.

^{13}C-NMR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate along with assignments of the carbon atoms is shown in **Figure 3.18**

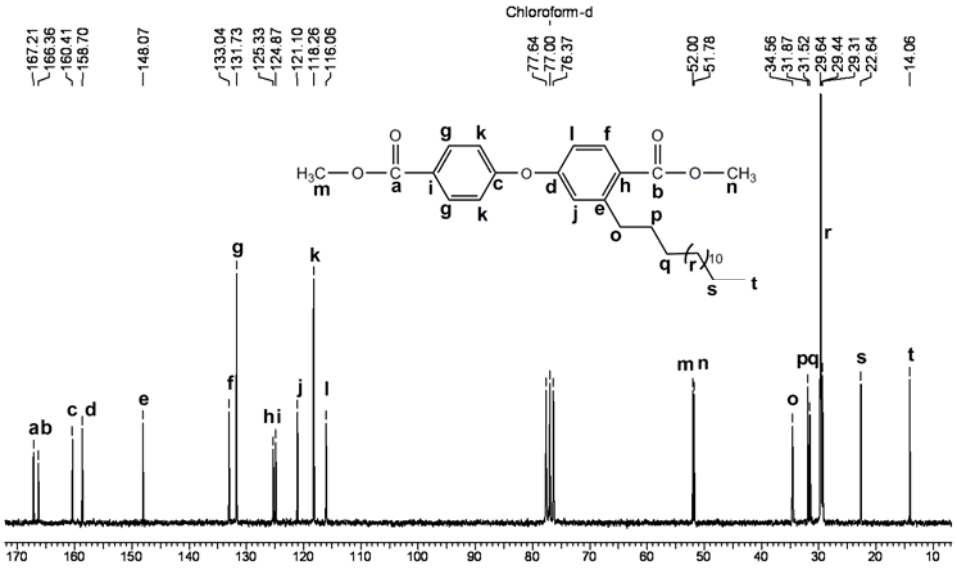


Figure 3.18 ^{13}C-NMR spectrum of 4-(4'-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate in $CDCl_3$

The carbonyl carbons of the ester groups gave rise to two distinct resonances at 167.21 and 166.36 δ ppm. Carbons (c,d) adjacent to oxygen resonated at 160.41 and 158.70. Aromatic carbon attached to benzylic $–CH_2$ appeared at 148.07 δ ppm. Methyl carbons of methyl ester appeared as two separate peaks at 52.0 and 51.78 δ ppm.

The diester was converted to diacyl hydrazide *viz,* 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide. The hydrazinolysis of diester was carried out with hydrazine hydrate (99%) in ethanol and the product was crystallized twice from ethanol.

4-[4'-(Hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide is shown in **Figure 3.19.** Absorption band at 3289 cm^{-1} is assignable to $-NH_2$ and –NH- functions. Absorption band at 1662 cm^{-1} is attributed to the carbonyl of the acid hydrazide group.

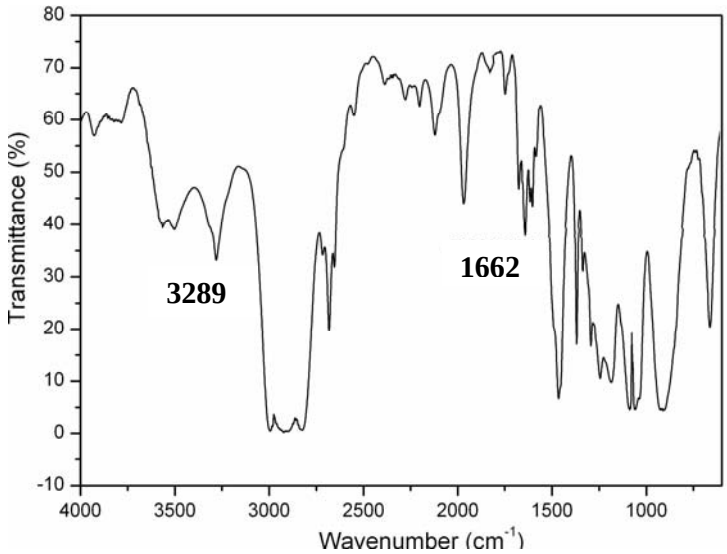


Figure 3.19 FTIR spectrum of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

^{1}H-NMR spectrum of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide is shown in **Figure 3.20**.

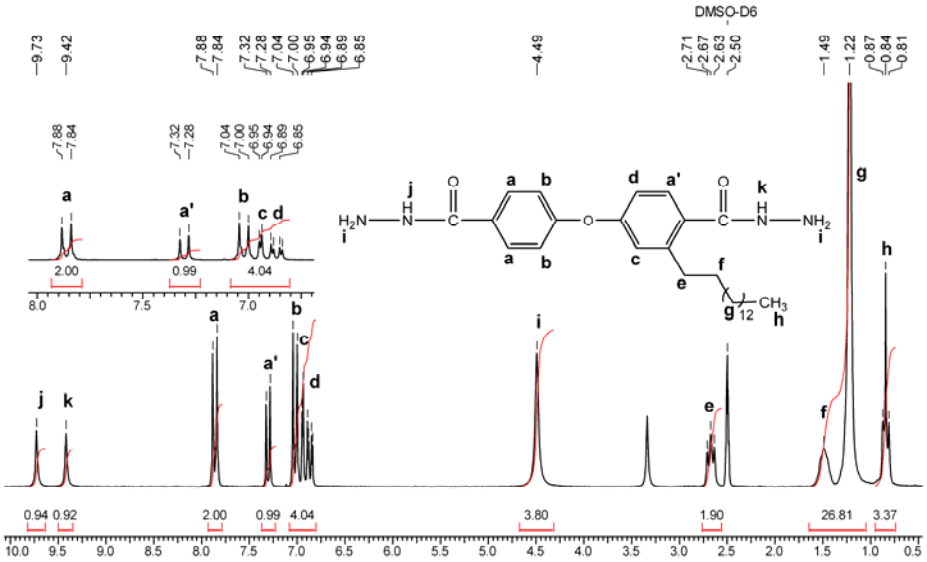


Figure 3.20 ^{1}H-NMR spectrum of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide in DMSO-d_6

Two braod singlet peaks observed at 9.70 and 9.42 δ ppm were assignable to the –NH- of the acid hydrazide group. The aromatic protons *ortho* to acid hydrazide group exhibited two doublets at 7.86 and 7.30 δ ppm. The remaining aromatic protons appeared as a multiplet in the range 6.83-7.06 δ ppm. A broad singlet at 4.49 δ ppm is due to the $–NH_2$ of the acid hydrazide group. The benzylic $–CH_2$ appeared as a triplet at 2.67 δ ppm; while, methylene $–CH_2$ appeared as a triplet at 1.49 δ ppm and a multiplet over the range 1.19-1.24 δ ppm. The termical $–CH_3$ appeared as a triplet at 0.84 δ ppm.

^{13}C-NMR spectrum of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide along with assignments is presented in **Figure 3.21.**

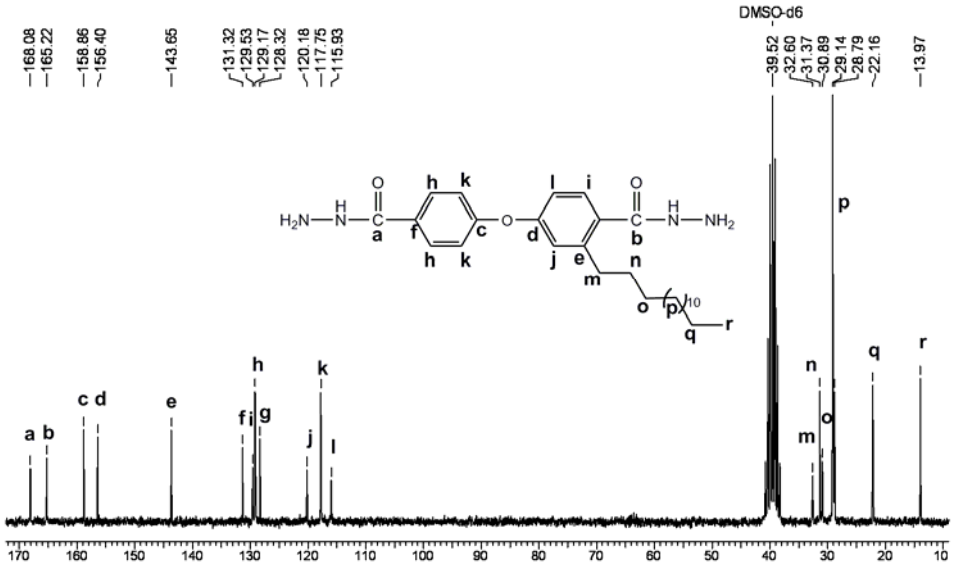


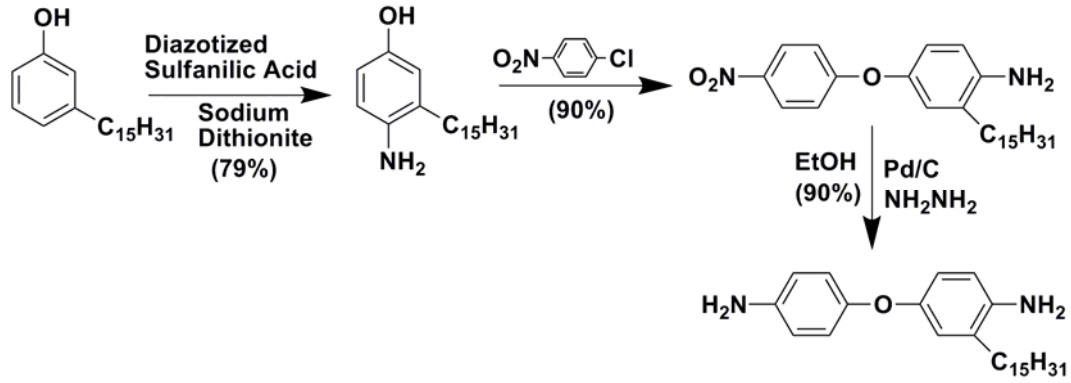
Figure 3.21 ^{13}C-NMR spectrum of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide in DMSO-d_6

3.4.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

Diamines constitute a highly important class of starting materials for the manufacture of a variety of polymers such as polyimides, polyamides, polyazomethines, polyurethanes, polyureas, etc. Various methods have been developed for the preparations of amines such as replacement of halogen,[93] hydroxyl,[94] reduction of nitro compounds,[95] alkaline hydrolysis of isocyanates, etc. Other methods used in the synthesis of diamines include (i) Hofmann degradation[96] (ii) Schmidt reaction[97] (iii) condensation of sodium salt of aminophenol with dihalo diphenyl sulfone[98,72] and (iv) condensation of amine or its hydrochloride with a ketone or an aldehyde.[99]

The diamines used in the synthesis of polymers are mainly synthesized by the catalytic hydrogenation of the respective dinitro compounds.[95] This is due to the fact that many substituted dinitro compounds can be readily prepared by simple substitution reactions of dinitro or mononitro halides and acid chlorides with compounds having an active hydrogen atom like bisphenols, phenols or amines. The most widely used catalysts for these reductions include palladium and platinum catalysts. Ruthenium and rhodium catalysts have also been used, but they have only limited and specialized use.

Scheme 3.3 depicts route for synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine. The synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine comprised of three steps; diazotization, condensation and reduction.[72]



Scheme 3.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

In the first step, 4-amino-3-pentadecyl phenol was obtained by reaction of 3-pentadecyl phenol with diazotized sulfanilic acid and sodium dithionite. The structure of 4-amino-3-pentadecyl phenol was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy and the data was in good agreement with the expected structure.

FTIR spectrum of 4-amino-3-pentadecyl phenol showed absorption bands at 3400 and 3350 cm^{-1} indicating the presence of primary amino group.

^{1}H-NMR spectrum **(Figure 3.22)** of 4-amino-3-pentadecyl phenol showed the presence of a multiplet in the range of 6.51-6.62 δ ppm which could be assigned to three aromatic protons. A broad peak at 3.65 δ ppm could be assigned to $–NH_2$. The benzylic $–CH_2$ appeared as a triplet at 2.43 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.57 δ ppm. The other methylene protons exhibited a multiplet over the range 1.22-1.26 δ ppm.The terminal $–CH_3$ exhibited a triplet at 0.87 δ ppm.

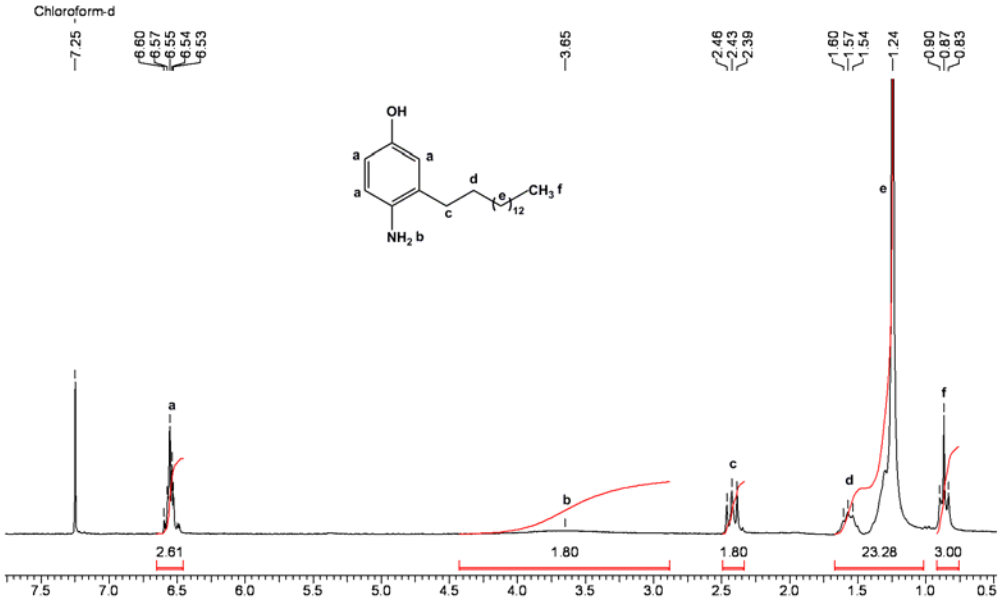


Figure 3.22 ^{1}H-NMR spectrum of 4-amino-3-pentadecyl phenol in $CDCl_3$

^{13}C-NMR spectrum of 4-amino-3-pentadecyl phenol along with assignments of the carbon atoms is shown in **Figure 3.23.**

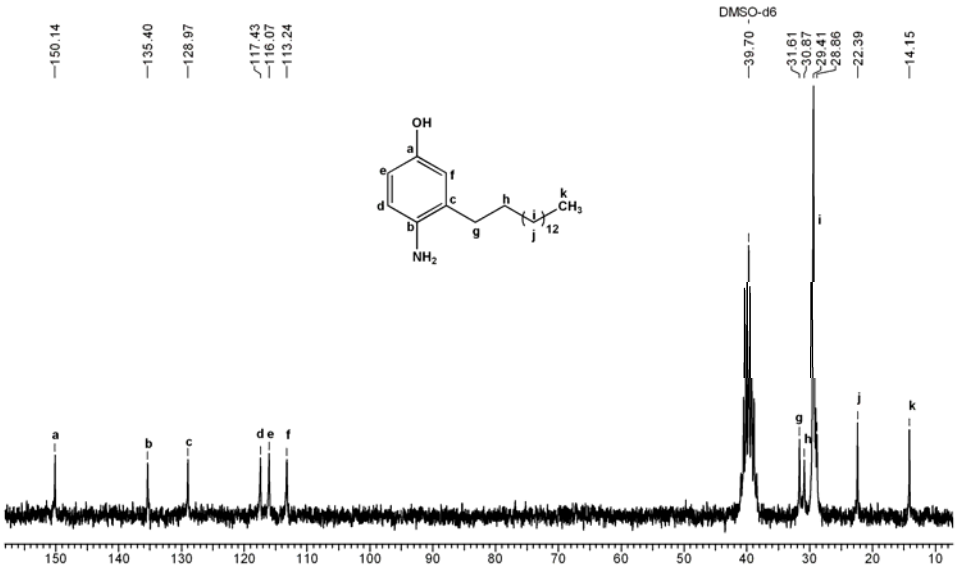


Figure 3.23 ^{13}C-NMR spectrum of 4-amino-3-pentadecyl phenol in DMSO-d_6

The second step involved condensation of 4-amino-3-pentadecyl phenol with 1-chloro-4-nitrobenzene in the presence of potassium carbonate to yield 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine. The pure product was obtained after recystallisation from ethanol. The formation of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

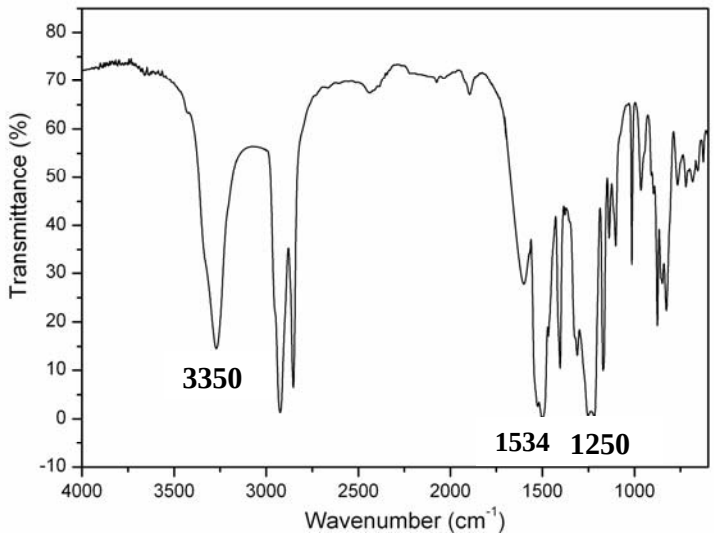


Figure 3.24 FTIR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine

In FTIR spectrum **(Figure 3.24)** of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine, a strong absorption band at 3350 cm^{-1} appeared due to the –NH_2 group. The absorption bands characteristic of the nitro group were observed at 1534 cm^{-1} (asymmetric stretching) and 1340 cm^{-1} (symmetric

stretching). The peak at 1250 cm^{-1} was assigned to –C-O-C- stretching.

^{1}H-NMR spectrum **(Figure 3.25)** of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine exhibited the presence of a doublet at 8.15 δ ppm which corresponds to protons *ortho* to $–NO_2$ group. The doublet at 6.93 δ ppm is assigned to aromatic protons *meta* to $–NO_2$ group. The protons on pentadecyl- substituted ring exhibited multiplet in the region 6.66-6.81 δ ppm. A broad peak at 3.62 δ ppm is attributed to $–NH_2$ group. The benzylic $–CH_2$ appeared as a triplet at 2.45 δ ppm; while, methylene protons appeared as triplet at 1.60 δ ppm and a multiplet in the region 1.24-1.26 δ ppm. The termical $–CH_3$ appeared as a triplet at 0.86 δ ppm.

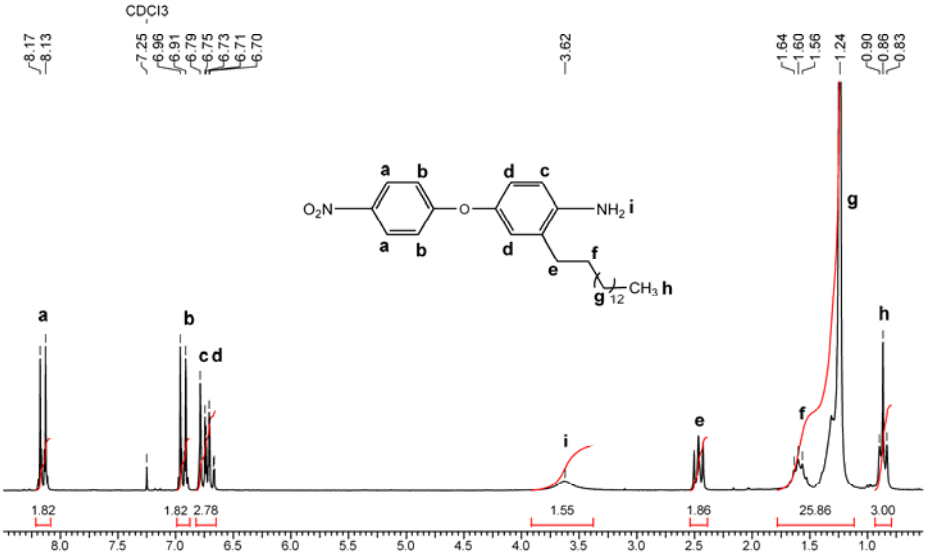


Figure 3.25 ^{1}H-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine in $CDCl_3$

^{13}C-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine along with assignments of the carbon atoms is shown in **Figure 3.26**.

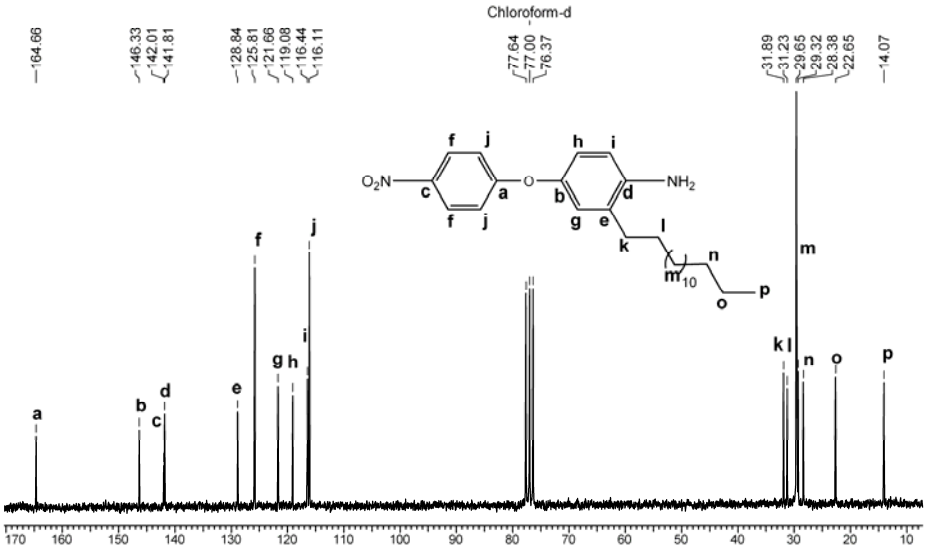


Figure 3.26 ^{13}C-NMR spectrum of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine in $CDCl_3$

In the next step, conversion of 4-(4'-nitrophenoxy)-2-pentadecylbenzenamine to 4-(4'-aminophenoxy)-2-pentadecylbenzenamine was accomplished using Pd/C as catalyst and hydrazine hydrate. The synthesized dimaine was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum **(Figure 3.27)** of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine showed broad band in the region 3300-3400 cm^{-1} (-N-H stretching).

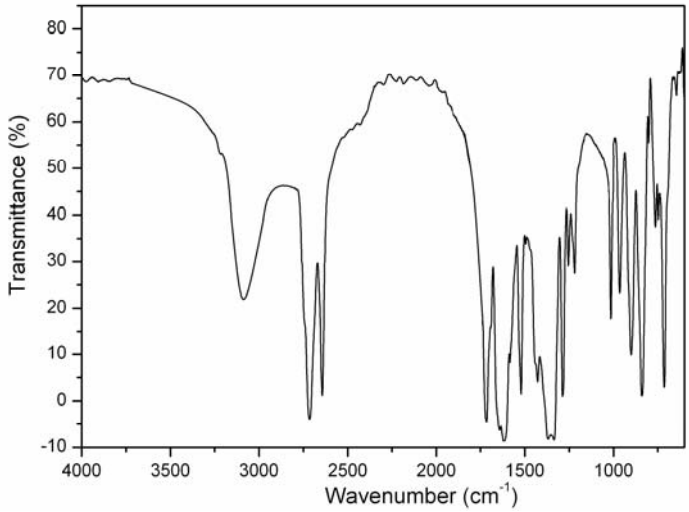


Figure 3.27 FTIR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

In the ^{1}H NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine **(Figure 3.28)**, the multiplet in the region 6.60-6.82 δ ppm corresponds to seven aromatic protons. A broad signal at 3.12 δ ppm was due to $-NH_2$ group. The triplet at 2.43 δ ppm corresponds to benzylic $-CH_2$ of pentadecyl group. The methylene protons β to aromatic ring exhibited a triplet 1.57 δ ppm and a multiplet in the range 1.23-1.27 δ ppm could be assigned to the remaining methylene protons in the pentadecyl chain. The $-CH_3$ protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

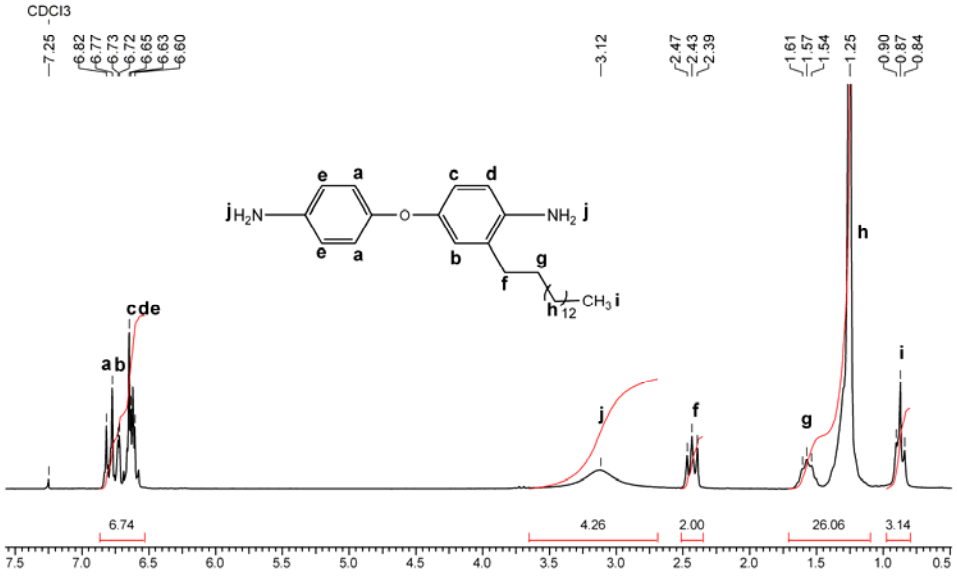


Figure 3.28 ^{1}H-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine in $CDCl_3$

^{13}C-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine along with assignments of the carbon atoms is shown in **Figure 3.29** and is in good agreement with the structure**.**

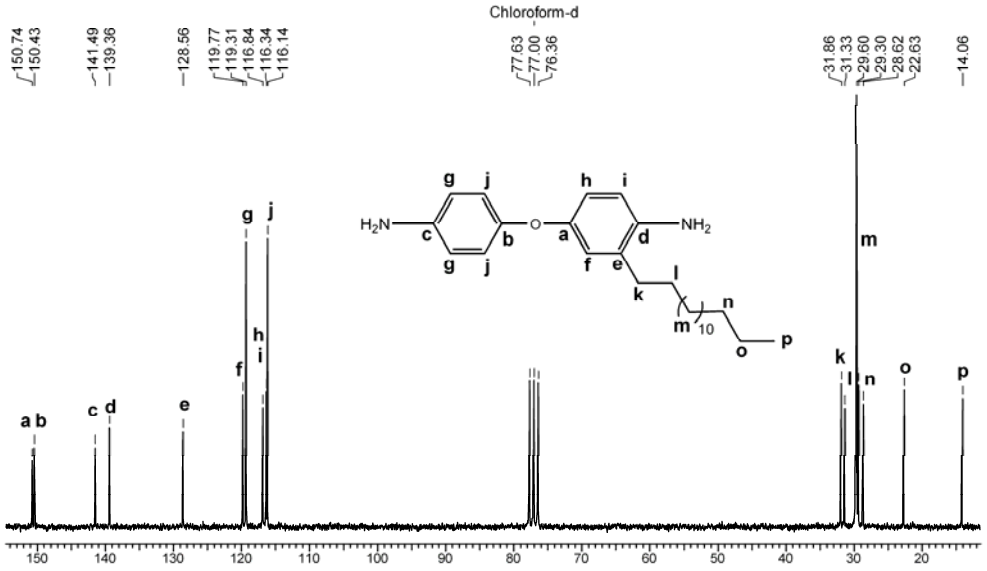
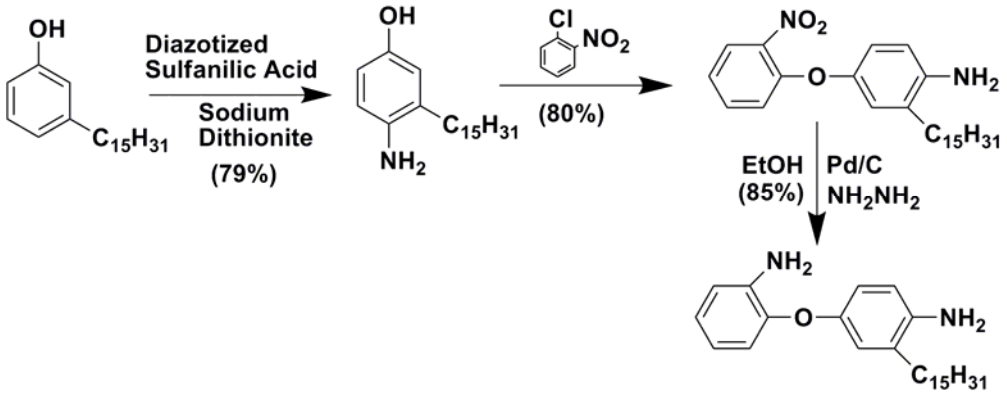


Figure 3.29 ^{13}C-NMR spectrum of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine in $CDCl_3$

3.4.4 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

Aromatic polyamides and polyimides are well accepted as advanced materials for thin-film application in microelectronic devices and liquid crystal displays due to their outstanding mechanical, chemical, thermal, and physical properties.[100] However, the technological applications of most of these polymers are limited by processing difficulties because of high melting or glass transition temperatures and limited solubility in most organic solvents due to their rigid backbones. One of the common approaches for increasing solubility and processability of polyamides and polyimides without sacrificing high thermal stability is the use of asymmetric monomer. It is generally recognized that aryl-ether linkage and asymmetric structure impart properties such as better solubility and melt-processing characteristics and improved toughness to the polymers. The introduction of asymmetric ether-diamine moieties decreases the chain-to-chain interactions, which interrupts the close packing of polymer chains, thereby leading to an enhancement in solubility and decrease in crystallinity.[101-104]

In this work, a new aromatic asymmetrical ether diamine, 4-(2-aminophenoxy)-2'-pentadecylbenzenamine was synthesized as shown in **Scheme 3.4**. In the first step, 4-amino-3-pentadecyl phenol was synthesized as reported in previous section **(3.4.3 Synthesis of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine)**.



Scheme 3.4 Synthesis of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine

In the second step, 4-amino-3-pentadecyl phenol was reacted with 1-chloro-2-nitrobenzene in the presence of K_2CO_3 to obtain 4-(4'-nitrophenoxy)-2'-pentadecylbenzenamine. The pure product was obtained by column chromatographic purification and was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine exhibited the bands at 1532 and 1346 cm^{-1} due to asymmetric and symmetric –NO_2 stretching vibrations. The band at 1280 is due to –C-O-C- stretching vibration. A broad band at 3400-3456 cm^{-1} corresponds to–N-H stretching.

^{1}H NMR spectrum of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine is presented in **Figure 3.30.**

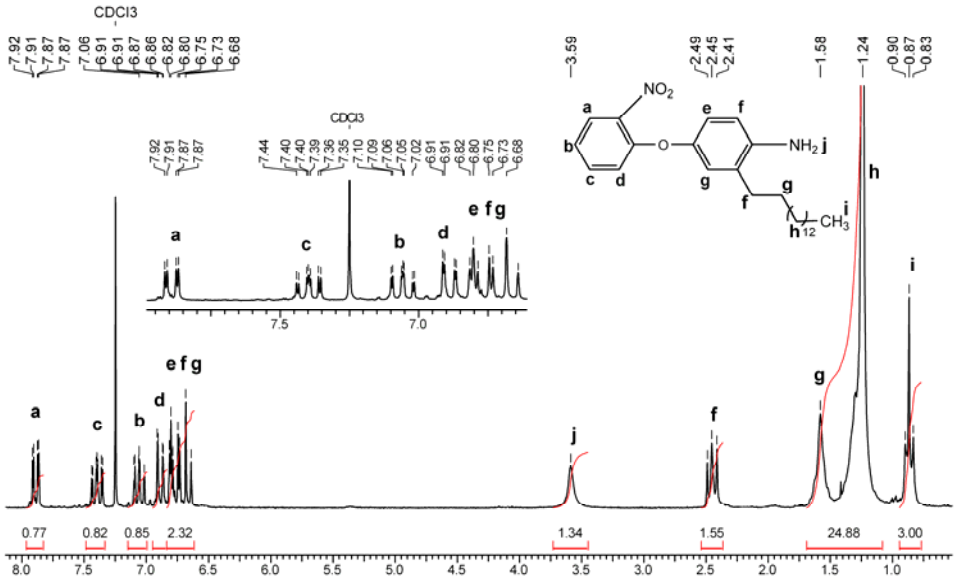


Figure 3.30 ^{1}H-NMR spectrum of 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine in $CDCl_3$

In the aromatic region, proton *ortho* to –NO_2 group exhibited doublet of doublet at 7.89 δ ppm. The rest of the aromatic protons exhibited multiplet over the range 6.66-7.46 δ ppm. In the aliphatic region, the triplet at 2.45 δ ppm corresponds to benzylic –CH_2 of pentadecyl group. The

methylene protons β to aromatic ring exhibited a triplet 1.58 δ ppm and a multiplet in the range 1.22-1.26 δ ppm could be assigned to the remaining methylene protons in the pentadecyl chain. The $–CH_3$ protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

In the next step, 4-(2-nitrophenoxy)-2'-pentadecylbenzenamine was hydrogenated with hydrazine hydrate and Pd/C to the corresponding diamine, viz, 4-(2-aminophenoxy)-2'-pentadecyl benzenamine. FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy confirmed the structure of the desired compound.

FTIR spectrum of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine showed a broad band at 3366-3456 cm^{-1} due to –N-H stretching vibration.

^{1}H-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecylbenzenamine is represented in **Figure 3.31.** Aromatic protons exhibited a multiplet over the range 6.62-6.96 δ ppm. A broad signal at 3.88 δ ppm was observed due to the $–NH_2$ group. The triplet at 2.47 δ ppm was due to benzylic $–CH_2$ of pentadecyl group. The methylene protons β to aromatic ring exhibited a triplet 1.59 δ ppm and a multiplet in the range 1.22-1.26 δ ppm could be assigned to the methylene protons in the pendant alkyl chain. The $–CH_3$ protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

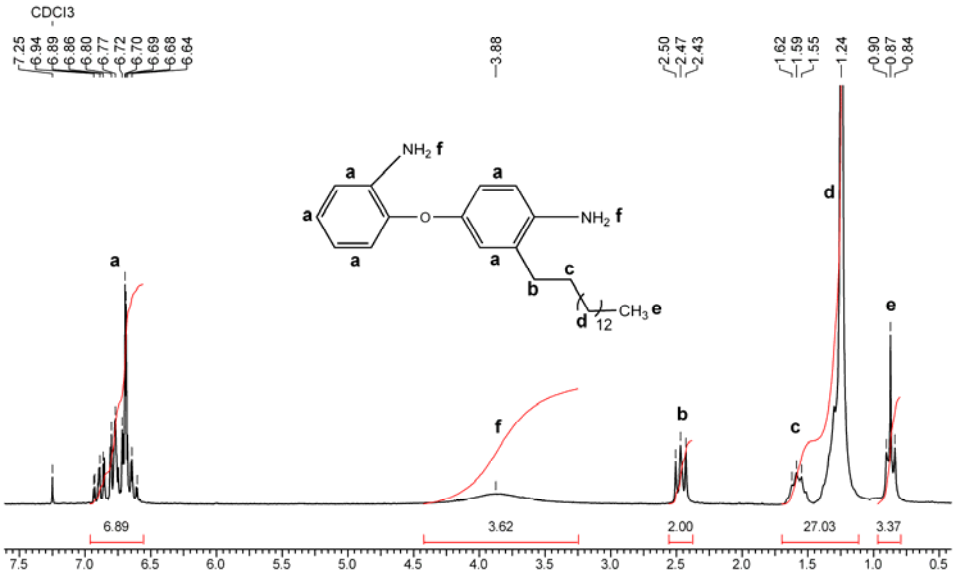


Figure 3.31 ^{1}H-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecyl benzenamine in $CDCl_3$

^{13}C-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecyl benzenamine alongwith assignment is presented in **Figure 3.32** and was in good agreement with the proposed structure.

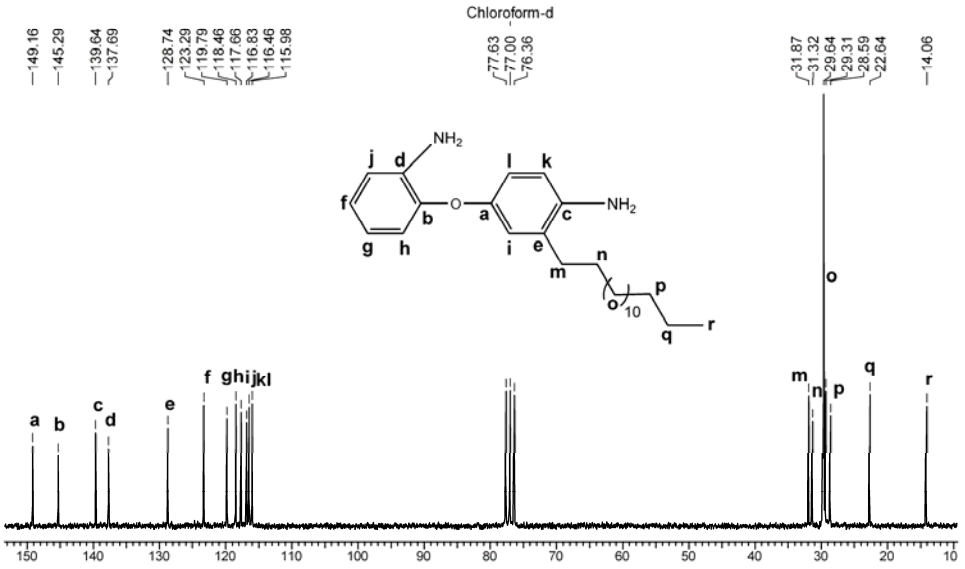
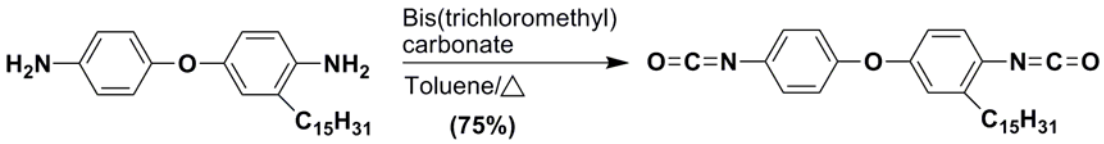


Figure 3.32 ^{13}C-NMR spectrum of 4-(2-aminophenoxy)-2'-pentadecyl benzenamine in $CDCl_3$

3.4.5 Synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

Aromatic diisocyanates are important raw materials in polymer chemistry as they are valuable precursors for the synthesis of polyurethanes, polyureas, polyimides, polyamides, etc. Various methods are available for the preparation of diisocyanates.[105] The phosgenation of an amine or its salt is the method of great importance.[106] The reaction of a nitro compound with carbon monoxide,[107] the reaction of isocyanic acid with an olefin,[108] Curtius rearrangement,[109] Loosen rearrangement[110] are some of the methods generally employed for synthesis of diisocyanates.

Scheme 3.5 depicts route for synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene starting from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine.



Scheme 3.5 Synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

The synthesis of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene was carried out starting from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine in a single step reaction using a well-known method, i.e. phosgenation of an amine with bis(trichloromethyl) carbonate (triphosgene). The phosgenation reaction of diamine was carried out in an inert atmosphere with excess bis(trichloromethyl) carbonate. The structure of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene is shown in **Figure 3.33**. A strong absorption band at 2256 cm^{-1} characteristic of the asymmetric stretching vibration of the isocyanate group was observed.

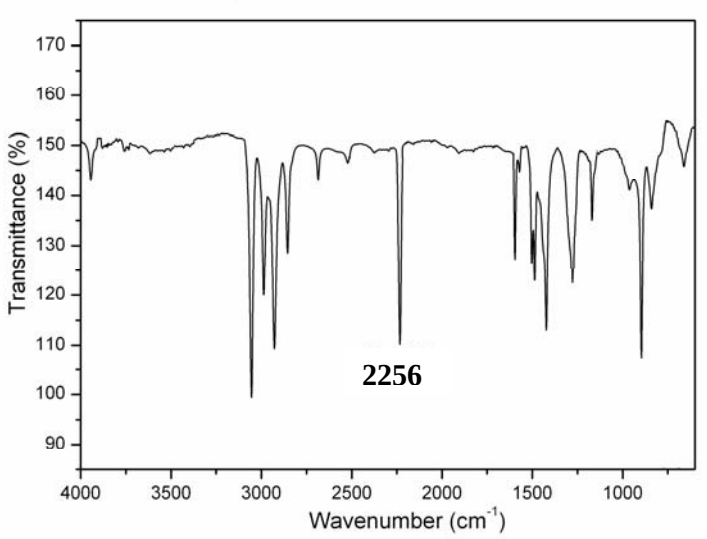


Figure 3.33 FTIR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

^{1}H-NMR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene is shown in **Figure 3.34**.

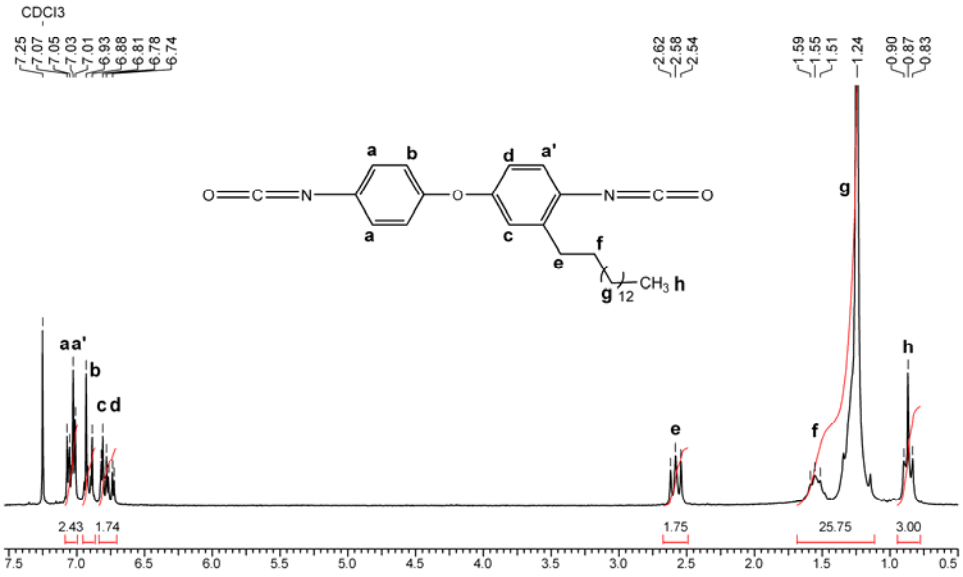


Figure 3.34 ^{1}H-NMR spectrum 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene in $CDCl_3$

Aromatic protons *ortho* to the -NCO group appeared as a multiplet in the range 7.0-7.08 δ ppm. Other four aromatic protons exhibited a multiplet in the region 6.72-6.95 δ ppm. Benzylic – CH_2 appeared as a triplet at 2.58 δ ppm. The other methylene protons appeared as a triplet at 1.55 δ ppm and a multiplet in the region 1.22-1.26 δ ppm. Terminal methyl protons of the aliphatic chain appeared as a triplet at 0.87 δ ppm.

^{13}C-NMR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene along with assignments of the carbon atoms is shown in **Figure 3.35**.

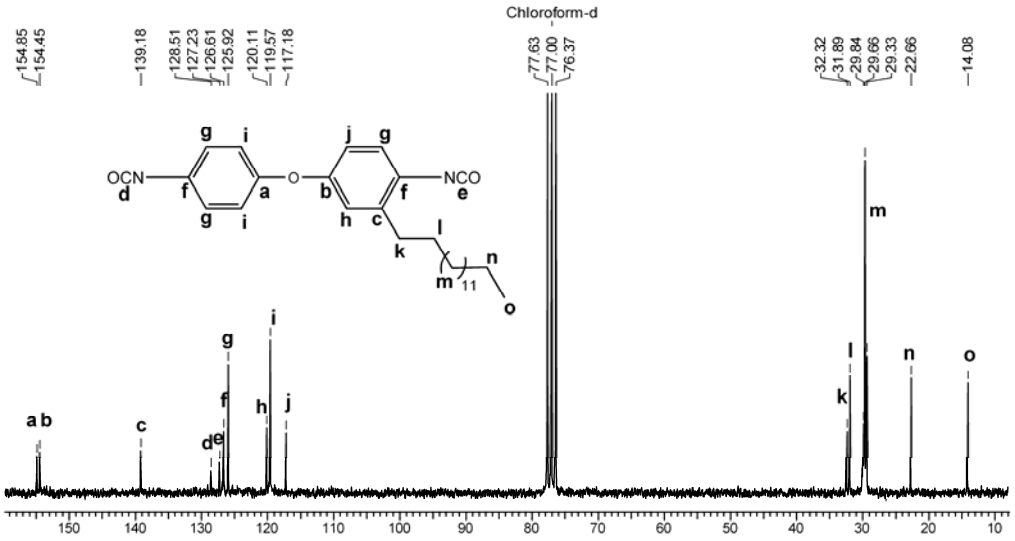


Figure 3.35 ^{13}C-NMR spectrum 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene in $CDCl_3$

In ^{13}C-NMR spectrum of 1-isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene the peaks at 127.23 and 128.51 were assigned to the carbon atoms of the -NCO group. The carbons 'a' and 'b' adjacent to ether linkage appeared at 154.45 and 154.58 δ ppm.

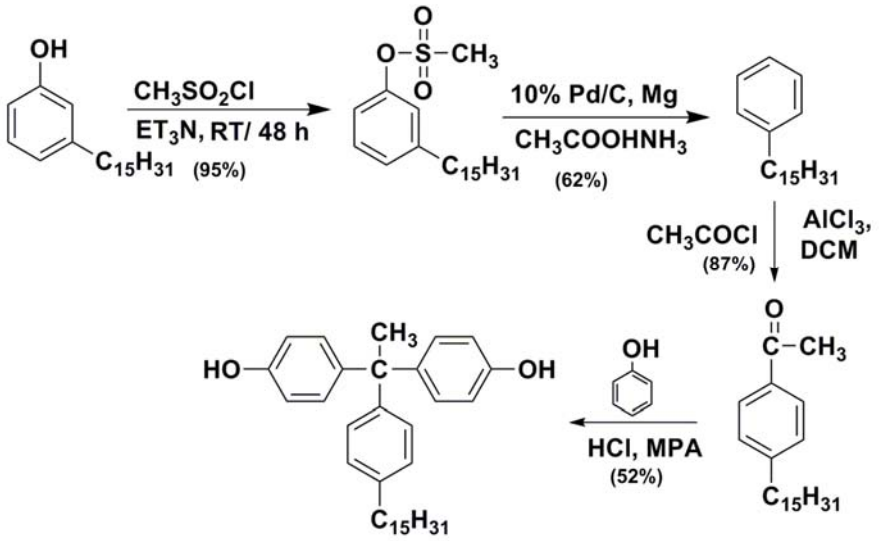
3.4.6 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

Bisphenols are an important class of monomers useful for the preparation of industrially useful epoxy resins, polycarbonates, polyesters, poly(ether sulfone)s, poly(ether ketone)s, etc. Bisphenols are usually synthesized by the acid-catalyzed condensation of aldehydes or ketones with phenols. A variety of aldehydes/ or ketones have been used for synthesis of bisphenols.

A new bisphenol monomer containing pendant pentadecyl chain was designed and synthesized starting from 3-pentadecyl phenol.

Scheme 3.6 depicts route for the synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane. The synthesis of bisphenol involved four steps.

The synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane proceeded through dehydroxylation of 3-pentadecyl phenol to obtain pentadecyl benzene. Since phenolic group is quite poor leaving group, it should be activated prior to deoxygenation. Several methods are available in the literature for dehydroxylation of phenol.[111] The conversion of the phenolic hydroxyl group to the corresponding sulfonate,[112] isourea,[113] dimethyl thiocarbamate,[112] aryl ether,[114] 5-phenyltetrazolyl ether,[115] and phosphate ester,[116] etc. are generally employed for activation as a substrate of reductive deoxygenation.



Scheme 3.6 Synthesis of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

In the first step, 3-pentadecyl phenol was converted into 1-methane sulfonyloxy-3-pentadecyl benzene. The obtained mesyl ester was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene is presented in **Figure 3.36.** The absence of band at 3300 cm^{-1} corresponding to hydroxyl group confirmed the replacement of –H of hydroxyl group by mesyl group.

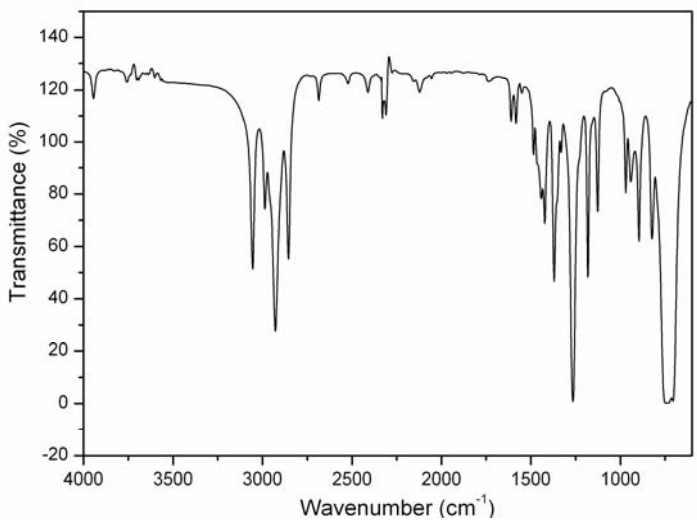


Figure 3.36 FTIR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene

^{1}H-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene is reproduced in **Figure 3.37.** Proton *meta* to mesyl group exhibited a triplet at 7.34 δ ppm. Protons *ortho* and *para* to mesyl group appeared as multiplet in the range 7.05-7.16 δ ppm. The singlet for methyl protons of mesyl ester appeared at 3.12 δ ppm. The triplet at 2.62 δ ppm was due to benzylic –CH_2 of pentadecyl group. The methylene protons β to aromatic ring exhibited a triplet 1.60 δ ppm and a multiplet in the

region 1.22-1.26 δ ppm could be assigned to the methylene protons in the pendant alkyl chain. The –CH_3 protons of pentadecyl chain appeared as a triplet at 0.87 δ ppm.

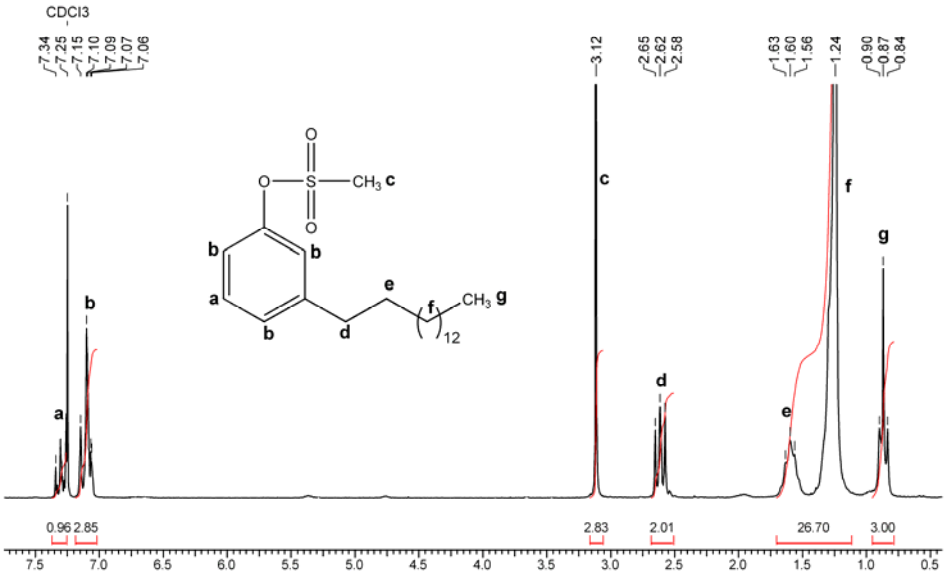


Figure 3.37 ^{1}H-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene in $CDCl_3$

^{13}C-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene alongwith assignments is presented in **Figure 3.38.**

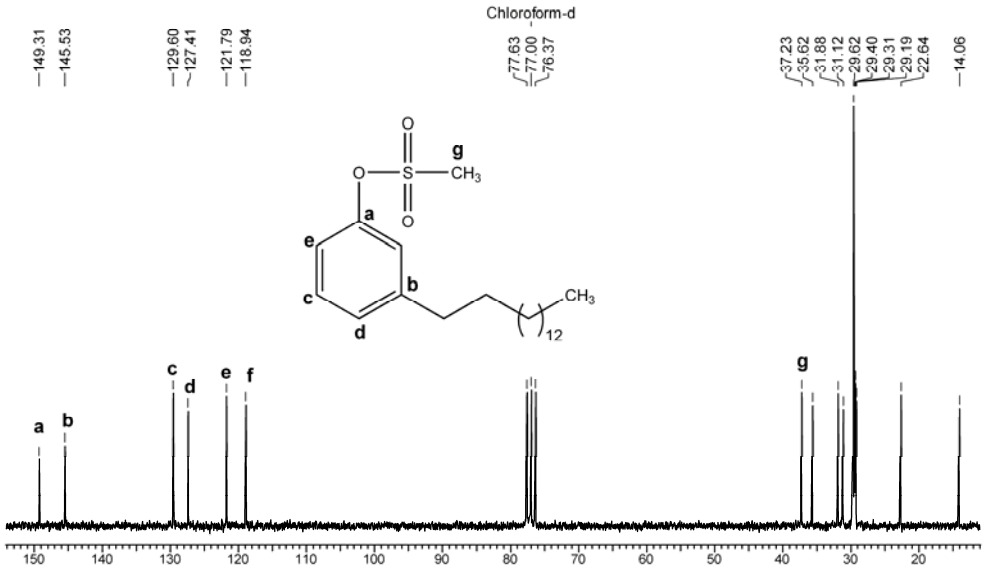


Figure 3.38 ^{13}C-NMR spectrum of 1-methyl sulfonyloxy-3-pentadecyl benzene in $CDCl_3$

Further, the mesyl ester of 3-pentadecyl phenol was converted into pentadecyl benzene using Mg metal and ammonium acetate with Pd/C as catalyst.[111] The obtained pentadecyl benzene was purified by column chromatography. The product was characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy.

In ^{1}H-NMR spectrum **(Figure 3.39)** of pentadecyl benzene aromatic protons appeared as a multiplet in the range 7.13-7.33 δ ppm. Benzylic –CH_2 splitted as a triplet at 2.60 δ ppm. The

methylene protons β to aromatic ring exhibited a triplet at 1.61 δ ppm, while rest of the methylene protons appeared as multiplet over the range 1.23-1.27 δ ppm. A triplet at 0.88 δ ppm could be attributed to the terminal $–CH_3$.

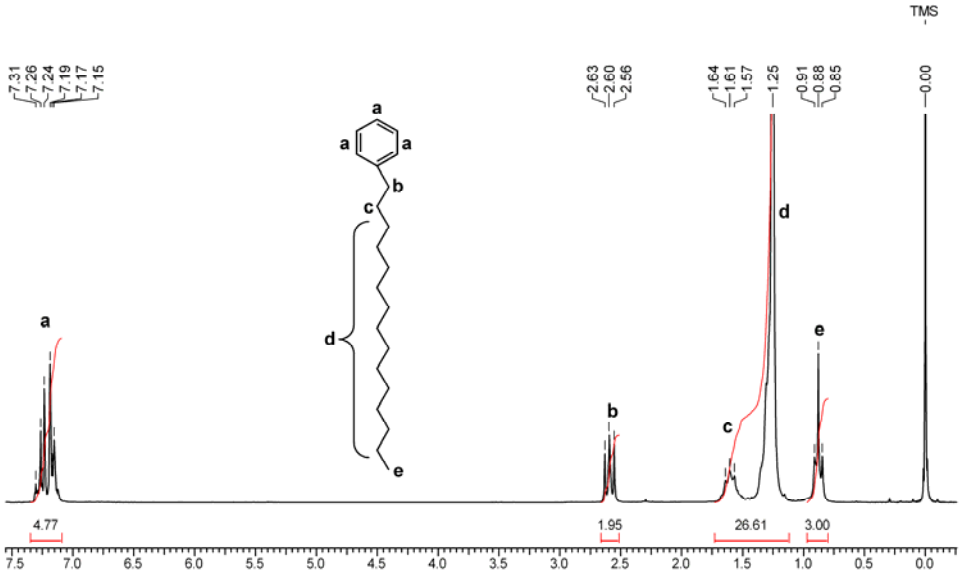


Figure 3.39 ^{1}H-NMR spectrum of pentadecyl benzene in $CDCl_3$

^{13}C-NMR spectrum of pentadecyl benzene along with assignments of the carbon atoms is shown in **Figure 3.40**.

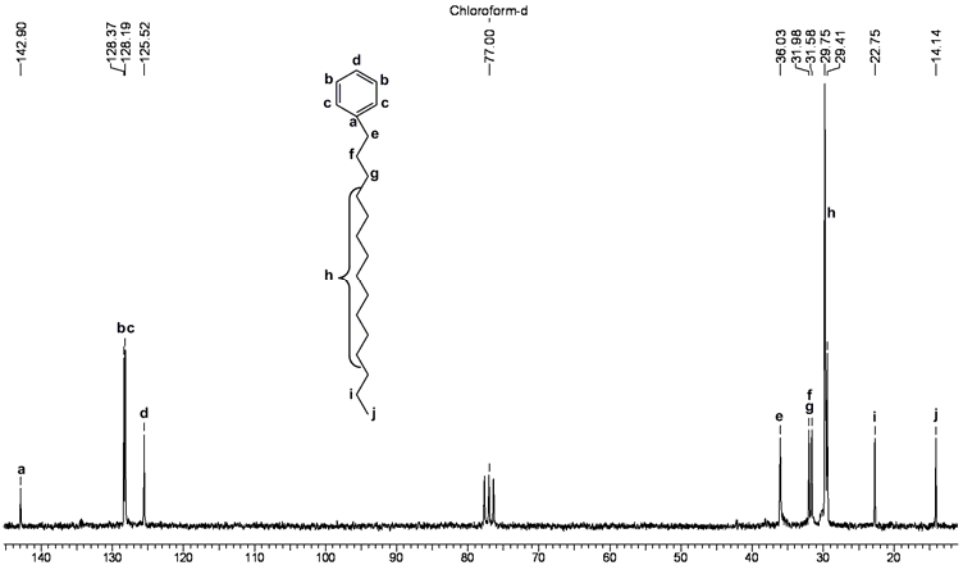


Figure 3.40 ^{13}C-NMR spectrum of pentadecyl benzene in $CDCl_3$

In the next step, monoacylation of pentadecyl benzene was carried out using acetyl chloride as acylating agent and aluminium chloride as catalyst. The pure monoacylated product was obtained after column chromatography.

4-Acetyl pentadecyl benzene was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 4-acetyl pentadecyl benzene (**Figure 3.41**) showed the presence of C=O stretching band at 1690 cm^{-1} confirming the presence of a ketone.

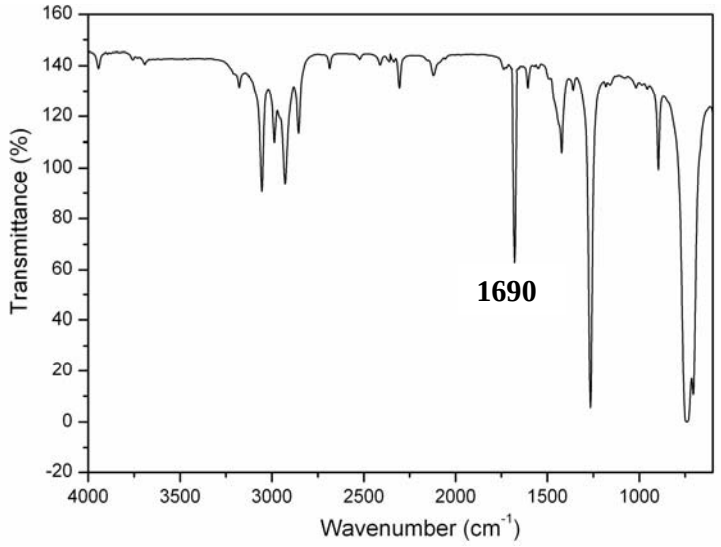


Figure 3.41 FTIR spectrum of 4-acetyl pentadecyl benzene

^{1}H-NMR spectrum of 4-acetyl pentadecyl benzene is reproduced in **Figure 3.42.** Downfield shift was observed for protons *ortho* to acetyl group. These two protons appeared as a doublet at 7.88 δ ppm. Protons *meta* to acyl group exhibited a doublet at 7.26 δ ppm. Methyl protons of acyl group appeared as a singlet at 2.58 δ ppm. Benzylic –CH_2 appeared as a triplet at 2.66 δ ppm. The methylene protons exhibited a triplet at 1.61 δ ppm and a multiplet over the range 1.22-1.1.27 δ ppm. The terminal –CH_3 appeared as a triplet at 0.88 δ ppm.

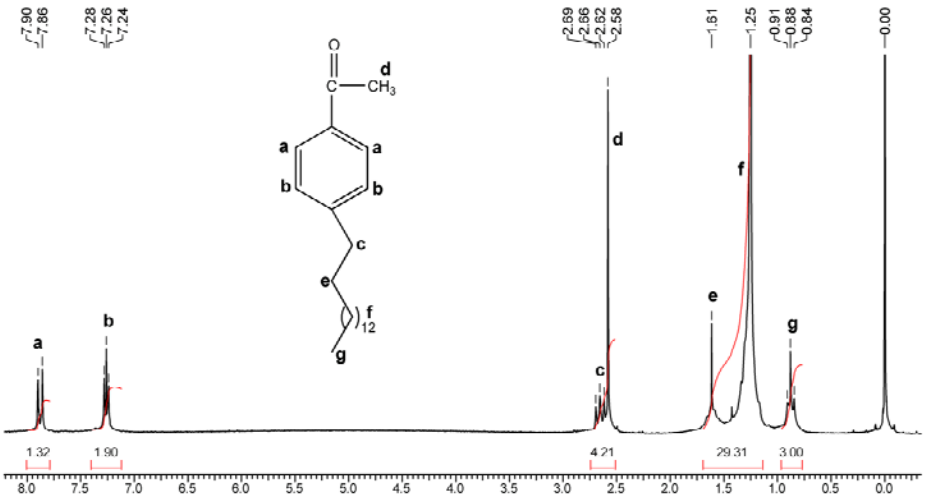


Figure 3.42 ^{1}H-NMR spectrum of 4-acetyl pentadecyl benzene in $CDCl_3$

In ^{13}C-NMR spectrum **(Figure 3.43)** of 4-acetyl pentadecyl benzene, the signal corresponding to acetyl carbon appeared at 197.68 and methyl carbon of acetyl group appeared at 29.33 δ ppm.

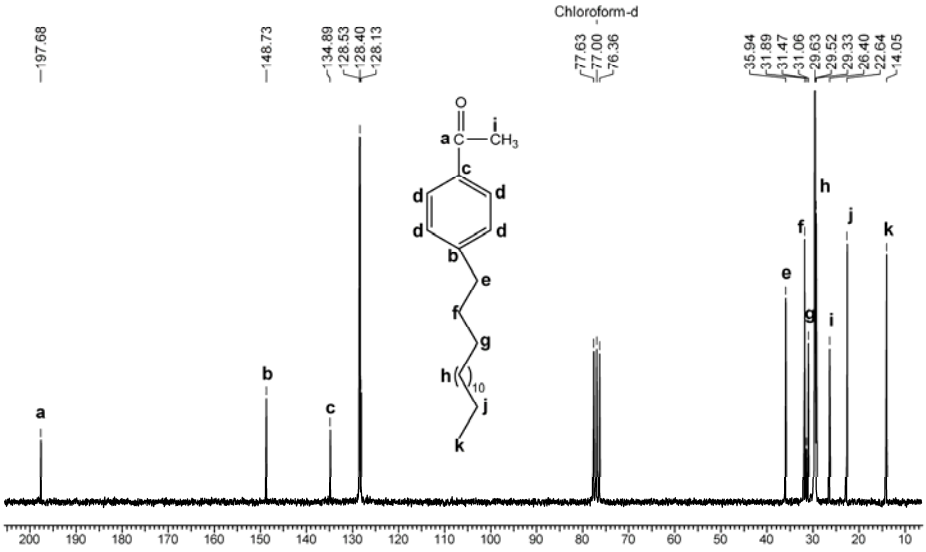


Figure 3.43 ^{13}C-NMR spectrum of 4-acetyl pentadecyl benzene in $CDCl_3$

In the fourth step, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane was prepared by condensation of 4-acetyl pentadecyl benzene with phenol using hydrogen chloride/3-mercaptopropionic acid catalyst system. The role of 3-mercaptopropionic acid for this reaction has been investigated in detail by various researchers.[117,118] When 3-mercaptopropionic acid is used for the condensation in combination with other strong acids, the rate and the selectivity for the formation of desired bisphenol (*p,p'*-isomer) is increased. The crude bisphenol was purified by column chromatography.

1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane **(Figure 3.44)** showed a broad band at 3490 cm^{-1} corresponsing to –OH stretching.

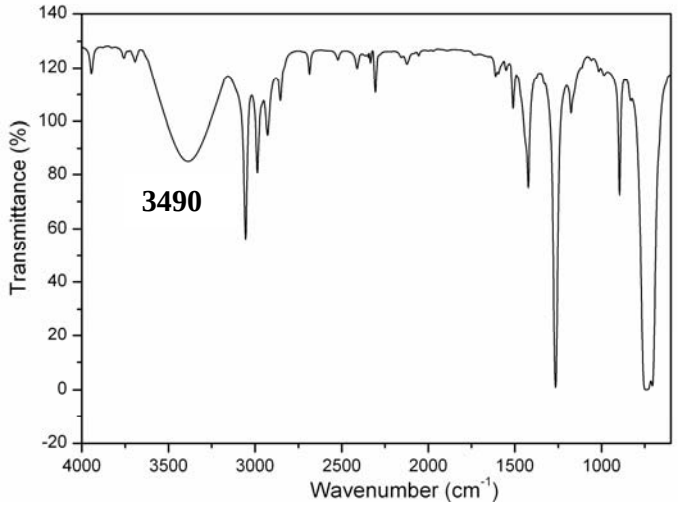


Figure 3.44 FTIR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

In ^{1}H-NMR spectrum **(Figure 3.45)** of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, aromatic protons *ortho* to –OH group appeared as a doublet at 6.70 δ ppm. Rest of the aromatic protons exhibited a multiplet in the region 6.91-7.10 δ ppm. Two proton of hydroxyl group appeared as a single peak at 4.82 δ ppm. The peak at 2.09 δ ppm is assigned to methyl protons attached to quaternary carbon. Benzylic –CH_2 appeared as a triplet at 2.56 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.59 δ ppm, while rest of the methylene protons appeared as a multiplet in the region 1.23-1.27 δ ppm. A triplet at 0.87 δ ppm could be attributed to the terminal –CH_3.

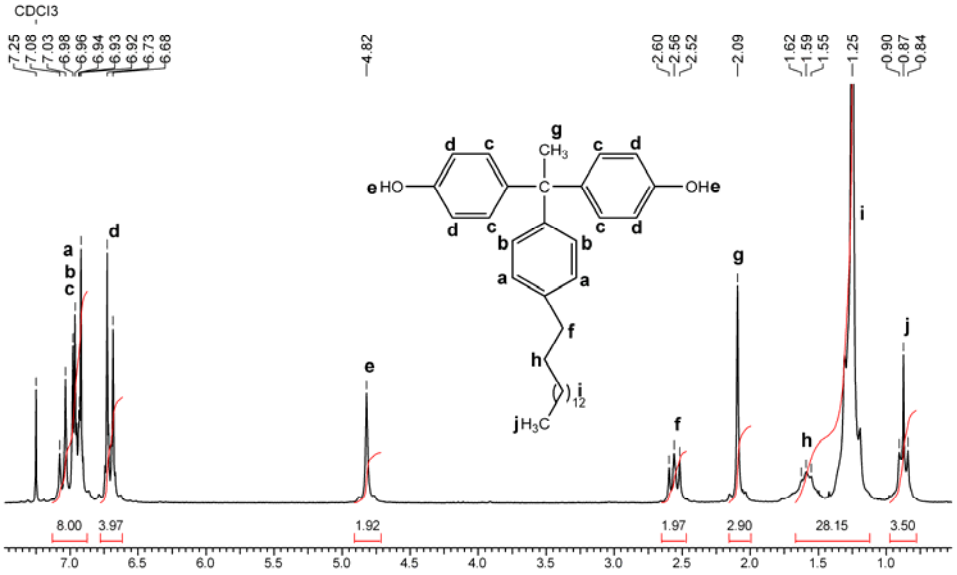


Figure 3.45 ^{1}H-NMR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane in $CDCl_3$

^{13}C NMR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane along with the assignments is presented in **Figure 3.46.**

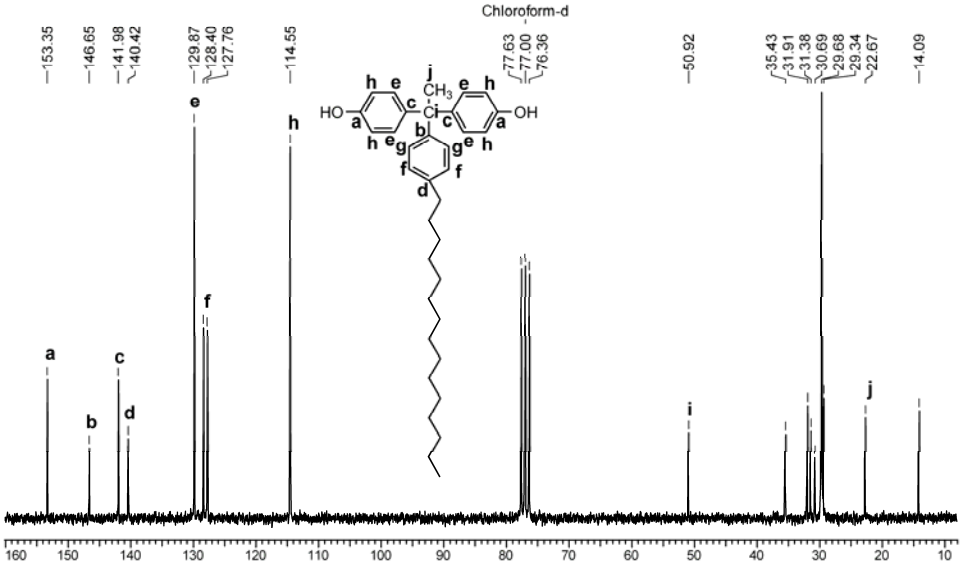
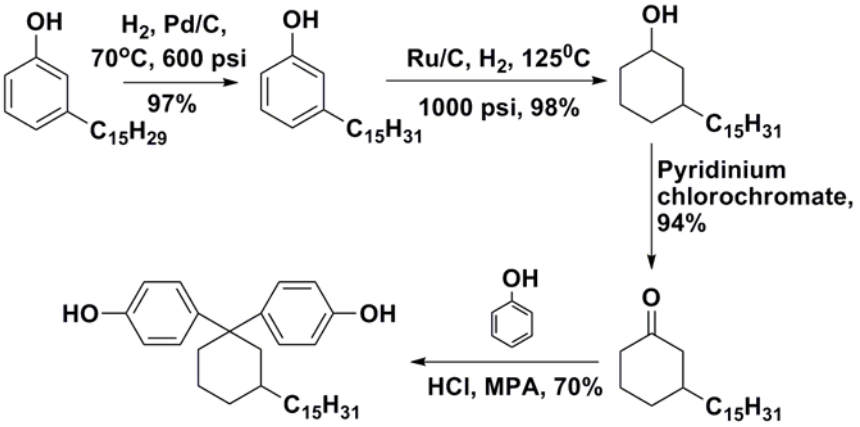


Figure 3.46 ^{13}C-NMR spectrum of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane in $CDCl_3$

Carbons 'a' next to –OH group appeared at 153.35 δ ppm. A peak at 50.92 δ ppm could be assigned to quaternary carbon 'i', while the aliphatic carbon 'j' and aromatic carbon 'b'appeared at 22.67 and 146.65 δ ppm, respectively. In aromatic region, the most upfield shift is observed in case of carbons *ortho* to –OH group. These four carbons appeared at 114.55 δ ppm.

3.4.7 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

Scheme 3.7 depicts route for the synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane. The synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane involved three steps: hydrogenation, oxidation and condensation.



Scheme 3.7 Synthesis of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

In the first step, 3-pentadecylphenol was prepared by the catalytic hydrogenation of freshly distilled cardanol in the presence of 5% Pd/C catalyst. The product obtained was recrystallized from petroleum ether (60-80°C) and was characterized by FTIR and ^{1}H NMR spectroscopy. FTIR spectrum showed absorption band at 3342 cm^{-1}, corresponding to –OH stretching.

Several researchers have studied the catalytic hydrogenation of cardanol at normal and elevated temperatures with different catalysts like nickel, Raney nickel, etc.[119,120] Effect of hydrazine hydrate on the reduction of cardanol was studied by Bhople et al and the products were compared to those obtained by catalytic hydrogenation. It was observed that increase in the molar ratio of hydrazine hydrate to cardanol (more than 1:15) gave better reduction of cardanol.[121] In the present study, Pd/C was used for high yields and reusability of the catalyst.

In the second step, 3-pentadecyl phenol was hydrogenated using 5% Ru/C to get 3-pentadecylcyclohexanol. Transition metal catalysts such as Ni, Pd, Co, Rh, Pt, Ru, etc can also be used for the hydrogenation of phenols.[122-124] After complete reduction, reaction mixture was filtered and the catalyst was recovered. The filtrate was passed through short column of silica gel (100-200 mesh) to obtain colorless solution. The evaporation of solvent under reduced pressure yielded 3-pentadecylcyclohexanol as white solid.

The reduction of 3-pentadecyl phenol gives cis- and trans-3-pentadecylcyclohexanols.[120] 3-

Pentadecylcyclohexanol was characterized by FTIR, ^{1}H-NMR and 13C-NMR spectroscopy.

The disappearance of the band around 1600 cm^{-1} corresponding to aromatic C=C stretching indicates the reduction of aromatic ring. The O-H stretching vibration was observed at 3334 cm^{-1}.

The complete reduction of aromatic ring was further indicated by the disappearance of peaks corresponding to aromatic protons in the region 6.65-7.18 ppm in ^{1}H NMR spectrum **(Figure 3.47)**. The two isomers can be distinguished by ^{1}H-NMR spectroscopy as proton 'a' and 'e' appear at 3.56 and 4.04 δ ppm, respectively.

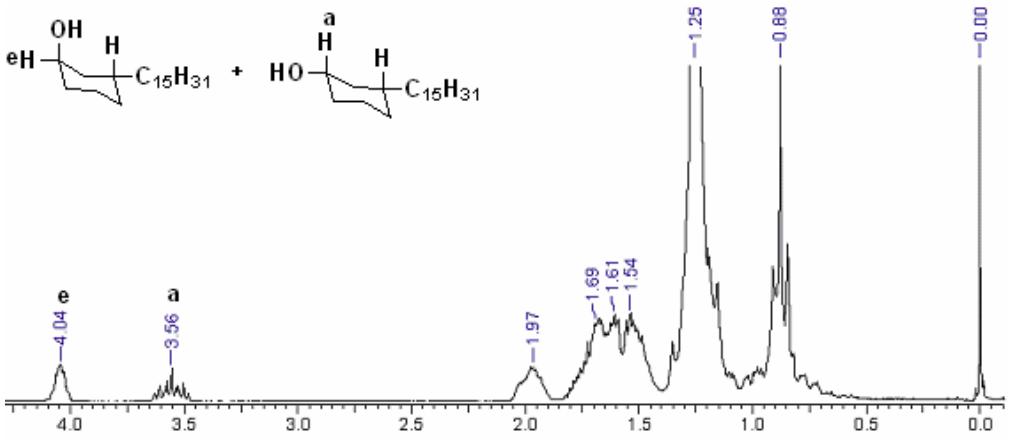


Figure 3.47 ^{1}H-NMR spectrum of 3-pentadecylcyclohexanol in $CDCl_3$

^{13}C-NMR spectrum of 3-pentadecylcyclohexanol with partial assignments is presented in **Figure 3.48**.

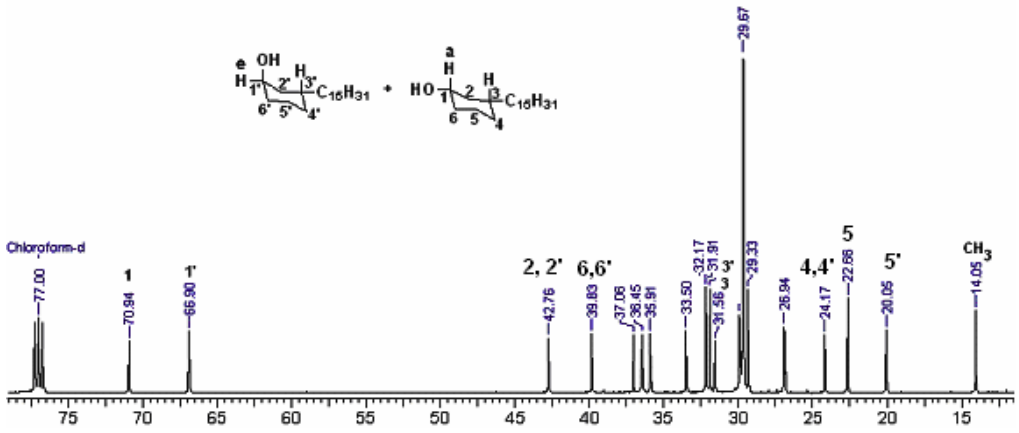


Figure 3.48 ^{13}C-NMR spectrum of 3-pentadecylcyclohexanol in $CDCl_3$

The assignment for the pentadecyl chain is not given because of the complexity of the system. The spectrum indicates the presence of *cis* and *trans* isomers. The carbon number 1 from cis isomer was observed at 70.94 ppm, where as carbon 1' from trans isomer was observed at 66.90 ppm. Carbon 3 and 3' were observed at same chemical shift value (31.56 ppm). The terminal CH_3 from pentadecyl chain appeared at 14.05 ppm. However, isomer separation and detailed spectral analysis was not carried out as it was outside the scope of present work.

The oxidation of alcohols to aldehydes and ketones is fundamental reaction in organic synthesis. Since the first experiment in 1820 by Davy who oxidized ethanol with air over a platinum catalyst, various reagents have been reported which include high valent chromium, and manganese compounds,[125] hypervalent iodine comounds,[126] *m*-chloroperbenzoic acid or sodium hypochlorite with 2,2,6,6-tetramethyl-1-piperidinyloxy,[127] etc. From the standpoint of the green and sustainable chemistry cleaner catalytic systems for oxidations have been in demand.[128] Recently metal-catalyzed oxidations of alcohols using clean and cheap oxidants such as H_2O_2, O_2, and/air have been investigated.[129]

In the present study, pyridinium chlorochromate (PCC) was used for oxidation of 3-pentadecylcyclohexanol because of the easy preparation as well as its demonstrated utility for moderate to large scale oxidations.[81]

In the second step, 3-pentadecyl cyclohexanol was oxidized to 3-pentadecyl cyclohexanone using PCC. After the completion of reaction, the reaction mixture was filtered through short column of Celite and silica gel to obtain colorless filtrate. The solvent was distilled off and solid was dissolved in ethyl acetate and washed with brine solution followed by water. 3-Pentadecylcyclohexanone was crystallized from methanol to obtain white solid.

3-Pentadecylcyclohexanone was characterized by FTIR and ^{1}H-NMR spectroscopy. FTIR spectrum showed the absence of band at 3300 cm^{-1} corresponding to hydroxyl group and appearance of characteristic band for the carbonyl stretch at 1705 cm^{-1}.

^{1}H NMR spectrum of 3-pentadecylcyclohexanone is reproduced in **Figure 3.49**, which shows absence of peaks at 3.56 and 4.04 ppm, corresponding to '**a**' and '**e**' protons of 3-pentadecylcyclohexanol.

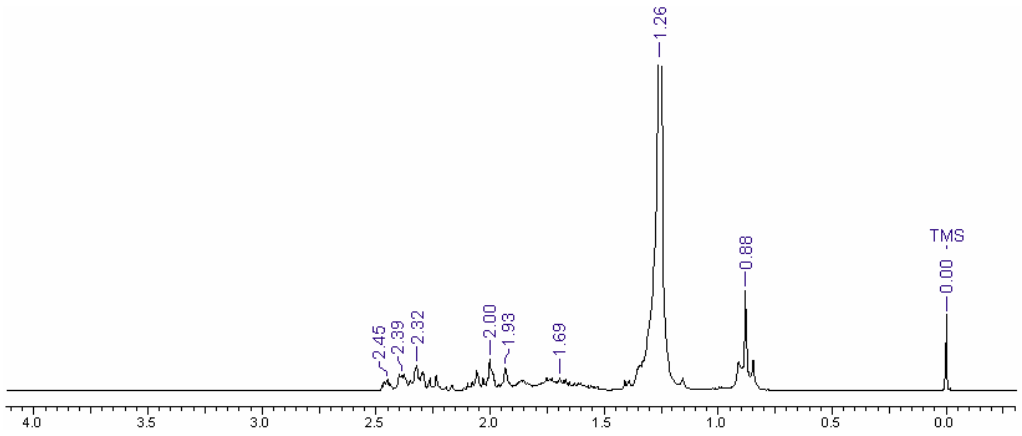


Figure 3.49 ^{1}H-NMR spectrum of 3-pentadecylcyclohexanone in $CDCl_3$

In the fourth step, 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane was prepared by condensation of 3-pentadecyl cyclohexanone with phenol using hydrogen chloride/3-mercaptopropionic acid catalyst system. Under these conditions, the reaction was complete within one hour. The pink colored solid mass was dissolved in ethyl acetate and was washed with sodium

bicarbonate solution and water. Ethyl acetate was removed under reduced pressure to get resinous mass. The excess phenol was removed by washing with hexane and crude 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane was crystallized two times from hexane:toluene mixture (9:1, v/v).

1,1-Bis(4-hydroxyphenyl)-3-pentadecylcyclohexane was characterized by FTIR, ^{1}H-NMR and ^{13}C NMR spectroscopy.

FTIR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane (**Figure 3.50**) showed broad band at 3291 cm^{-1} corresponding to –OH group.

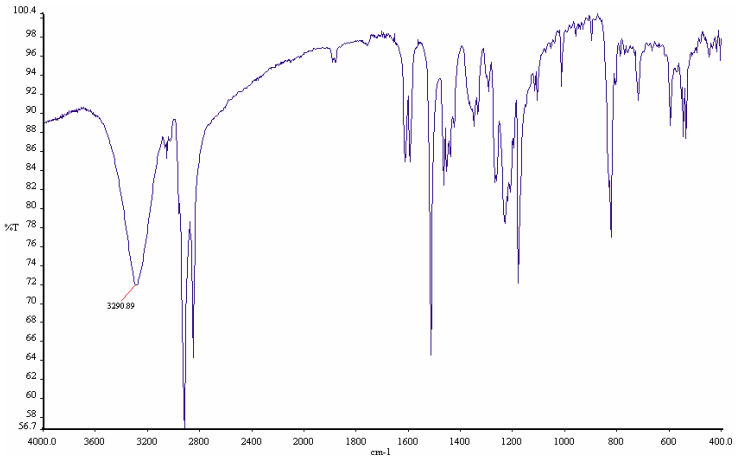


Figure 3.50 FTIR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane

^{1}H NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane along with assignments is presented in **Figure 3.51**.

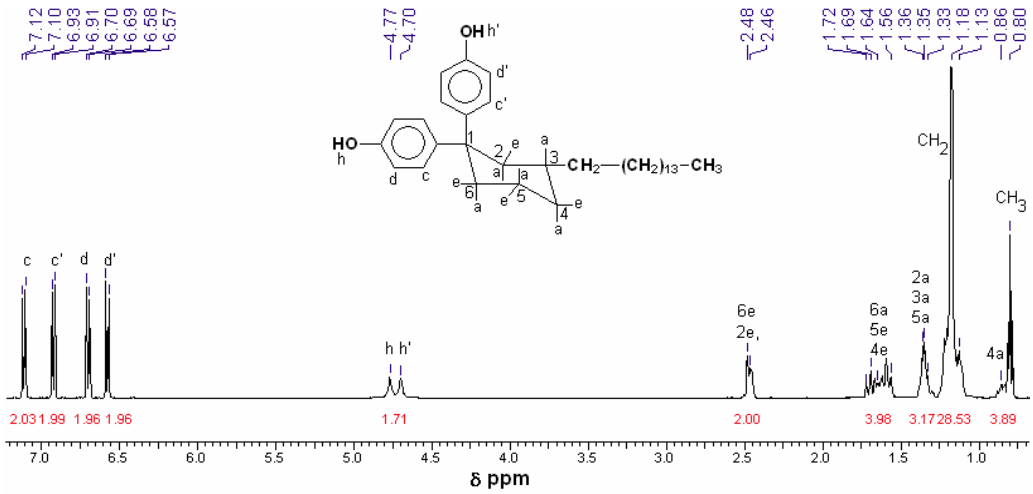


Figure 3.51 ^{1}H-NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane in CDCl3

^{1}H and ^{13}C NMR spectra of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane showed the presence of distereotopic phenyl rings, which are magnetically non-equivalent. 1,1-Bis(4-hydroxyphenyl)-3-pentadecylcyclohexane is not symmetrical about a C_2 axis between the two phenyl rings and this results in different environments for two phenyl rings. Because of this, the

aromatic rings showed four doublets in ^{1}H NMR spectrum and two sets of four aromatic shifts in ^{13}C spectrum as compared to only one set for symmetrical bis-phenols. The substitutent on the cyclohexyl ring prevents the ring inversion of cyclohexyl ring and axial and equatorial phenyl groups can hence be distinguished.

The protons of axial and equatorial phenyl rings can be distinguished. Two sets of doublets are observed in the region of 6.57 – 7.12 ppm. Protons *meta* to hydroxyl of equatorial phenyl ring appeared at 7.11 ppm, while those for axial ring appeared at 6.92 ppm. Protons ortho to hydroxyl of equatorial phenyl ring appeared at 6.70 ppm while those of axial ring appeared at 6.58 ppm.

^{13}C NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane along with assignments is presented in **Figure 3.52**. Equatorial phenyl ring carbons appeared downfield compared to their axial phenyl ring partners. Carbons attached to hydroxyl group appeared as two peaks at 153.07 and 153.01 ppm for equatorial and axial phenyl rings, respectively. Carbons *para* to hydroxyl group appeared at 144.78 and 138.19 ppm. Carbons *meta* to hydroxyl group appeared at 129.15 and 127.35 ppm, whereas carbons *ortho* to hydroxyl group showed signals at 115.20 and 114.78 ppm. Aliphatic carbons were observed at higher field. Carbon 1, 2, 6, 3, 4 and 5 appeared at 45.59, 44.46, 37.73, 33.56, 33.35 and 22.85 ppm, respectively. Terminal CH_3 of alkyl chain showed signal at 14.07 ppm.

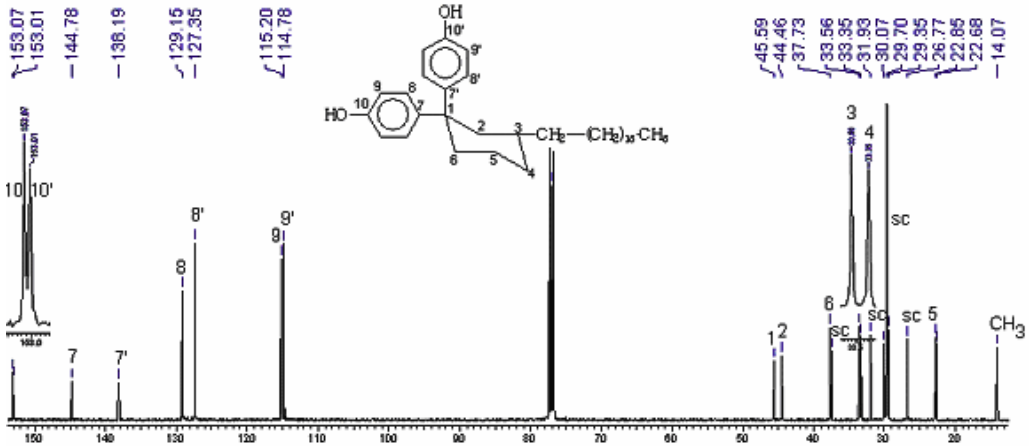


Figure 3.52 ^{13}C-NMR spectrum of 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane in $CDCl_3$

3.5 Conclusions

1. The potential of using a renewable resource material like Cashew Nut Shell Liquid (CNSL); as a raw material for the synthesis of variety of value-added condensation monomers viz; dihalide, diacid, diacylhydrazide, diamines, diisocyanate and bisphenols was explored.
2. Six novel difunctional monomers *viz*;
    1. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene
    2. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid
    3. 4-[4'-(Hydrazinecarbonyl)phenoxy]-2-pentadcyl benzohydrazide
    4. 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine
    5. 4-(2-Aminophenoxy)-2'-pentadecylbenzenamine
    6. 1-Isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene

    containing ether moiety and pendant linear pentadecyl chain were synthesized starting from CNSL.
3. Two bisphenols viz; 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane containing pendant pentadecyl chain and 1,1-bis(4-hydroxyphenyl)-3-pentadecylcyclohexane containing cyclohexylidene moiety with flexible pentadecyl substituent were synthesized starting from CNSL.
4. Difunctional monomers are potentially useful for the synthesis of a host of high performance polymers.

References

1. Lubi, M.C.; Thachil, E.T. *Des. Monomers Polym*. **2000**, 3, 123.
2. Harvey, M.T.; Caplan, C. *Ind. Eng. Chem*. **1940**, 10, 1306.
3. Suresh, K.I.; Kishanprasad, V.S. *Ind. Eng. Chem. Res*. **2005**, 44, 4504.
4. Shingte, R.D.; Wadgaonkar, P.P. US. 6,790,993, **2004**.
5. Avadhani, C.V.; Wadgaonkar, P.P.; Sivaram, S. US 6,255,439, **2001**.
6. David, D.J.; Misra, A. (Eds.) *Relating Materials Properties to Structure: Handbook and Software for Polymer Calculations and Material Properties* Technomic Publishing Company Inc. Lancaster, **1999**.
7. Ulmer II, C. W.; Smith, D.A.; Sumpter, B.G.; Noid, D.I. *Comput. Theor. Polym. Sci*. **1998**, 8, 311.
8. Bicerano, J. *Prediction of Polymer Properties* Marcel Dekker Inc. New York, **1996**.
9. Rogers, M.E.; Long, T.E. (Eds.) *Synthetic Methods in Step Growth Polymers*, John Wiley and Sons: New York , **2003**.
10. Mittal, H.K. (Ed.) *Polyimides and Other High Temperature Polymers* Vol. I, VSP BV, The Netherlands, **2001**.
11. Priebe, C.; Koch, D. PCT Int. Appl. WO 2008017476 A1 **2008**.
12. Roy, D.; Basu, P.K.; Raghunathan, P.; Eswaran, S.V. *J. Appl. Polym. Sci*. **2003**, 89, 1959.
13 Ittara, S.K.; Sarangapani, K.V. US 7,244,772 B2 **200**7.
14. Antony, M.J.; Jayakannan, M. *J. Phys. Chem. B*, **2007**, 111, 12772.
15. Jayakannan, M.; Pillai, C.K.S.; Dhawan, S.K.; Trivedi, D.C.; Subramaniam, R. PCT Int. Appl. WO 2007077569 A1 **2007**.
16. Anilkumar, P.; Jayakannan, M. *Langmuir* **2006**, 22, 5952.
17. Guo, Y.C.; Mele, G.; Martina, F.; Margapoti, E.; Vasapollo, G.; Xiao, W.J.; *J. Organometal. Chem*. **2006**, 691, 5383.
18. de Avellar, I.G.J. ; Godoy, K. ; de Magalhães, G.C. *J. Braz. Chem. Soc*. **2000**, 11, 22.
19. dos Santos, M.L.; de Magalhães, G.C. *J. Braz. Chem. Soc*. **1999**, 10, 13.
20. Antony, B.D. USP Application 20070287640 A1 **2007**.
21. Calo, E.; Maffezzoli, A.; Mele, G.; Martina, F.; Mazzetto, S.E.; Tarzia, A.; Stifani, C. *Green Chem*. **2007**, 9, 754.
22. Lubi, M.C.; Thachil, E.T. Inter. *J. Polym. Mater*. **2008**, 57, 17.
23. Sudha, J.D.; Sasikala, T.S. *Polymer* **2007**, 48, 338.
24. Prasad, V.S.; Pillai, C.K.S. *J. Appl. Polym. Sci*. **2000**, 77, 2631.
25. Philip, J.Y.N.; Buchweishaija, J.; Mkayula, L.L.; Ye, L. *J. Agri. Food Chem*. **2007**, 55, 8870.
26. Suresh, K.I.; Jaikrishna, M. *J. Polym. Sci. Polym. Chem*. **2005**, 43, 5953.
27. Nguyen, L.H.; Koerner, H.; Lederer, K. *J. Appl. Polym. Sci*. **2003**, 88, 1399.
28. Agarwal, S.; Choudhary, V.; Varma, I.K. *J. Appl. Polym. Sci*. **1992**, 46, 1707.
29. John, G.; Pillai, C.K.S.; *Makromol. Chem., Rapid Commun*. **1992**, 13, 255.
30. Sitaramam, B.S.; Chatterjee, P.C. *J. Appl. Polym. Sci*. **1989**, 37, 33.
31. Tyman, J.H. GB 2429455 A **2007**.
32. Syamakumari, A.; Pillai, C.K.S. PCT Int. Appl. WO 2007077564 A1 **2007**.
33. Vikram, T.; Nando, G.B. *J. Appl. Polym. Sci.* **2007**, 105, 1280.
34. Guo, Y.C.; Mele, G.; Martina, F.; Margapoti, E.; Vasapollo, G.; Xiao, W.J.; *J. Organometal. Chem*. **2006**, 691, 5383.
35. Devi, A.; Srivastava, D. *J. Appl. Polym. Sci.* **2006**, 102, 2730.
36. John, G.; Vemula, P.K. *Soft Matter* **2006**, 2, 909.

37. Attanasi, O.A.; Berretta, S.; Favi, G.; Filippone, P.; Mele, G.; Moscatelli, G.; Saladino, R. *Org. Lett*. **2006**, 8, 4291.
38. Arcadi, A.; Attanasi, O.A.; Berretta, S.; Bianchi, G.; Filippone, P. *Synthesis* **2006**, 15, 2523.
39. Attanasi, O.A.; Berretta, S.; Fiani, C.; Filippone, P.; Mele, G.; Saladino, R. *Tetrahedron* **2006**, 62, 6113.
40. Ghatge, N.D.; Yadav, S.D.; Ranade, A.C. *J. Appl. Polym. Sci.* **1968**, 12, 447.
41. Ghatge, N.D.; Patil, V.S. *Die Angew. Makromol. Chem*. **1971**, 19, 75.
42. Tyman, J.H.P. GB 2421503 A **2006**.
43. Khaokhum, L.; Sawasdipuksa, N.; Kumthong, N.; Tummatorn, J.; Roengsumran, S. J. Scientific Res. Chulalongkorn University **2005**, 30, 23.
44. Rao, B.S.; Pathak, S.K. *J. Appl. Polym. Sci.* **2006**, 100, 3956.
45. Springsted, P.; Hahn, L.; Tzap, G.P. US 7,084,103 B1 **2006**.
46. Pillot, J.P.; Birot, M.; Tran, T.T.T.; Dao, T.M.; Belin, C.; Desbat, B.; Lazare, S. *Langmuir* **2005**, 21, 3338.
47. Shedge, A.S.; Lele, A.K.; Wadgaonkar, P.P.; Hourdet, D.; Perrin, P.; Chassenieux, C.; Badiger, M.V. *Macromol. Chem. Phys*. **2005**, 206, 464.
48. Suresh, K.I.; Kishanprasad, V.S. *Ind. Eng. Chem.Res*. **2005**, 44, 4504.
49. Bhunia, H.P.; Nando, G.B.; Basak, A.; Lenka, S.; Nayak, P.L. *Eur. Polym. J*. **1999**, 35, 1713.
50. Saminathan, M.; Pillai, C.K.S.; Pavithran, C. IN 186686 A **2001**.
51. Saminathan, M.; Pillai, C.K.S. US 6,887,632 **2005**.
52. Saminathan, M.; Pillai, C.K.S. *J. Polym. Mater*. **2001**, 18, 83.
53. Saminathan, M.; Pillai, C.K.S.; Pavithran, C. *Macromolecules* **1993**, 26, 7103.
54. Attanasi, O.A.; Del Sole, R.; Filippone, P.; Ianne, R.; Mazzetto, S.E.; Mele, G.; Vasapollo, G. *Synlett* 2004, 5, 799.
55. Nayak, R.R.; Ray, G.; Guru, B.; Lenka, S. *Polym-Plast Technol Eng*. **2004**, 43, 261.
56. Chowdhury, S.K.; Wadgaonkar, P.P.; Hoeks, T.L.; Scholten, A.B.; Rajaraman, S.K.; Sarwade, B.D.; Avadhani, C. US 6,841,598 **2005**.
57. Luboch, E.; Wagner-Wysiecka, E.; Biernat, J. F. *J. Supramol. Chem*. **2002**, 2, 279.
58. Wasserman, D.; Caplan, S. US 2,571,092 **1951**.
59. Nasar, A. S.; Shrinivas, V.; Shanmugam, T.; Raghavan, A., *J. Polym. Sci. Polym. Chem*. **2004**, 42, 4047.
60. Somsaluay, S.; Thumnoon, N.; Sophon, R.; Amorn, P. *Ind. Eng. Chem. Res*. **2004**, 43, 4973.
61. Castro Dantas, T.N.; Dantas, M.S.G.; Dantas Neto, A.A.; D'Ornellas, C.V.; Queiroz, L.R. *Fuel* **2003**, 82, 1465.
62. Saladino, R.; Mincione, E.; Attanasi, O.A.; Filippone, P. *Pure Appl. Chem*. **2003**, 75, 265.
63. Saminathan, M.; Pillai, C.K.S. *Polymer* **2000**, 41, 3103.
64. Paul, R.K.; Pillai, C.K.S. *J. Appl. Polym. Sci.* **2002**, 84, 1438.
65. a) Mathew, J.S., *Ph. D. Dissertation* University of Pune, Pune, India, **2001**. (b) Mathew, J.S.; Vernekar, S.P.; Mercier, R.; Kerboua, R. US 6,500,913 B2 **2002**.
66. Swain, J.R.; Biswal, S.K.; Lenka, S. Polym-Plast Technol. Eng. **2000**, 39, 927.
67. Bhunia, H.P.; Basak, A.; Chaki, T.K.; Nando, G.B. *Eur. Polym. J*. **2000**, 36, 1157.
68. Bhunia, H.P.; Nando, G.B.; Chaki, T.K.; Basak, A.; Lenka, S.; Nayak, P.L. *Eur. Polym. J*. **1999**, 35, 1381.
69. Bhunia, H. P.; Jana, R.N.; Basak, A.; Lenka, S.; Nando, G.B. *J. Polym. Sci. Polym. Chem*. **1998**, 36, 391.
70. Mhaske, S.B.; Bhingarkar, R.V.; Sabne, M.B.; Mercier, R.; Vernekar, S.P. *J. Appl. Polym. Sci*. **2000**, 77, 627.
71. Ning, S.; Bradshaw, J.S.; Savage, P.B.; Krakowiak, K.E.; Izatt, R.M.; De Wall, S.L.; Gokel, G.W. *Tetrahedron* **1999**, 55, 9737.
72. Jadhav, A.S.; Vernekar, S.P.; Maldar, N.N. *Polym Int*. **1993**, 32, 5.

73. Tan, T.T.M. *J. Appl. Polym. Sci.* **1997**, 65, 507.
74. Rupavani, J.N.; Vijayalakshmi, V.; Sitaramam, B.S.; Krishnamurti, N. *Eur. Polym. J*. **1993**, 29, 863.
75. Madhusudhan, V.; Murthy, B.G.K. *Prog. Org. Coat*. **1992**, 20, 63.
76. Ramasri, M.; Rao, Srinivasa, G.S.; Sampathkumaran, P.S.; Shirsalkar, M.M. J. *Appl. Polym. Sci*. **1990**, 39, 1993.
77. Ghatge, N.D.; Mahajan, S.S. *Indian J. Technol*. **1979**, 17, 55.
78. Vernekar, S.P. *Eur. Polym. J*. **1970**, 6, 1547.
79. Ghatge, N.D.; Patil, V.S. *Die Angew. Makromol. Chem*. **1971**, 19.
80. Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals* Pergamon Press: NewYork, **1989**.
81. Corey, E.J.; Suggs, J.W. *Tet. Lett*. **1975**, 31, 2647.
82. a) Ullmann, F. *Chem. Ber*. **1904**, 37, 853. b) Lindley, J. *Tetrahedron* **1984**, 40, 1433.
83. a) Mann, G.; Hartwig, J.F. *Tett. Lett*. **1977**, 38, 8005. b) Aranyos, A.; Old, D.W.; Kiyomori, A.; Wolfe, J.P.; Sadighi, J.P.; Buchwald, S.L. *J. Am. Chem. Soc*. **1999**, 121, 4369. c) Marcoux, J.F.; Doye, S.; Buchwald, S. L. *J. Am. Chem. Soc*. **1997**, 119, 10539. d) Ma, D.; Cai, Q. *Org. Lett*. **2003**, 5, 3799. e) Buck, E.; Song, Z.J.; Tschaen, D.; Dormer, P.G.; Volante, R.P. Reider, P.J. *Org. Lett*. **2002**, 4, 1623. f) Palomo, C. *Chem. Commun*. **1998**, 2091. g) Xu, L.W.; Xia, C.G.; Li, J.W.; Hu, X.X. *Synlett* **2003**, 13, 2071.
84. a) Mamuzic, R.I.; Bhattacharya, B. US 4,835,322 **1989**. b) Garman, J.A.; Mamuzic, R.I. US. 4,214,103 **1980**. c) Herbert, J. US 3,285,965 **1966**.
85. a) Ellis, G.P.; Romney-Alexander, T.M. *Chem. Rev*. **1987**, 87, 779. b) Grushin, V.V.; Alper, H. *Chem. Rev*. **1994**, 94, 1047. c) Subramanian, L.R. *Science of Synthesis*, Georg Thieme: Stuttgart, **2004**, 19, 163.
86. a) Rosenmund, K.W.; Struck, E. *Ber. Dtsch. Chem. Ges*. **1919**, 2, 1749. b) Mowry, D.F. *Chem. Rev*. **194**8, 42, 189. c) Friedrich, K.; Wallenfels, K. *The Chemistry of the Cyano Group*; Rappoport, Z. (Ed.) Interscience: London, **1970**, 67. d) Lindley, J. *Tetrahedron* **1984**, 40, 1433. e) Kurtz, P. *Methoden der Organischen Chemie*, Müller, E. (Ed.) Georg Thieme: Stuttgart, **1952**, 8 (3) 302.
87. a) Takagi, K. *Handbook of Organopalladium Chemistry for Organic Synthesis* John Wiley and Sons, Inc.: New York, **2002**, 1, 657. b) Sundermeier, M.; Zapf, A.; Mutyala, S.; Baumann, W.; Sans, J.; Weiss, S.; Beller, M. *Chem. Eur. J*. **2003**, 9, 1828. c) Polshettiwar, V.; Hesemann, P.; Mreau, J.J.E. *Tetrahedron* **2007**, 63, 6784. d) Dolakova, P.; Masojidkova, M.; Holy, A. *Heterocycles* **2007**, 71, 1107. e) Sundermeier, M.; Zapf, A.; Beller, M. *Angew. Chem. Int. Ed*. **2003**, 42, 1661.
88. a) Sakakibara, Y.; Ido, Y.; Sasaki, K.; Sakai, M.; Uchino, N. *Bull. Chem. Soc. Jpn*. **1993**, 66, 2776. b) Arvela, R.K.; Leadbeater, N.E. *J. Org. Chem*. **2003**, 68, 9122.
89. a) Cristau, H.J.; Ouali, A.; Spindler, J.F.; Taillefer, M. *Chem. Eur. J*. **2005**, 11, 2483. b) Zanon, J.; Klapers, A.; Buchald, S. L. *J. Am. Chem. Soc*. **2003**, 126, 2890. c) Schareina, T.; Zapf, A.; Beller, M. *Tet. Lett*. **2005**, 46, 2585. d) Wang, D.; Kuang, L.; Li, Z.; Ding, Ke. *SynLett* **2008**, 1, 69.
90. a) Mathews, J.A. *J. Am. Chem. Soc*. **1896**, 18, 679. b) Chemat, F.; Poux, M.; Berlan, J. *J. Chem. Soc. Perkin Trans*. 1994, 2, 2597. c) Rounds, W.D.; Eaton, J.T.; Urbanowicz, J.H.; Gribble, G.W. *Tet. Lett*. **1988**, 29, 6557.
91. Yu, V.; Kukushkin, A.; Pombeiro, J. L. *Inorg. Chim. Acta*. **2005**, 358, 1.
92. Brady, D.; Dube, N.; Petersen, R. *S. Afr. J. Sci*. **2006**, 102, 339.
93. a) Muhlbauer, H.G. US 3,394,186 **1966**. b) Azuma, H.; Ota, J.; Watanabe, H.C. JP 7659824 **1976**. c) Ohshio, M., Matsubara, S.Y., Kikuchi, M. JP 7795617 **1977**.
94. a) Mackenize, G.F. US 2,861,995 **1958**. b) Habermann, C.E. US 4,153,581 **1979**. c) Enomoto, S.; Kamiyama, T.; Takahashi, Y.; Sahuro, K. JP 7723030 **1977**.
95. Haberman, C. E. US 4,153,581 **1979**.
96. Nobis, J.F.; Greenberg, H. US 2,865,940 **1958**.
97. Alfred Nobel and Co. GB 701789 **1954**.
98. Kwiatkowski, G.T.; Brode, G.L.; Bedwin, A.W. *J. Polym. Sci. Polym. Chem. Ed*. **1974**, 12, 565.
99. Sillion, B.J.; Aude, R. Fr. Pat. 1422852 **1966**.
100. Ghosh, M.K.; Mittal, K.L. (Eds.) *Polyimides: Fundamentals and Applications* Marcel Dekker: New York, **1996**.

101. Hsiao, S.H.; Lin, K.H. *Polymer* **2004**, 45, 7877.

102. Chung, I.S.; Kim, S.Y. *Macromolecules* **2000**, 33, 3190.

103. Ghatge, N.D.; Shinde, B.M.; Mulik, U.P. *J. Polym. Sci. Polym. Chem*. **1984**, 22, 3359.

104. Imai, Y.; Maldar, N.N.; Kakimoto, M. *J. Polym. Sci. Polym. Chem*. **1989**, 22, 2189.

105. Ozaki, S. *Chem. Rev*. **1972**, 72, 5.

106. Ulrich, H. *The Chemistry and Technology of Isocyanates* John Wiley, **1996**, 342.

107. a) Wang, Y.; Zhao, X.; Li, F.; Wang, S.; Zhang, J. *J chem. Technol. Biotechnol*. **2001**, 76, 857. b) Ccnini, S.; Pirrotti, M.; Crotti, C. *Aspects of Homogeneous Catalysis* Ugo, R. (Ed.). D. Reidei Publishing Company **1988**, 6, 97.

108. a) Cross, J.M.; Metzger, S.H. US 3,471,541 **1969**.Chem. Abstr.: 71 : 123533z. b) Ragaini, F.; Longo, T.; Cenini, S. *J. Mol. Catal. A: Chemical* **1996**, 110, L171.

109. a) Curtius, T. *Ber.* **1890**, 23, 3023. b) Wolff, O.; Waldvogel, S.R. *Synthesis* **2004**, 1303.

110. a) Lossen, W. *Ann*. **1872**, 161, 347. b) Anilkumar, R.; Chandrasekhar, S.; Sridhar, M. *Tet. Lett*. **2000**, 41, 5291.

111. Sajiki, H.; Mori, A.; Mizusaki, T.; Ikawa, T.; Maegawa, T.; Hirota, K. *Org. Lett*. **2006**, 8, 987.

112. a) Evans, D.A.; Wood, M.R.; Trotter, B.W.; Richardson, T.I.; Barrow, J.C.; Katz, J.L. *Angew. Chem. Int. Ed*. **1998**, 37, 2700. b) Sebo¨k, P.; Timar, T.; Eszenyi, T.; Patonay, T. *J. Org. Chem*. **1994**, 59, 6318. c) Pan, Y.; Holmes, C.P. *Org. Lett*. **2001**, 3, 2769. d) Cammidge, A.N.; Ngaini, Z. *Chem. Commun*. **2004**, 1914. e) Revell, J.D.; Ganesan, A. *Chem. Commun*, **2004**, 1916.

113. Vowinkel, E.; Wolff, C. *Chem. Ber*. **1974**, 107, 907.

114. Pirkle, W.H.; Zabriskie, J.L. *J. Org. Chem*. **1964**, 29, 3124.

115. Hussey, J.; Johnstone, R.A.Q. *Tetrahedron* **1982**, 38, 3775.

116. a) Goldkamo, A.H.; Hoehn, W.M.; Mikulec, R.A.; Nutting, E.F.; Cook, D.L. *J. Med. Chem*. **1965**, 8, 409. b) Rossi, R.A.; Bunnett, J.F. *J. Org. Chem*. **1973**, 38, 2314.

117. Yamada, M.; Sun, J.; Suda, Y.; Nakaya, T. *Chem. Lett*. **1998**, 1055.

118. Wehmeyer, R.; Walters, M.; Tasset, E.; Brewster, S. US 5,463,140, **1995**.

119. Madhusudhan, V.; Ramaiah, M.S.; Naidu, N.B.; Sivasamban, M.A. *Indian J. Technol*. **1973**, 11, 347.

120. Sethi, S.C.; Subba Rao, B.C. *Indian J. Chem*. **1964**, 2, 178.

121. Bhople, R.D.; Rao, B.Y.; Rao, C.V.N. *J. Oil. Technol. Ass. India*. **1969**, 15.

122. Tobicik, J.; Cerveny, L. *J. Mol. Catal. A: Chemical* **2003**, 194, 249.

123. Silberova, B.; Cerveny, L. *React. Kinet. Catal. Lett*. 1999, 67, 29.

124. Murzin, D.Y.; Allachverdiev, A.I.; Kulkova, N.V. *Heterogeneous Catalysis and Fine Chemical III*, Guisnet. M. (Ed.) Elsevier Science Publishers, **1993**.

125. Mijs, W.J.; de Jonge, C.R.H.I. (Eds.) *Organic Synthesis by Oxidation with Metal Compounds*, Plenum Press, New York, **1986**.

126. Dess, D.B.; Martin, J.C. *J.Org. Chem*. **1983**, 48, 4155.

127. de Nooy, A.E.J.; Besemer, A.C.; Van Bekkum, H. *Synthesis* **1996**, 1153.

128. Satov, K.; Aoki, M.; Takagi, J.; Zimmermann, K.; Noyori, R. *Bull. Chem. Soc. Jpn*. **1999**, 72, 2287.

129. a) Markao, I.E.; Gautier, A.; Chelle-Regnaut, I.; Giles, P.R.; Tsukazaki, M.; Urch, C.J.; Brown, S.M. *J. Org. Chem*. **1998**, 63, 7576. b) Kakiuchi, N.; Maeda, Y.; Nishimura, T.; Uemura, S. *J. Org. Chem*. **2001**, 66, 6620. c) Vocanson, F.; Guo, Y.P.; Namy, J.L.; Kagan, H.B. *Synth. Commun*. **1998**, 28, **2577**. d) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura. *J. Org. Chem*. **1999**, 64, 6750.

141. Ghatge, N.D.; Maldar, N.N. *Polymer* **1984**, 25, 1353.

142 Shingate, R.D. *Ph.D. Dissertation*, The University of Pune, Pune, **2006**.

143 Sadavarte, N.V.; Halhalli, M.R.; Avadhani, C.V.; Wadgaonkar, P.P. *Eur. Polym. J*. **2009**, 45, 582.

144 Kadam, V.S.; Badiger, M.V.; Wadgaonkar, P.P.; Ducouret, G.; Hourdet,D. *Polymer*, **2008**, 49, 4635.

Chapter 4

Synthesis and Characterization of Polyazomethines and Polyamides

Chapter 4a

Synthesis and Characterization of Polyazomethines Based on 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine

4a.1 Introduction

Polyazomethines or polymeric Schiff bases are an interesting class of polymers having carbon–nitrogen double bonded units in the main chain capable of protonation and complexation. They have been studied intensively owing to their good thermal stability, mechanical strength, nonlinear optical properties, ability to form metal chelates, semiconducting properties, environmental stability, and fiber-forming properties, which are associated mainly with their conjugated backbone and the presence of imine sites.[1] These polymers could become materials suitable for use in polymer electronics, especially in view of the recent discovery that the photoluminescence of conjugated polymers containing basic sites in the main chain can be strongly modified by protonic (acid–base) doping.[2]

A major drawback of polyazomethines is their limited solubility in most common organic solvents.[1,3-5] High molecular weight polymers are difficult to obtain because the growing macromolecular chains precipitate out of the solution during polycondensation. Moreover, their high melting temperature and insolubility makes them intractable for processing by conventional techniques. Efforts devoted towards obtaining soluble and fusible polyazomethines include: insertion of flexible spacer between main chain aromatic rings; introduction of pendant groups, i.e. aromatic or alkyl substituents, insertion of fluorine into the polymer chain, introduction of structural irregularities such as kinks, bents, crankshaft-shaped units, etc.[6-16,18-22] It is generally recognized that presence of an alkyl chain and ether linkage in polymer backbone imparts segmental mobility to the polymer, enhances the solubility and lowers the glass transition temperature.

In order to obtain processable polyazomethines, a new diamine monomer with ether linkage and pendant pentadecyl chain *viz*, 4-(4'-aminophenoxy)-2-pentadecylbenzenamine was utilized. A series of (co) polyazomethines was synthesized by solution polycondensation of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with commercially available aromatic dialdehydes such as terephthaldehyde, isophthaldehyde and a mixture of terephthaldehyde and isophthaldehyde.

To study the effect of ether linkage and pentadecyl chain on solubility behavior, a series of copolyazomethines was synthesized by polycondensation of terephthaldehyde with varying molar ratios of 4,4'-oxydianiline and 4-(4'-aminophenoxy)-2-pentadecylbenzenamine.

(Co) polyazomethines were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, gel permeation chromatography, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

4a.2 Experimental

4a.2.1 Materials

4-(4'-Aminophenoxy)-2-pentadecylbenzenamine (APPB) was synthesized as described in **Chapter 3**. Terephthaldehyde (TPA), isophthaldehyde (IPA), and 4,4'-oxydianiline (ODA), all received from Aldrich, USA, were sublimed before use. Hexamethylphosphoramide (HMPA)

received from Aldrich, USA, was used as received. Anhydrous lithium chloride, received from Aldrich, USA, was dried at 180°C for 8 h under reduced pressure. 1-Methyl-2-pyrrolidinone (NMP) received from Aldrich, USA, was dried and distilled according to reported procedure.[17] The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[17]

4a.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in chloroform at 30±0.1°C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

Molecular weights of (co) polyazomethines were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5 Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 ml chloroform and filtered through 0.2 µ SS-filter.

FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker 200 and 400 MHz spectrometer at resonance frequency of 200 MHz for ^1H and 100 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 15 °C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

The solubility of (co) polyazomethines was determined at 3 wt.% concentration in various solvents at room temperature or upon heating.

4a.3 Synthesis of (co) polyazomethines

4a.3.1 Synthesis of polyazomethines from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and terephthaldehyde / isophthaldehyde

A representative procedure for synthesis of polyazomethines is described below.

Into a 100 mL three necked round bottom flask equipped with a nitrogen gas inlet, a calcium guard tube and a magnetic stirrer were placed 4-(4'-aminophenoxy)-2-pentadecylbenzenamine (1.0

g, 2.4 mmol), a mixture of 1-methyl-2-pyrrolidinone (8 mL): hexamethylphosphoramide (8 mL) and lithium chloride (300 mg) under nitrogen atmosphere. Terephthaldehyde (327 mg, 2.4 mmol) was added to the solution in one portion and the reaction was allowed to proceed for 48 h at room temperature under a thin stream of nitrogen. The viscous solution, thus obtained, was poured into aqueous methanol to precipitate the polymer and the precipitated polymer was filtered and washed several times with water and then with methanol. The polymer was dried at 50 ^{o}C under reduced pressure.

4a.3.2 Synthesis of (co) polyazomethines from a mixture of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and 4,4'-oxydianiline with terephthaldehyde

A representative procedure for synthesis of polyazomethines is described below.

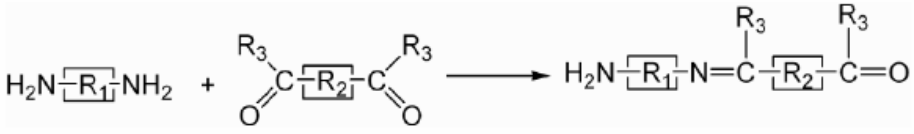
Into a 100 mL three necked round bottom flask equipped with a nitrogen gas inlet, a calcium chloride guard tube and a magnetic stirrer were placed 4-(4'-aminophenoxy)-2-pentadecyl benzenamine (800 mg, 1.95 mmol), 4,4'-oxydianiline (390 mg, 1.95 mmol), a mixture of 1-methyl-2-pyrrolidinone (8 mL): hexamethylphosphoramide (8 mL) and lithium chloride (400 mg) under nitrogen atmosphere. Terephthaldehyde (523 mg, 3.9 mmol) was added to the solution in one portion and the reaction was allowed to proceed for 5 h at room temperature under a thin stream of nitrogen. The reaction mixture was poured into aqueous methanol to precipitate the polymer and the precipitated polymer was filtered and washed several times with water and then with methanol. The polymer was dried at 50 ^{o}C under reduced pressure for 6 h.

A similar procedure was followed for the synthesis of other (co) polyazomethines.

4a.4 Results and discussion

4a.4.1 Synthesis and characterization of (co) polyazomethines

Polymeric Schiff bases are synthesized mainly by polycondensation reaction between a diamine or hydrazine and a dialdehyde or diketone. **(Scheme 4a.1)**:



R_1, R_2 can be aryl or alkyl, R_3 can be aryl, alkyl or H

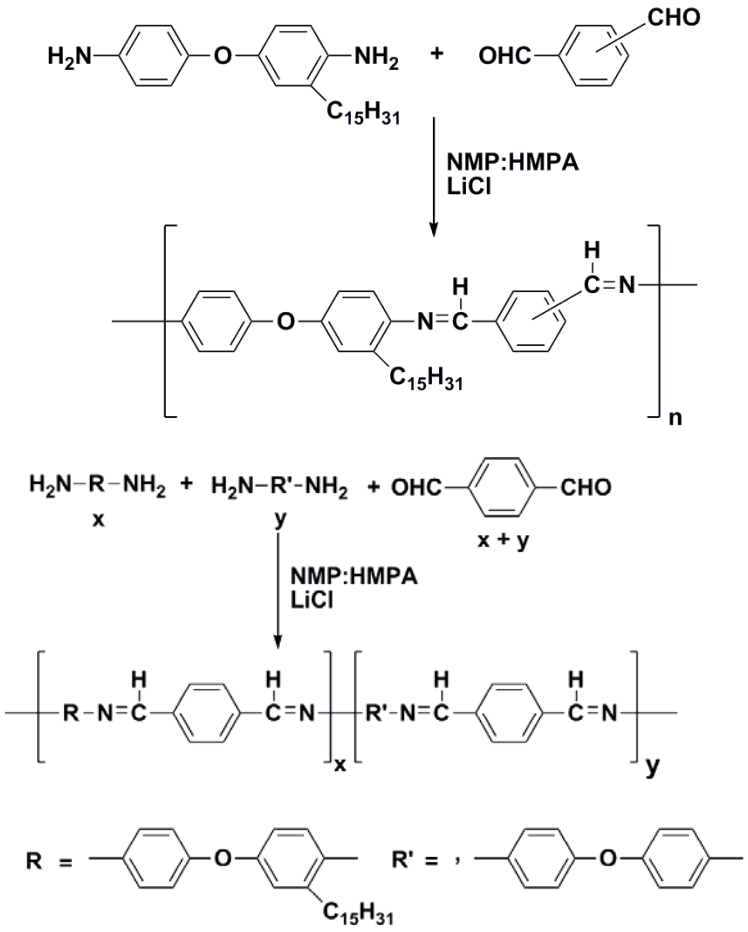
Scheme 4a.1 Synthesis of polymeric Schiff bases

These polymers are also named polyazomethines or polyazines when diamines or hydrazine, respectively, are used in a reaction with dialdehyde compounds and polyketimines or polyketazines when diketones are used as dicarbonyl compounds in reaction with diamine or hydrazine.

In the present study, (co) polyazomethines containing pendant flexible pentadecyl chains and ether moieties in the backbone were synthesized to study the effect of incorporation of flexible pentadecyl chains and ether moieties on the polymer properties. Copolyazomethines based on

varying molar ratios of 4,4'-oxydianiline and 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with terephthaldehyde were synthesized to study the effect of incorporation of pentadecyl chain on solubility behavior.

Polyazomethines were prepared by polycondensation of diamine and dialdehyde to form the azomethine or imine linkage **(Scheme 4a.2)**.



Scheme 4a.2 Synthesis of (co) polyazomethines

The reaction between aromatic diamines and dialdehydes is rapid at room temperature**.** Polymerisation can be initiated in solvents such as DMAc, THF, DMF, NMP, HMPA, ethanol or benzene. Better results are obtained when polar aprotic solvents are used. No catalyst is necessary but removal of water expedites the polymerization. In the present work, polycondensation **(Scheme 4a.2)** of diamine with dialdehyde was carried out in solution using a mixture of freshly distilled 1-methyl-2-pyrrolidinone and hexamethylphospharamide as the reaction medium and LiCl was used to absorb the water formed during the polycondensation. It was observed during the course of reaction that extended reaction time gave high molecular weight polymers.

The results of polymerizations are summarized in **Tables 4a.1** and **4a.2.** Polymerization reactions based on 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and terephthaldehyde and / or isophthaldehyde proceeded in a homogeneous manner and (co) polyazomethines did not phase out

of the reaction medium. All the reactants remained homogeneous in solution and gradual increase in the viscosity could be observed. However, copolyazomethines derived form varying molar ratio of 4,4'-oxydianiline and 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with terephthaldehyde precipitated out of the reaction medium in the early stages of reaction.

Inherent viscosities of (co) polyazomethines were in the range 0.50 – 0.70 dL/g indicating formation of medium to reasonably high molecular weight polymers. Transparent and flexible films of (co) polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine could be cast from chloroform solutions. Furthermore, the films of (co) polyazomethines **(PAZ-II to PAZ-V)** based on isophthaldehyde were stretchable in nature.

Table 4a.1 Synthesis of (co) polyazomethines from aromatic diamines with terephthaldehyde and / or isophthaldehyde

Polymer	APPB, mol%	ODA, mol%	TPA, mol%	IPA, mol%	Yield, (%)	η_{inh} ,(dL/g)[a]
PAZ-I	100	0	100	0	95	0.70
PAZ-II	100	0	0	100	92	0.56
PAZ-III	100	0	50	50	94	0.52
PAZ-IV	100	0	25	75	92	0.50
PAZ-V	100	0	75	25	96	0.52
PAZ-VI	50	50	100	0	91	-[b]
PAZ-VII	75	25	100	0	95	-[b]

a: η_{inh} was measured with 0.5% (w/v) solution of polyazomethine in $CHCl_3$ at 30±0.1 °C., b: insoluble in $CHCl_3$

(Co) polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and terephthaldehyde and/ or isophthaldehyde were soluble in chloroform and the results of GPC measurements on polyazomethines are presented in **Table 4a.2.**

Table 4a.2 GPC data for (co) polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with terephthaldehyde and / or isophthaldehyde

Polymer	Diamine	Dialdehyde		Molecular weight[a]		Polydispersity Index M_w/M_n
		TPA	IPA	M_n	M_w	
PAZ-I	APPB	100	0	12,400	27,200	2.2
PAZ-II	APPB	0	100	25,900	47,900	1.8
PAZ-III	APPB	50	50	40,800	63,200	1.5
PAZ-IV	APPB	25	75	10,490	27,450	2.6
PAZ-V	APPB	75	25	14,500	32,650	2.2

a: measured by GPC in chloroform, polystyrene was used as the calibration standard

Inherent viscosity **(Table 4a.1)** and GPC data **(Table 4a.2)** indicated the formation of medium to reasonably high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards.

4a.4.1.1 Structural Characterization

The formation of polyazomethines was confirmed by FT-IR and ^{1}H-NMR spectroscopy.

A representative FTIR spectrum of polyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and terephthaldehyde is reproduced in **Figure 4a.1**. The bands at 1618 cm^{-1} and 1244 cm^{-1}correspond to azomethine or imine linkage (-CH=N-) and –C-O-C- linkage, respectively.

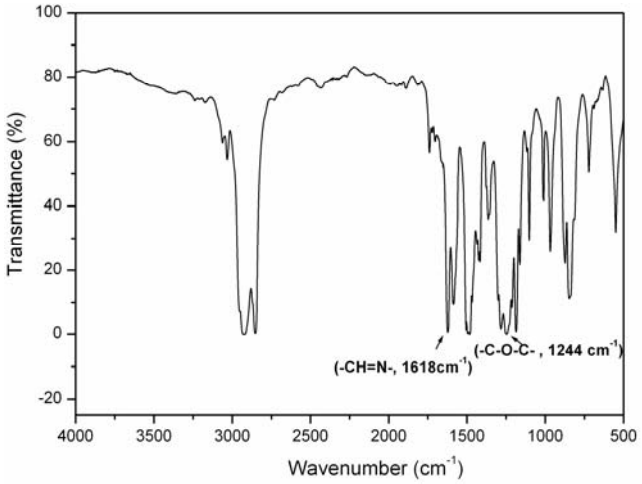


Figure 4a.1 FTIR spectrum of polyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine and terephthaldehyde

^{1}H-NMR spectrum of polyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and terephthaldehyde along with tentative assignments is shown in **Figure 4a.2**.

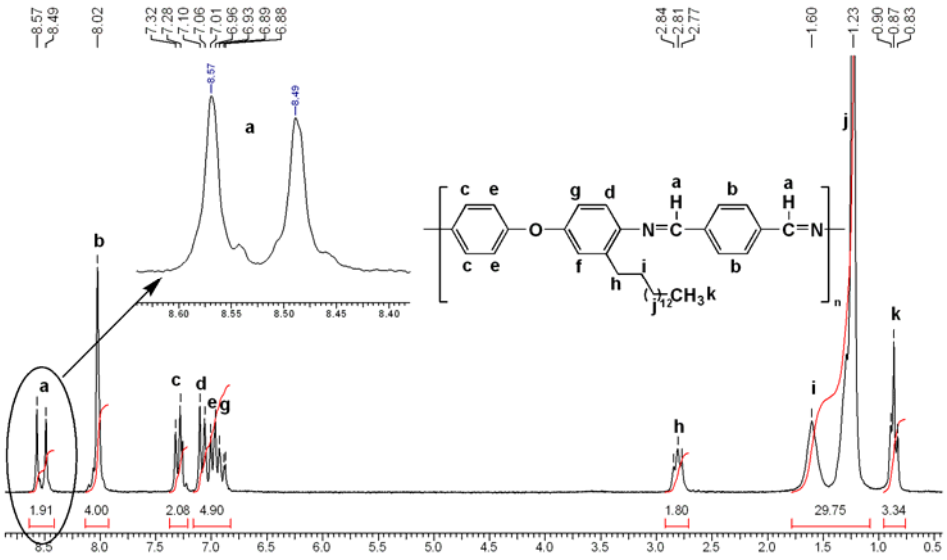


Figure 4a.2 ^{1}H-NMR spectrum of polyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine and terephthaldehyde in $CDCl_3$

Two separate singlets of azomethine protons were observed at 8.49 and 8.57 δ ppm. Two protons 'c' *ortho* to azomethine linkage exhibited a doublet at 7.30 δ ppm, while rest of the aromatic protons displayed a multiplet in the range 6.86-7.12 δ ppm. The benzylic $-CH_2$ appeared as a triplet at 2.81 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.60 δ ppm. Rest of the methylene protons exhibited a multiplet over the range 1.21-1.25 δ ppm. The terminal $-CH_3$ appeared as a triplet at 0.87 δ ppm.

Two distinct singlets were observed corresponding to proton in the azomethine linkage. The appearance of two singlets could be due to the constitutional isomerism present in polyazomethine resulting from the use of unsymmetrical diamine monomer.

It is reported[30,31] that when an asymmetric monomer reacts with a symmetric monomer, constitutional isomerism would arise. Pino and coworkers[31] have reported a series of studies on the influence of constitutional isomerism on the physical properties of polycondensates, where the theoretical aspects of structural regularity of polycondensation were systematically investigated. Generally, the probable structural orientations are four *viz,* (a) Head-to-Head, (b) Tail-to-Tail, (c) Head-to-Tail and (d) Tail-to-Head; where the two structures, i.e. Head-to-Tail and Tail-to-Head would be indistinguishable. In ^{1}H-NMR spectrum of polyazomethine, theoretically one would expect four signals corresponding to azomethine protons, if constitutional isomers were present. However, 200 MHz NMR spectrum of **PAZ-I** displayed only two distinct singlets at 8.49 and 8.57 δ ppm for imine protons.

The possible structural orientations of polyazomethine **(PAZ-I)** is depicted in **Figure 4a.3**.

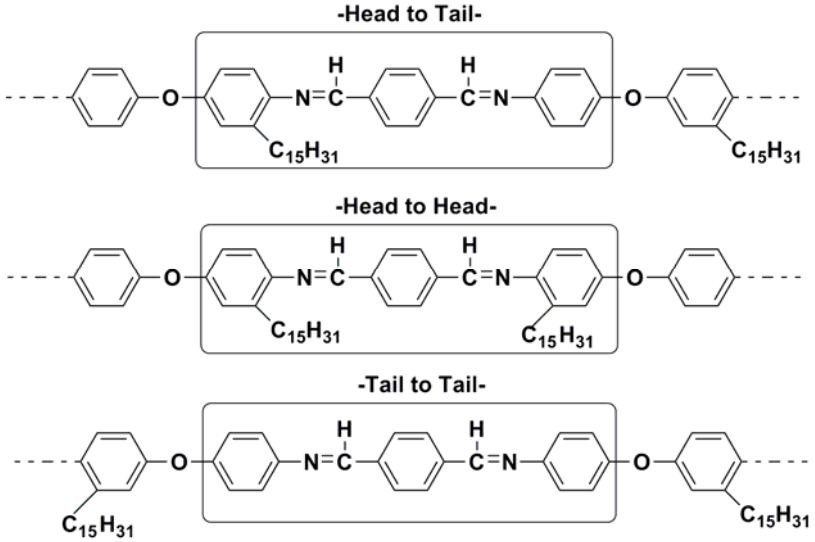


Figure 4a.3 Possible sequences in polyazomethine chains derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine and terephthaldehyde

There also exists possibility of syn and anti isomers at imine linkages[29] which further complicated the interpretation of ^{1}H-NMR spectral data. In order to make definitive conclusions, ^{13}C-NMR and DQF-COSY spectral data would be required.

^{1}H-NMR spectrum of polyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and isophthaldehyde along with assignments is shown in **Figure 4a.4**. Two separate signals of imine protons were observed at 8.50 and 8.59 δ ppm. Proton 'b' of isophthalic moiety exhibited a triplet at 8.36 δ ppm. Protons 'c' appeared as a multiplet in the range 8.01-8.10 δ ppm while proton 'd' exhibited a triplet at 7.59 δ ppm. The remaining aromatic protons appeared as a multiplet over the range 6.91-7.33 δ ppm. The benzylic $-CH_2$ appeared as a triplet at 2.80 δ ppm. The methylene protons β to aromatic ring appeared as a triplet at 1.60 δ ppm. Rest of the methylene protons exhibited a multiplet over the range 1.19-1.23 δ ppm. The terminal $-CH_3$ appeared as a triplet at 0.86 δ ppm.

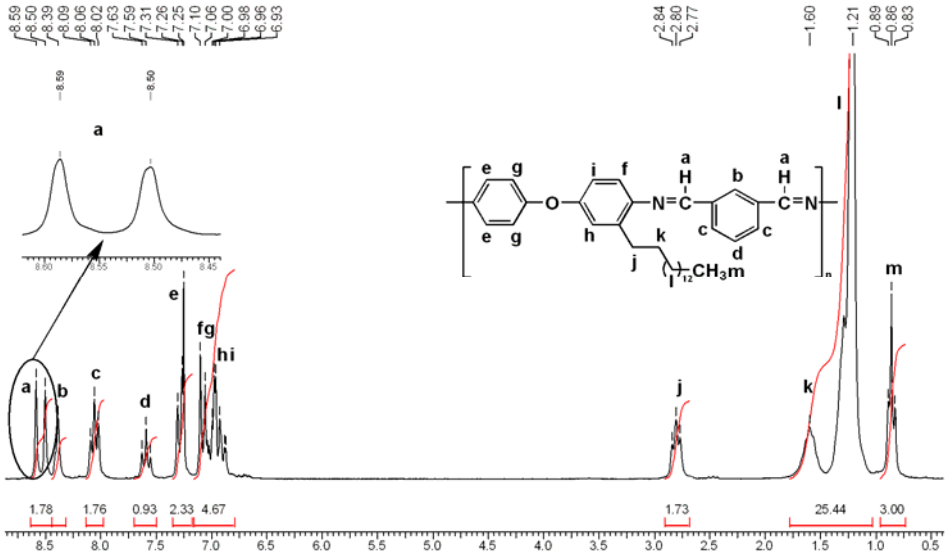


Figure 4a.4 ^{1}H-NMR spectrum of polyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine and isophthaldehyde in $CDCl_3$

^{1}H-NMR spectrum **(Figure 4a.5)** of (co)polyazomethine derived form 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with a mixture of terephthaldehyde and isophthaldehyde **(50:50 mol%, PAZ-III)** in $CDCl_3$ showed the presence of four different signals for imine protons in the range of 8.47-8.61 δ ppm. Protons corresponding to terephthaldehyde ring 'd' and isophthaldehyde protons 'c' and 'd', exhibited singlet and triplet at 8.02 and 8.04 δ ppm, respectively. A triplet at 7.60 δ ppm could be assignable to isophthaldehyde proton 'e'. Aromatic protons of diamine appeared as a multiplet in the range 6.87-7.35 δ ppm.

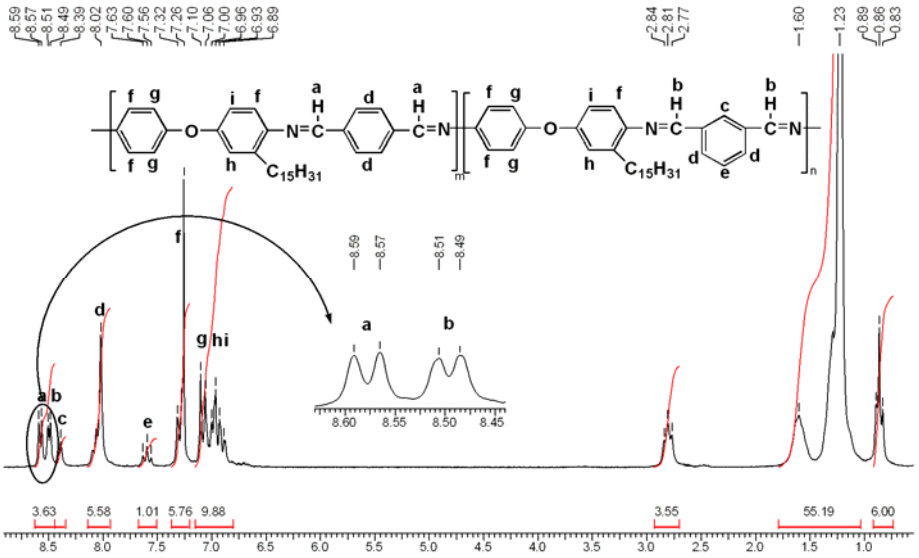


Figure 4a.5 ^{1}H-NMR spectrum of copolyazomethine derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with a mixture of terephthaldehyde and isophthaldehyde in $CDCl_3$

Figure 4a.6 shows stacked partial ^{1}H-NMR spectra of different compositions of polyazomethines synthesized from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with a mixture of terephthaldehyde and isophthaldehyde.

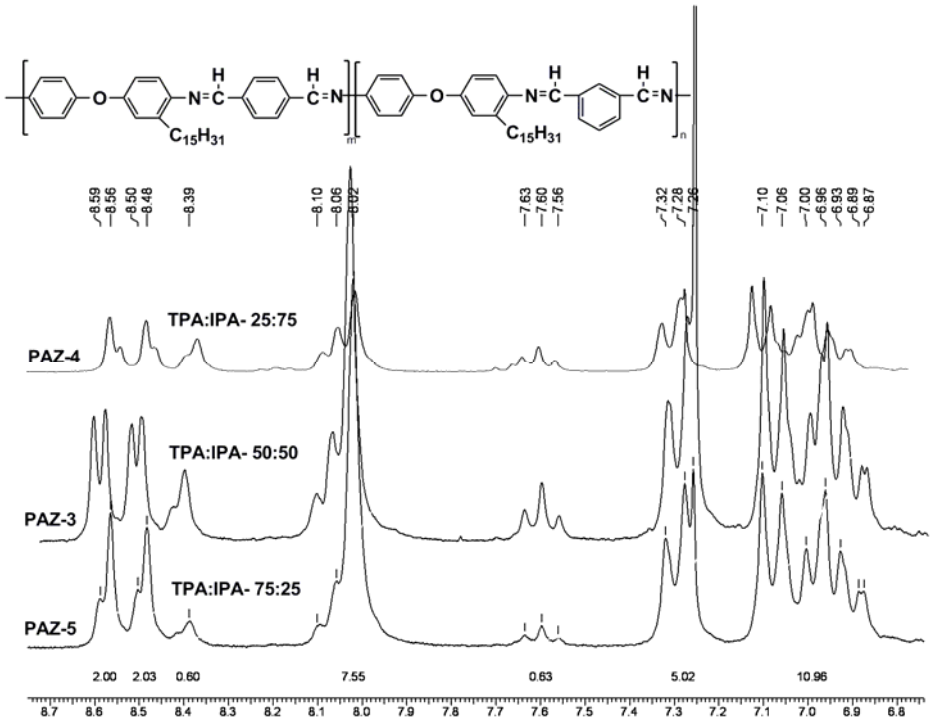


Figure 4a.6 Stacked partial ^{1}H-NMR spectra of copolyazomethine of varying compositions derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with terephthaldehyde and isophthaldehyde in $CDCl_3$

In a representative example, composition of copolyazomethine **(PAZ-III)** containing 50:50 mol% of TPA:IPA ratio was determined from ^{1}H-NMR spectrum **(Figure 4a.6).** For calculating the composition of copolyazomethine the integration of terephthaldehyde ring protons at 8.02 δ ppm was compared with that of the benzylic –CH_2 protons at 2.81 δ ppm. There was a reasonably good agreement between the observed incorporation of TPA (49.54 mol%) and the amount taken for polymerization (50 mol%).

4a.4.1.2 Solubility measurements

Solubility of (co) polyazomethines was tested in various organic solvents at 3 wt % concentration and the data is summarized in **Table 4a.3.**

Table 4a.3 Solubility data of (co) polyazomethines derived from diamines and terephthaldehyde / isophthaldehyde

Polymer	Diamines		Dialdehydes		$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
	APPB	ODA	TPA	IPA									
PAZ-I	100	0	100	0	++	++	+-	--	--	--	+-	++	--
PAZ-II	100	0	0	100	++	++	++	--	+-	+-	++	++	--
PAZ-III	100	0	50	50	++	++	++	--	+-	+-	++	++	--
PAZ-IV	100	0	25	75	++	++	++	--	+-	+-	+-	++	--
PAZ-V	100	0	75	25	++	++	+-	--	+0	+0	+-	++	--
PAZ-VI	50	50	100	0	+0	+0	+0	+0	+0	+0	+0	+0	+0
PAZ-VII	75	25	100	0	+0	+0	+0	+0	+0	+0	+0	+0	+0

++ : soluble at room temperature; +- : soluble on heating; +0 : partially soluble on heating; -- : insoluble

(Co) polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and dialdehydes were found to be soluble in chloroform, DCM, THF, pyridine and *m*-cresol at room temperature or upon heating. The presence of C_{15} alkyl chain disrupted the packing of polymer chains as well as provided the additional 'handle' for interaction with solvents. (Co) polyazomethines were comparatively less soluble or insoluble in amide solvents. The insolubility or less solubility of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine-based (co) polyazomethines in amide solvents could be due to the presence of long aliphatic chain present in the backbone. It is well known that, amides are not good solvents for polyolefins. It was observed that, as the terephthaldehyde composition increased in the polymer, solubility decreased gradually. This may be attributed to the rigidity of the 1,4-phenylene linkages.

Polyazomethine derived from 4,4'-oxydianiline and terephthaldehyde is reported to be insoluble in organic solvents such as chloroform, DCM, THF, pyridine, *m*-cresol, etc..[23] Hence, in order to study the effect of incorporation of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine on solubility behavior of copolyazomethine- based on 4,4'-oxydianiline and terephthalaldehyde, two copolyazomethines with varying molar ratios of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine

and 4,4'-oxydianiline with terephthaldehyde were synthesized and tested for solubility. However, even after the incorporation of 75 mol% of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine **(PAZ-VII)** the copolyazomethine was still found to be insoluble in all organic solvents tested at room temperature and only partially soluble upon heating.

4a.4.1.3 X-Ray diffraction studies

X-Ray diffraction patterns of (co) polyazomethines are reproduced in **Figure 4a.7.**

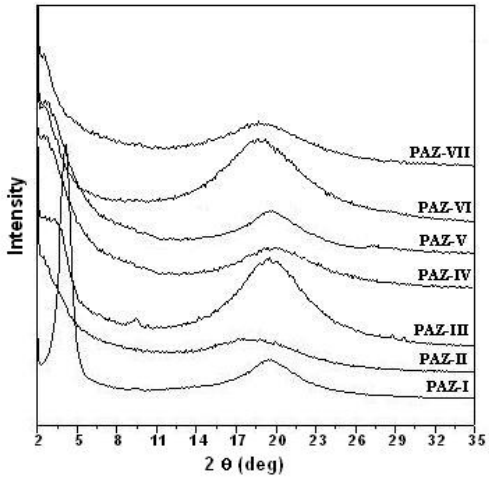


Figure 4a.7 X-Ray diffraction patterns of (co) polyazomethines derived from aromatic diamines and terephthaldehyde and / or isophthaldehyde

All (co) polyazomethines exhibited broad halo at about $2\theta = \sim 19^{o}$ in the wide-angle region, indicating that polymers are amorphous in nature **(Figure 4a.7).** This is attributed to the flexible pendant pentadecyl chain which increases the disorder in polymer chains thereby causing less chain packing.

As reported in the literature, [21,25-29] rigid-rod polymers with flexible long chains strongly tend to form layered crystalline structure in the solid state. If a layered structure is perfectly developed with high degree of crystallinity, the main chains get together to form a rigid backbone and the flexible side-chains fill the space between the rigid backbone in fully extended zig-zag configuration to form their own crystalline phase. In the phase, the side-chains can be interdigitated with those emanating from neighboring backbones, the degree of interdigitation being governed by chemical structure of the rigid rod polymers.

Such layered structures of (co) polyazomethines synthesized in the present study were investigated. X-Ray diffractograms indicated a diffuse reflection for **PAZ-II** to **PAZ-VII** in the small-angle region at $2\theta = \sim 3^{o}$ and a sharp, strong reflection for **PAZ-I** at $2\theta = \sim 5^{o}$. This indicates that in case of **PAZ-II** to **PAZ-VII** the interaction of flexible pentadecyl side chains with polyazomethine backbone is too weak for the layered structures to develop well, while in the case of **PAZ-I,** interactions of flexible pentadecyl side-chains is so strong that the layered structures are

developed more tightly.

4a.4.1.4 Thermal properties

In the present study, thermal stability of (co) polyazomethines was determined by thermogravimetric analysis (TGA) at a heating rate of 15 ^{o}C /minute under nitrogen. Thermogravimetric (TG) curves for polyazomethines are shown in **Figure 4a.8**.

The initial decomposition temperature (IDT), the temperature at 10% weight loss (T_{10}) and the residual weight at 900^{o}C for (co) polyazomethines are given in **Table 4a.4**.

The initial decomposition temperature (IDT) and the temperature for 10% weight loss (T_{10}) are some of the main criteria to determine the thermal stability of polymers. It is noteworthy that the decomposition of (co) polyazomethines is a one-step process. An examination of data showed that T_{10} values of (co) polyazomethines were in the range 435-443^{o}C, indicating good thermal stability of (co) polyazomethines.

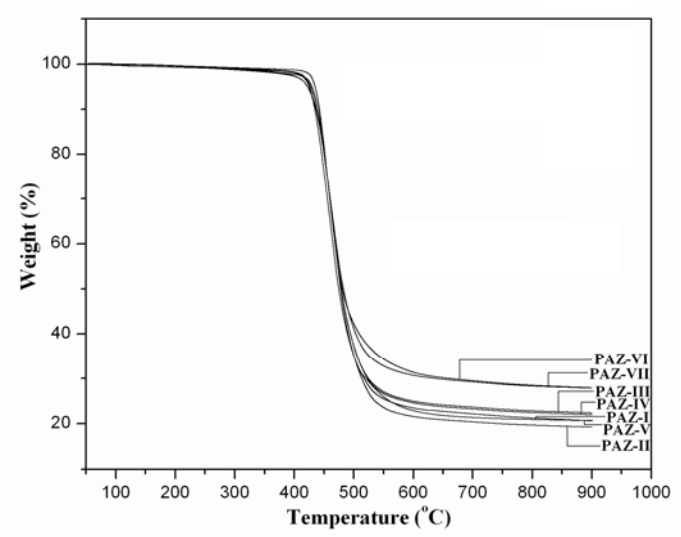


Figure 4a.8 TG curves of (co) polyazomethines derived from aromatic diamines with terephthaldehyde and/ or isophthaldehyde

Table 4a.4 Thermal properties of (co) polyazomethines derived from aromatic diamines and terephthaldehyde and / or isophthaldehyde

Polymer	Diamine		Dialdehyde		T_0 [a] (^{o}C)	T_{10} [b] (^{o}C)	Weight residue at 900^{o}C (%)	T_g (^{o}C)
	APPB	ODA	TPA	IPA				
PAZ-I	100	0	100	0	372	435	20	48
PAZ-II	100	0	0	100	346	438	19	21
PAZ-III	100	0	50	50	359	441	22	27
PAZ-IV	100	0	25	75	362	434	21	22
PAZ-V	100	0	75	25	368	439	20	42
PAZ-VI	50	50	100	0	380	443	27	59
PAZ-VII	75	25	100	0	363	438	27	57

a : Initial decomposition temperature, *b* : temperature at which 10% weight loss is observed

Glass transition (T_g) temperature of (co) polyazomethines was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of (co) polyazomethine samples at a heating rate of 10°C / minute. DSC curves for (co) polyazomethines are shown in **Figure 4a.9** and T_g values are given in **Table 4a.4.**

None of the (co) polyazomethines, except **PAZ-I**, showed a melt transition in DSC measurements. It is interesting to note that in contrast with the fact that polyazomethines are high T_g materials, the polymers synthesized in the current study exhibited glass transitions in the range 21-59 °C. Even in the case of copolymers with ODA **(PAZ-VI and PAZ-VII)**, the observed T_g was 59 °C and 57 °C. The literature data[23] for polymer of ODA with terephthaldehyde reported its melting transition above 400°C.

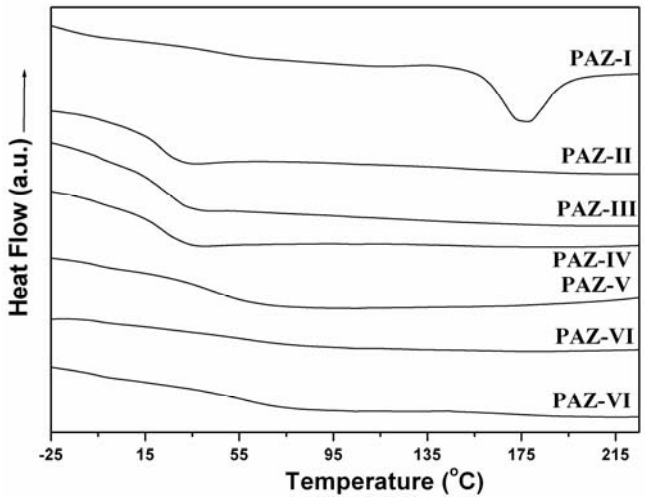


Figure 4a.9 DSC thermograms of (co) polyazomethines derived from aromatic diamines with terephthaldehyde and/ or isophthaldehyde

The large depression in T_g values resulted from the presence of flexible ether linkages and pendant pentadecyl chains. The flexible pentadecyl side chains are thought to act as a bound solvent or internal plasticizer for the rigid polymer backbone. A similar observation has been reported for polyazomethines containing alkoxy side-chains.[24-27] For example, polyazomethine derived from 2,5-bis(*n*-dodecyloxy)terephthaldehyde and p-phenylenediamine exhibited a glass transition at 39 °C.[24] A comparison of the T_g values of polyazomethines derived from terephthaldehyde **(PAZ-I)** and isophthaldehyde **(PAZ-II)** indicated that former had a higher T_g (48 °C) compared to T_g of isophthaldehyde- based polyazomethine (21 °C). This could be attributed to the rigid 1,4-phenylene linkages present in terephthaldehyde- based polyazomethines. In polyazomethines synthesized utilizing different molar proportions of TPA and IPA with 4-(4'-aminophenoxy)-2-pentadecylbenzenamine, the T_g values tend to increase as the molar proportion of TPA was increased.

A very large difference between glass transition (21-59 °C) and initial decomposition temperature (346-380°C) was observed. This offers (co)polyazomethines a wide processing window.

4a.5 Conclusions

1. A series of (co) polyazomethines containing pendant pentadecyl chains and ether linkages was synthesized by the solution polycondensation of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with commercially available dialdehydes *viz,* terephthaldehyde and/ or isophthaldehyde.
2. A series of copolyazomethines was synthesized by polycondensation of terephthaldehyde and varying molar ratios of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and 4,4'-oxydianiline.
3. Inherent viscosities of (co) polyazomethines were in the range 0.50 – 0.70 dL/g indicating formation of medium to reasonably high molecular weight polymers.
4. Polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with commercially available dialdehydes were soluble in organic solvents such as chloroform, DCM, THF, pyridine and *m*-cresol indicating that the incorporation of pentadecyl chains leads to a significant improvement in solubility.
5. ^{1}H-NMR analysis of the polyazomethines obtained by polycondensation of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and aromatic dialdehydes showed presence of constitutional isomerism.
6. WAXD patterns indicated that (co) polyazomethines containing pendant pentadecyl chains were amorphous in nature. The formation of layered structures was observed due to packing of pentadecyl chains.
7. T_{10} values of (co) polyazomethines were in the range 435-443^{o}C indicating good thermal stability of the polymers.
8. The flexible ether linkages and pentadecyl side chains along the polymer backbone was effective in lowering the T_g values (21-59 ^{o}C) of polyazomethines considerably.
9. Overall, internal plasticization effect of the pentadecyl chain was shown to be effective in achieving processable polyazomethines.

References

1. Grigoras, M. ; Catanescu, C. *J. Macromol. Sci; Part C. Polym. Rev.* **2004**, C44, 131.
2. Iwan, A.; Sek, D., Rannou, P. ; Kasperczyk, J. ; Janeczek, H. ; Mazurak Z. ; Pron, A. *Synth. Met.* **2004**, 143, 331.
3. Grigoras, M. ; Catanescu, C.O. ; Simionescu, C.I. *Rev. Roum. Chim*. **2001**, 46, 927.
4. D'Alelio, G.F.; Hornback, J.M.; Strazik, W.F.; Dehner, T.R. *J. Macromol Sci*. **1967**, 7, 1161.
5. Yang, C.J.; Jenekhe, S.A. *Macromolecules*, **1995**, 28, 1180.
6. Park, K.H.; Tani, T.; Kakimoto, M.; Imai, Y. *Macromol. Chem. Phys*. **1998**, 31, 501.
7. Kim, H.C.; Kim, J.S.; Kim, K.S.; Park, K.H.; Baek, S.; Ree, m. *J. Polym. Sci.: Polym Chem*. **2004,** 42, 825.
8. Thoms, O.; Inganas, O.; Andersson, M.R. *Macromolecules*, **1998**, 31, 2676.
9. Jeffries-EI M.; Ambrosio, K.C.; Tarkka, R.M. *Polym. Preprints*, **2001,** 42, 446.
10. Farcas, A.; Grigoras, M. *Polym. Int*. **2003**, 52, 1315.1320.
11. Farcas, A.; Grigoras, M. *High Perform. Polym*. **2001**, 13, 201.
12. Weng, J.; Sun, W.; Jiang, L.; Shen, Z. *Macromol. Rapid Commun*. **2000**, 21, 1099.
13. Imai, Y.; Maldar, N.N.; Kakimoto, M.J. *J. Polym Sci., Polym Chem. Ed*., **1984**, 22, 3771.
14. Spiliopoulos, I.K.; Mikroynnidis, J.A. *Macromolecules,* **1996**, 29, 5313.
15. Mohite, S.S.; Wadgaonkar, P.P.; *Polym. Preprints*, *(Am. Chem. Soc., Div. Polym. Chem.)*, **1990**, 31, 482.
16. Wang, C.; Shieh, S.; LeGoff, E.; Kanatzidis, M.G. *Macromolecules*, **1996**, 29, 3147.
17. Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; Pergamon Press: NewYork, **1989**.
18. Yang, C.J.; Jenekhe, S.A. *Chem. Mater*. 1991, 3, 878.
19. Puértolas, J.A.; Carod, E.; Diaz-Calleja, R.; Cerrada, P.; Oriol, L.; Pinol, M.; Serrano, J.L. *Macromolecules,* **1997**, 30, 773.
20. Adell, J.M.; Alonso, M.P.; Barbera, L.; Pinol, M.; Serrano, J.L. *Polymer*, **2003**, 44, 7829.
21. Park, S; Kim, H.; Zin, W.; Jung, J. *Macromolecules* **1993**, 26, 1927.
22. Destri, S.; Pasini, M.; Pelizzi, C.; Porzio W.; Predieri G.; Vignali C. *Macromolecules*, **1999**, 32, 353.
23. Kolot, V.N.; Chernykh, T.E.; Shugaeva, T.V.; Batik'yan, B.A.; Shchetinin, A.M.; Kudryavtsev, G.I. *Fibre Chemistry*, **1987**, 285. Translated from *Khimicheskie Volokna*, **1986**, 4, 30.
24. Park, S.; Kim, H.; Zin, W.; Jung, J. *Macromolecules*, **1993**, 26, 1627.
25. Liu, C. L.; Chen, W. C. *Macromol. Chem. Phys*. **2005**, 206, 2212.
26. Cerrada, P.; Oriol, L.; Pinol, M.; Serano, J. L.; Alonso, P.J.; Pueltolas, J.A.; Iribarren, I.; Munoj. S.; *Macromolecules* **1999**, 32, 3565.
27. Adell, J.M.; Alonso, M.P.; Barbera, J.; Oriol, L.; Pinol, M. J.; Serano, L. *Polymer*, **2003**, 44, 7829.
28. Mikroyannidis, J.A. *J. Polym. Sci.: Polym Chem*. **1989**, 27, 3465.
29. Destri, S.; Khotina, I.A.; Porzio, W. *Macromolecules* **1998**, 31, 1079
30. Pal, R.R.; Patil, P.S.; Salunkhe, M.N.; Maldar, N.N.; Wadgaonkar, P.P. Eur. Polym. J. **2009**, 45, 953
31. Pino, P.; Lorenzi, G.P.; Suter, U.W.; Casartelli, P.; Steinman, I.; Bonner, F.J. *Macromolecules* **1978**, 11, 624.

Chapter 4b

Synthesis and Characterization of Polyamides Based on 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid

4b.1 Introduction

Aromatic polyamides (aramids) are thermally stable polymers with an attractive combination of excellent chemical, physical and mechanical properties.[1] However, the applications of aramids are often hampered by problems in their fabrication. For instance, the poor solubility and high softening or melting temperatures caused by the high crystallinity and high stiffness of the polymer backbone leads to difficulties in processing of polyamides.

A lot of efforts have been made to synthesize structurally modified aromatic polyamides having improved solubility and processability with retention of their high thermal stability.[2-15] The introduction of flexible chains into polyamide backbone,[16] the use of *meta*-oriented monomers,[17,18] synthesis of polyamides with non-coplanar units in the polymer chains,[19] introduction of bulky side groups into the polymer chains, etc.,[20-24] resulted in a number of modified polyamides. These modifications work by breaking chain symmetry and regularity and by destroying hydrogen bonding, generally leading to better solubility and processability.

It is known that ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. Also, the presence of alkyl chain in polymer backbone aids in enhanced solubility and processability. In general, these structural modifications lead to lowering of glass transition temperatures, as well as significant improvement in solubility and processability. Aramids containing ether linkages or asymmetrical groups are significantly more flexible and soluble than conventional aramids.[25-28]

In view of the above, dicarboxylic acid monomer *viz*, 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid containing an ether linkage and a pendant pentadecyl chain was considered as a useful monomer for synthesis of processable polyamides.

The objective of the present work was to synthesize a series of polyamides containing pendant pentadecyl chains and ether linkages in the backbone and to examine the effect of their incorporation on the polymer properties such as solubility and thermal behavior. Thus, a series of polyamides was synthesized by solution polycondensation of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid with various diamines, *viz*, 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenedianiline, 4,4'-(hexafluoroisopropylidene) dianiline and 4-(4'-aminophenoxy)-2-pentadecylbenzenamine.

The synthesized polyamides were characterized by inherent viscosity measurements, solubility tests, FTIR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

4b.2 Experimental

4b.2.1 Materials

4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid (CPPB) and 4-(4'-aminophenoxy)-2-pentadecylbenzenamine (APPB) were synthesized as described in **Chapter 3**. The diamines, 1,4-phenylenediamine (*p*-PD), 1,3-phenylenediamine (*m*-PD), 4,4'-oxydianiline (ODA), 4,4'-methylenedianiline (MDA), 4,4'-(hexafluoroisopropylidene) dianiline (HFDA) all received from Aldrich, USA, were sublimed before use. Anhydrous lithium chloride, received from Aldrich, USA, was dried at 180°C for 8 h under reduced pressure. Triphenyl phosphite (TPP), received from Fluka, Germany, was purified by distillation under reduced pressure. 1-Methyl-2-pyrrolidinone (NMP) and pyridine, both from Merck, India, were dried over calcium hydride and distilled under reduced pressure. The solvents were of reagent grade quality and were purified prior to use according to reported procedures.[29]

4b.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in N,N-dimethylacetamide (DMAc) at 30±0.1°C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 15 °C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

The solubility of polyamides was determined at 3 wt.% concentration in various solvents at room temperature or on heating.

4b.3 Synthesis of polyamides

A representative procedure for the synthesis of polyamides is given below:

Into a 50 mL two necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube and a magnetic stirring bar were charged NMP (6 mL), 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid (600 mg, 1.28 mmol), 4,4'-oxydianiline (256 mg, 1.28 mmol), lithium

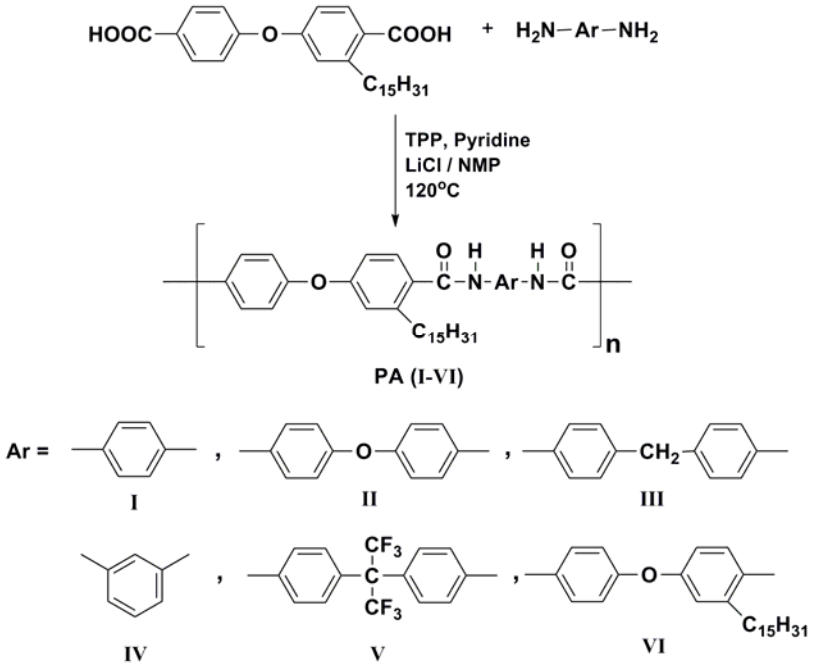
chloride (558 mg), triphenyl phosphite (875 mg, 2.82 mmol), and pyridine (1.2 mL). The reaction mixture was heated with stirring at 120°C for 8 h. The viscous reaction mixture was poured into methanol (100 mL) when a fibrous precipitate was obtained which was filtered, washed thoroughly with hot water and methanol. The polymer was dried at 50°C for 12 h under reduced pressure.

A similar procedure was followed for the synthesis of other polyamides.

4b.4 Results and discussion

4b.4.1 Synthesis and characterization of polyamides

Scheme 4b.1 illustrates synthesis of polyamides from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and various diamines.



Scheme 4b.1 Synthesis of polyamides from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines

Conventionally, aromatic polyamides are prepared by the polycondensation of diacid chlorides with diamines. However, the preparation, purification, and storage of diacid chlorides is troublesome. Since 1975, the direct polycondensation technique reported by Yamazaki et al[30-32] is routinely used in the laboratory for synthesis of polyamides.

As outlined in **Scheme 4b.1,** aromatic polyamides were synthesized by the phosphorylation polycondensation reaction of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid with diamines **(I-VI)** in NMP solution containing lithium chloride using triphenyl phosphite and pyridine as condensing agents. The polycondensation reactions were carried out at 120°C for 8 h. In the preparation of polymer **PA-I,** the reaction mixture became hazy while in case of **PA-VI** precipitation occurred

during the polymerization. These heterogeneous reactions could not produce high molecular weight polymers. All other reaction solutions were homogeneous throughout the reaction and the obtained polyamides had inherent viscosities in the range 0.45 to 0.66 dL/g indicating formation of medium to reasonably high molecular weight polymers. Except for **PA-VI**, tough, transparent and flexible films of polyamides could be cast from DMAc solutions.

The results of polymerization are summarized in **Table 4b.1**.

Table 4b.1 Synthesis of polyamides from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines

Polymer	Diacid	Diamine	Yield (%)	η_{inh} (dL/g)[a]
PA-I	CPPB	*p*-PD	92	0.45
PA-II	CPPB	ODA	96	0.66
PA-III	CPPB	MDA	96	0.62
PA-IV	CPPB	*m*-PD	98	0.58
PA-V	CPPB	HFDA	95	0.66
PA-VI	CPPB	APPB	91	--[b]

a: η_{inh} was measured with 0.5% (w/v) solution of polyamide in DMAc at 30 ± 0.1°C; *b*: η_{inh} could not be determined as polymer was insoluble in DMAc

4b.4.1.1 Structural Characterization

The formation of polyamides was confirmed by FTIR spectroscopy.

Figure 4b.1 shows FTIR spectrum of polyamide derived from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and 4,4'-oxydianiline (ODA) as an example.

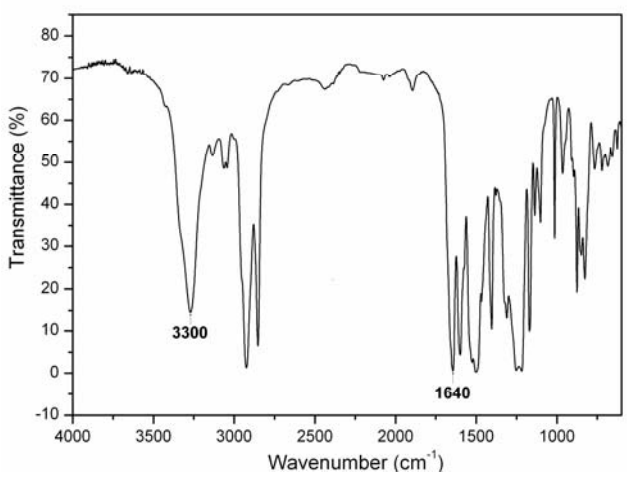


Figure 4b.1 FTIR spectrum of polyamide derived from 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid and 4,4'-oxydianiline

FTIR spectrum of polyamide showed –NH stretching frequency as a broad band around 3300 cm^{-1}. This lowering of frequency could be attributed to the involvement of -NH groups in hydrogen bonding. The amide band, associated with stretching vibration of the carbonyl group,

appeared at around 1640 cm^{-1}. The band at 1256 cm^{-1} could be attributed to the overlapped C-O-C ether linkage in CPPB and ODA.

^{1}H-NMR spectra of polyamides could not be recorded because of their insolubility in $CDCl_3$ and DMSO-d_6 at room temperature.

4b.4.1.2 Solubility measurements

Solubility of polyamides was tested in various organic solvents at 3 wt % concentration and data is summarized in **Table 4b.2.**

Table 4b.2 Solubility data of polyamides derived from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines

Polymer	Diacid	Diamine	$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
PA-I	CPPB	*p*-PD	--	--	--	--	+0	+0	--	--	--
PA-II	CPPB	ODA	--	--	--	+0	++	+-	--	+0	--
PA-III	CPPB	MDA	--	--	--	+-	++	++	+-	++	--
PA-IV	CPPB	*m*-PD	--	--	++	++	++	++	++	++	+0
PA-V	CPPB	HFDA	--	--	++	++	++	++	++	++	+0
PA-VI	CPPB	APPB	--	--	--	--	--	--	--	--	--

++ : soluble at room temperature; +- : soluble on heating; +0 : partially soluble on heating; -- : insoluble

With the exceptions of **PA-I and PA-VI**, polyamides were soluble in polar aprotic solvents such as DMF, DMAc, and NMP at room temperature or upon heating. In addition, polyamides **PA-IV and PA-V** were found to be soluble even in solvents such as THF, *m*-cresol and pyridine. This increase in solubility may be attributed to the unsymmetrical monomer *m*-PD and bulky CF_3 group in HFDA, which increased the disorder in the polymer chain and hindered chain packing, thereby reducing chain interactions.[33,34] In the case polyamide **PA-III**, the presence of methylene groups in the backbone further increased flexibility and also disturbed the planarity of aromatic units, resulting in a reduction of the close packing, and hence was found to be soluble even in pyridine and *m*-cresol at room temperature or upon heating. Polyamide **PA-I** showed insolubility or limited solubility in most of the solvents, because of the presence of symmetrical and rigid 1,4-phenylene rings.

Polyamide derived from 4,4'-oxybisbenzoic acid and 4,4'-oxydianiline is reported to be insoluble in polar aprotic solvents such as, NMP, DMAc, DMF and DMSO. However, polyamide **PA-II** synthesized by polycondensation of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and 4,4'-oxydianiline was soluble in DMAc and NMP either at room temperature or upon heating. The improved solubility if **PA-II**, is apparently due to the presence of packing- disruptive pendant pentadecyl chains in the polymer backbone which results in increased chain packing distances and decreased inter-molecular interactions. It is interesting to note that polyamide **PA-VI** derived from

4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and 4-(4'-aminophenoxy)-2-pentadecyl benzenamine was insoluble in amide-type solvents. The poorer solubility of polyamide **PA-VI** could be attributed to the presence of two pentadecyl chains in each repeat unit. The increased hydrocarbon content is presumably responsible for the insolubility of **PA-VI** in amide-type solvents which are known to be poor solvents for polyolefins.

4b.4.1.3 X-Ray diffraction studies

The crystallinity in polyamides results in their insolubility and is dependent on the rigidity of both diacid and diamine used in their synthesis. It is known that less symmetrical monomers[35] and those having pendant groups[36] reduce the crystallinity in polyamides and improve their solubility.

X-Ray diffractograms of polyamides derived from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and various aromatic diamines are shown in **Figure 4b.2**.

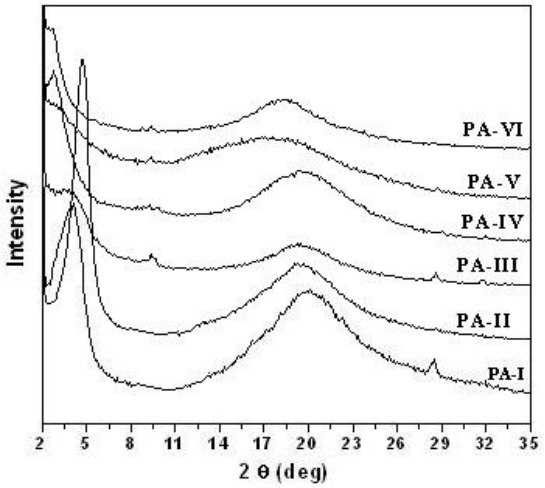


Figure 4b.2 X-Ray diffraction patterns of polyamides derived from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines

Polyamides showed broad halo at around $2\theta = \sim 19^{o}$ indicating that the polymers are amorphous in nature **(Figure 4b.2).** This result could be explained in terms of the presence of the pendant pentadecyl chain in the polymer backbone which hindered packing of the polymer chains and decreased the intermolecular forces, subsequently causing a decrease in crystallinity.

It is generally known that rigid-rod polymers having long flexible side chains crystallize into layered structures[37-40] in which the rigid backbones come together to form backbone layers and the side chains to form a separate crystal region. A sharp reflection peak for **PA-I** and **PA-II** ($2\theta = \sim 5^{o}$) and reflections for rest of the polyamides were observed in the small angle region ($2\theta = \sim 3^{o}$). These reflections resulted from the packing of pentadecyl side chains.

4b.4.1.4 Thermal properties

In the present study, thermal stability of the polyamides was determined by thermogravimetric analysis (TGA) at a heating rate of 15°C/ minute under nitrogen. TG curves of polyamides are shown in **Figure 4b.3**. The initial decomposition temperature (IDT), the temperature at 10% weight loss (T_{10}) and the weight residues at 900°C for polyamides are given in **Table 4b.3**.

T_{10} values obtained from TG curves for polyamides were in the range 425-455°C indicating their good thermal stability. The weight residue of polyamides when heated to 900°C in nitrogen was in the range 21-38 %.

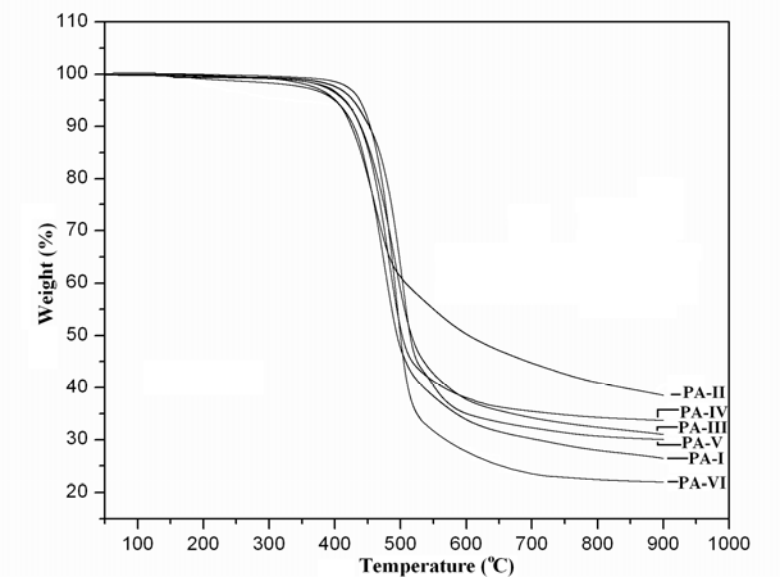


Figure 4b.3 TG curves of polyamides derived from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines

Table 4b.3 Thermal properties of polyamides derived from 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid and aromatic diamines

Polymer	Diacid	Diamine	T_0[a] (°C)	T_{10}[b] (°C)	Weight residue at 900°C (%)	T_g (°C)
PA-I	CPPB	*p*-PD	345	430	26	189
PA-II	CPPB	ODA	335	425 (515)[c]	38	160 (231)[c]
PA-III	CPPB	MDA	349	440 (483)[c]	32	139 (255)[c]
PA-IV	CPPB	*m*-PD	348	439 (467)[c]	33	148 (250)[c]
PA-V	CPPB	HFDA	376	453	29	154
PA-VI	CPPB	APPB	371	455	21	--[d]

a : Initial decomposition temperature, *b* : temperature at which 10% weight loss is observed,
c: 4,4'-oxybisbenzoic acid derived polyamides[41]; *d* : Not detected

Glass transition (T_g) temperature of the polyamides was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polyamide samples at a heating rate of 10°C / minute. DSC curves are reproduced in **Figure 4b.4** and T_g values are given in

Table 4b.3.

Most of the polyamides displayed distinct glass transitions on the second heating DSC traces. These polyamides had glass transition temperatures (T_g's) in the range 139-189 °C. Glass transition temperature of polyamide **PA-VI** derived from 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid and 4-(4'-aminophenoxy)-2-pentadecylbenzenamine could not be detected under the present experimental conditions. The increasing order of T_g generally corresponds to an increase in the rigidity and bulkiness of the diamine monomer. For example, polyamide **PA-I** with a stiff 1,4-phenylene unit in the polymer backbone exhibited the highest T_g value among these polyamides. Due to presence of long pentadecyl chain in the polymer backbone, the derived polyamides showed lower glass transition temperatures in comparison with those synthesized from 4,4'-oxybisbenzoic acid and various diamines.[41] For example, polymer derived from 4,4'-oxybisbenzoic acid and 1,3-phenylenediamine showed a T_g at 250 ^oC, whereas, when diacid was replaced by 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid, a glass transition temperature was observed at 148^oC. This result is very reasonable and can be attributed to the fact that long pentadecyl chains along the polymer backbone, which is acting as an internal plasticizer, increases free volume and thereby increases segmental mobility, thus resulting in a reduction in the T_g.

A large difference between glass transition (139-189 ^oC) and initial decomposition temperature (335-376^oC) was observed. This offers polyamides a wide processing window.

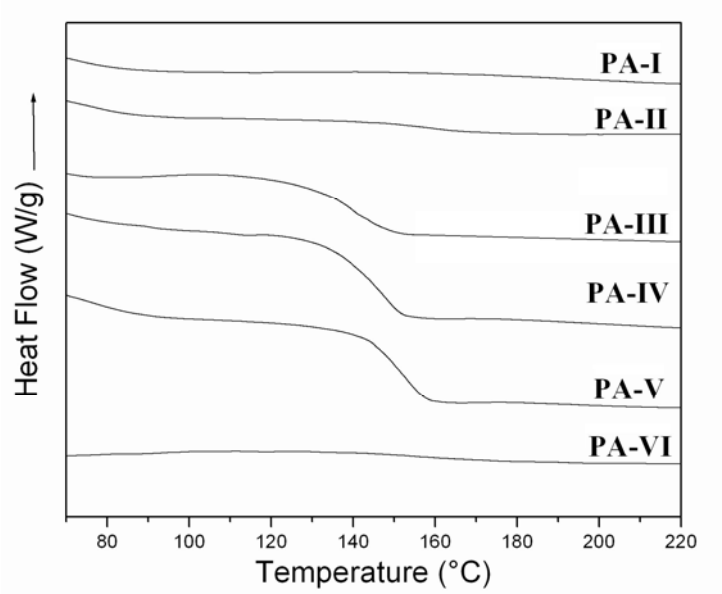


Figure 4b.4 DSC curves of polyamides derived from 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid and aromatic diamines

4b.5 Conclusions

1. A series of polyamides containing pendant pentadecyl chains and ether moieties in the backbone was synthesized by the direct polycondensation of 4-(4'-carboxyphenoxy)-2-pentadecyl benzoic acid with various diamines. Inherent viscosities of polyamides were in the range 0.45-0.66 dL/g indicating formation of medium to reasonably high molecular weight polymers.
2. Most of the polyamides were found to be soluble in DMF, DMAc, NMP, pyridine and *m*-cresol at room temperature or upon heating. Tough, transparent and flexible films of most of the polyamides could be cast from DMAc solution.
3. Wide angle X-ray diffraction patterns indicated that polyamides containing pendant pentadecyl chains were amorphous in nature. The formation of layered structure was observed due to the packing of pentadecyl chains.
4. T_{10} values for polyamides were in the range 425-455°C indicating good thermal stability of polyamides.
5. T_g values of polyamides were in the range 139 to 189°C. The depression in T_g values of polyamides could be attributed to the presence of flexibilizing ether linkages in the backbone and pendant pentadecyl chains.

References

1. Cassidy, P. E. *Thermally Stable Polymers*, Dekker, New York, **1980**.
2. Abid, S.; Gharbi, R.E.; Gandini, A. *Polymer* **2004**, 45, 5793.
3. Ferrero, E.; Espeso, J.F.; de la Campa, J.G.; de Abajo, J.; Lozano, A.E. *J. Polym. Sci. Polym. Chem.* **2002**, 40, 3711.
4. Garcia, J.M.; Garcia, F.; Sanz, R.; de la Campa, J.G.; Lozano, A.E.; de Abajo, J. *J. Polym. Sci. Polym. Chem.* **2001**, 39, 1825.
5. Sagar, A.D.; Shingte, R.D.; Wadgaonkar, P.P.; Salunkhe, M.M. *Eur. Polym. J.* **2001**, 37, 1493.
6. Morikawa, A.; Hatakeyama, T. *Polym. J.* **1999**, 31, 66.
7. Sagar, A.D.; Salunkhe, M.M.; Wadgaonkar, P.P.; Sarwade, B.D.; Mahajan, S.S. *J. Polym. Sci. Polym. Chem.* **1997**, 35, 1077.
8. de Abajo, J.; de la Campa, J.G.; Lozano, A.E.; Alvarez, J.C. *Adv. Mater.* **1995**, 7, 148.
9. Ferreieo, J. J.; de la Campa, J. G.; Lozano, A.; de Abajo, J.; Preston, *J. J. Polym. Sci. Polym. Chem.* **2007,** 45, 4671.
10. Yang, C. P.; Oishi, Y.; Kakimoto, M.A.; Imai, Y. *J. Polym. Sci. Polym. Chem.* **1989**, 27, 3895.
11. Mahajan, S.S.; Wadgaonkar, P.P.; Chavan, N.N. *Intern. J. Polym. Mater.* **1988**, 12, 101.
12. Spiliopoulos, I.K.; Mikroyannidis, J.A. *Polymer* **1996**, 37, 3331.
13. Wang, C. S.; Yang, R. W. *Polymer* **1997**, 38, 6109.
14. Melendez, A.; de la Campa, J.G.; de Abajo, J. *Polymer* **1988**, 29, 1142.
15. Garcia, J.M.; Alvarez, J.C.; de la Campa, J.G.; de Abajo, J. *Macromol. Chem. Phys.* **1997**, 198, 727.
16. Mallakour, S. ; Kowsari, E. *Polym. Adv. Technol*. **2005**, 16, 732.
17. Liaw, D.J.; Liaw, B.Y. *Polymer* **2001**, 42, 839.
18. Nakata, S. ; Brisson, J.J. *J. Polym. Sci. Polym. Chem*. **1997**, 35, 2379.
19. Liaw, D.J. ; Hsu, P.N. ; Liaw, B.Y. *J. Polym. Sci. Polym. Chem*. **2001**, 39, 63.
20. Liaw, D.J.; Liaw, B.Y.; Yang, C.M. *Macromol. Chem. Phys*. **2001**, 202, 1866.
21. Ferrero, E.; Espeso, J.F. ; de la Campa, J.G. ; de Abajo, J. ; Lozano, A. E. *J. Polym. Sci. Polym. Chem.* **2002**, 40, 3711.
22. Ayala, V. ; Maya, E.M. ; Garcia, J.M.; de la Campa, J.G. ; Lozano, A.E. ; de Abajo, J. *J. Polym. Sci. Polym. Chem.* **2005**, 43, 112.
23. Hsiao, S.H.; Yang, C.P.; Chen, C.W. ; Liou, G.S. *Eur. Polym. J*. 2005, 41, 511.
24. Sava, I. ; Bruma, M. *Macromol. Symp*. **2006**, 239, 36.
25. Zulfiqar, S.; Zahoor, A.; Sarwar, M. *Colloid Polym. Sci.* **2007**, 285, 1749.
26. Yang, C.P.; Hsiao, S.H. ; Jang, C.C. *J. Polym. Sci. Polym. Chem*. **1995**, 33, 1095.
27. Yang, C.P.; Lin J. H. *J. Polym. Sci. Polym. Chem*. **1996**, 34, 341.
28. Hsiao S. H.; Yang C.P.; Chen, S.H. *Polymer*, **2000**, 41, 6537.
29. Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; Pergamon Press: NewYork, **1989**.
30. Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. Polym. Chem.* **1975**, 13, 1373.
31. Higashi, F.; Ogata, S.; Aoki, Y. *J. Polym. Sci. Polym. Chem.* **1982**, 20, 75.

32. Krigbaum, W.R.; Kotek, R.; Mihara, Y.; Preston, J. *J. Polym. Sci. Polym.Chem.* **1985**, 23, 1907.
33. Banerjee, S.; Maier, G.; Burger, M. *Macromolecules* **1999**, 32, 4279.
34. Kute, V.; Banerjee, S. *J. Appl. Polym. Sci.* **2007**, 103, 3025.
35. Yang, C. P.; Hsiao, S. H.; Yang, C.C. *J. Polym. Sci. Polym. Chem*. **1997**, 35, 2147.
36. Liaw, D. J.; Liaw, B. Y.; Chen, J. J. *J. Polym. Sci. Polym. Chem*. **2000**, 38, 797.
37. Shia, H.; Zhaoa, Y.; Zhanga, X.; Zhoua, Y.; Xub, Y.; Zhoua, S.; Wanga, D.; Hana, C. C.; Xua, D. *Polymer* **2004**, 45, 6299.
38. Kim, H.; Park, S.B.; Jung, J.C.; Zin, W.C. *Polymer* **1996**, 37, 2845.
39. Park, S.B.; Kim, H.; Zin, W.C.; Jung, J.C. *Macromolecules* **1993**, 26, 1627.
40. Ballauff, M. *Makromol. Chem. Rapid Commun*. **1987**, 8, 93.
41. Hsiao S. H.; Yu. C.H. *J. Polym. Res*. **1996,** 3, 239.

Chapter 5

Synthesis and Characterization of Poly(amideimide)s, Polyhydrazides and Polyoxadiazoles

Chapter 5a

Synthesis and Characterization Poly(amideimide)s Based on 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

5a.1 Introduction

Aromatic polyimides are well recognized as a class of high performance materials due to their remarkable thermal and oxidative stabilities, and excellent electrical and mechanical properties.[1-3] The difficulties in processing conventional aromatic polyimides are due to the inherent molecular features of aromatic polyimides. Molecular stiffness, high polarity and high intermolecular association forces make these polymers virtually insoluble in organic medium, and shift the transition temperatures to well above the decomposition temperatures.

The strategies to processable aromatic polyimides have focused on chemical modifications, mainly by preparing new monomers that provide less molecular order, better torsional mobility and lower intermolecular interactions. Of the various alternatives to design novel processable polyimides, some general approaches have been universally implemented: introduction of aliphatic or another kind of flexible segments which reduce chain stiffness;[3-12] introduction of bulky side substituents which help for separation of polymer chains and hinder molecular packing and crystallization;[13-28] use of enlarged monomers containing angular bonds which suppress coplanar structures; use of 1,3-disubstituted instead of 1,4-disubstituted monomers and/or asymmetric monomers which lower regularity and molecular ordering;[29-38] preparation of co-polyimides from two or more dianhydrides or diamines, etc.[39-51] However, factors leading to better solubility or lower T_g or T_m in a polymer often conflict with other important requirements such as mechanical properties, thermal resistance or chemical resistance. Therefore, an adjusted degree of modification should be applied to optimize the balance of properties.

Among various strategies adapted so far in order to improve processability of polyimides, insertion of an amide moiety in imide backbone has proven very satisfactory. Poly(amideimide)s (PAIs) combine the thermal stability property of polyimides and ease of processability of polyamides and be intermediate in properties between polyimides and polyamides. PAIs, as a family, have deserved particular attention as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and moldability. It is expected that a combination of these structural modifications will give rise to polyimides with a favorable balance of properties.

The objective of the present work was to synthesize and characterize poly(amideimide)s containing flexibilizing ether linkages in the backbone and pendant pentadecyl chains by polycondensation of diacylhydrazide monomer *viz*; 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide with commercially available aromatic dianhydrides, *viz*, benzene-1,2,4,5-tetracarboxylic dianhydride or pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoro isopropylidene)diphthalic anhydride.

The synthesized poly(amideimide)s were characterized by inherent viscosity measurements, solubility tests, FTIR spectroscopy, ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

5a.2 Experimental

5a.2.1 Materials

4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide (HPPB) was synthesized as described in **Chapter 3**. The dianhydrides, benzene-1,2,4,5-tetracarboxylic dianhydride or pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA), benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA), all received from Aldrich, USA, were sublimed before use. N,N-Dimethylacetamide (DMAc) received from Merck, India, was dried over calcium hydride and distilled under reduced pressure. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[52]

5a.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in DMAc at 30±0.1^{o}C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker 200 MHz spectrometer at a resonance frequency of 200 MHz in DMSO-d_6.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 15 °C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

The solubility of poly(amideimide)s was determined at 3 wt % concentration in various solvents at room temperature or on heating.

5a.3 Synthesis of poly(amideimide)s

A representative procedure for the synthesis of poly(amideimide)s is given below:

Into a 50 mL two necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube and a magnetic stirring bar were charged 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide (650 mg, 1.31 mmol) and N,N-dimethylacetamide (10 mL). After complete dissolution of diacyl hydrazide, benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA) (285 mg, 1.31 mmol) was added in portions to the stirred solution of diacylhydrazide. The reaction was allowed to proceed for an additional 18 h at room temperature under nitrogen atmosphere.

The obtained poly(hydrazide-acid) was imidized thermally in the following way:

Thermal imidization of poly(hydrazide acid) [54]

The solution of poly(hydrazide-acid) was cast onto a glass plate and the solvent was evaporated at 80^{o}C under nitrogen atmosphere for 1 h. The semi-dried film was heated at 220^{o}C for 12 h under reduced pressure to effect imidization.

A similar procedure was followed for the synthesis of other poly(amideimide)s.

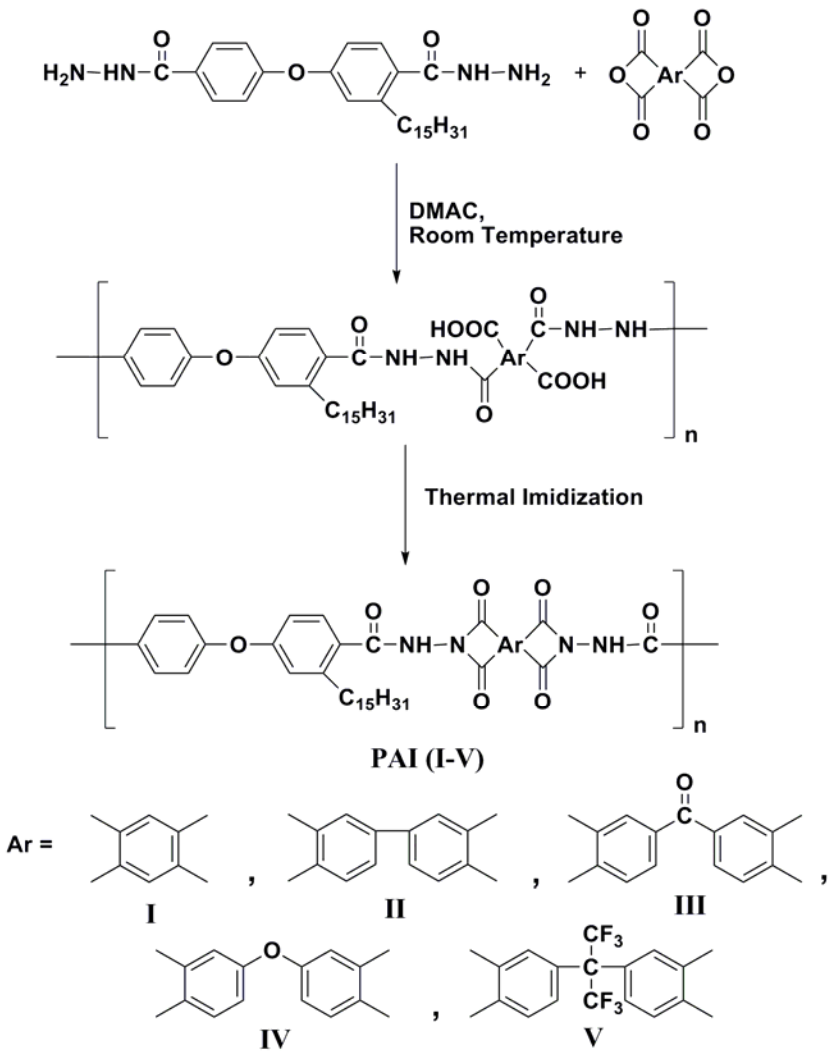
5a.4 Results and discussion

5a.4.1 Synthesis and characterization of poly(amideimide)s

Scheme 5a.1 illustrates synthesis of poly(amideimide)s from 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide and commercially available dianhydrides.

The preparation of poly(amideimide)s by the reaction of an aromatic diacylhydrazide and a dianhydride is a two stage process.[53-58] The first stage is the ring opening polyaddition reaction of a dianhydride and a diacylhydrazide to form poly(hydrazide acid), while the second step consists of the subsequent cyclodehydration of poly(hydrazide acid) to form poly(amideimide). It has been established that the cyclodehydration reaction involving NH and COOH groups in poly(hydrazide acid) gives selectively imide functions, without formation of any detectable 1,3,4-oxadiazole rings by cyclodehydration of the O=C–NH–NH–C=O moieties.[49,50,53]

4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide was reacted with various aromatic dianhydrides at room temperature in DMAc. All the reactions proceeded in a homogeneous fashion. The cyclodehydration of poly(hydrazide acid)s can be achieved either chemically or thermally. In the present work, the cyclization of poly(hydrazide acid)s was carried out using thermal imidization.[54] In the thermal cyclodehydration, the solution of poly(hydrazide acid) was spread onto a glass plate and the solvent was evaporated at 80^{o}C/ 1 h in a slow stream of nitrogen flow. Then, the semi-dried film was kept in a vacuum oven at 220^{o}C for 12 h to obtain a tough, pale yellow film of polyamideimide.



Scheme 5a.1 Synthesis of poly(amideimide)s from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

The results of polymerization are summarized in **Table 5a.1**.

Table 5a.1 Synthesis of poly(amideimide)s from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

Polymer	Diacylhydrazide	Dianhydride	Yield (%)	η_{inh} (dL/g)[a]
PAI-I	HPPB	PMDA	95	0.62
PAI-II	HPPB	BPDA	93	0.62
PAI-III	HPPB	BTDA	96	0.64
PAI-IV	HPPB	ODPA	92	0.60
PAI-V	HPPB	6-FDA	92	0.60

a: η_{inh} was measured with 0.5% (w/v) solution of poly(amideimide)s in DMAc at 30 ± 0.1°C

Inherent viscosities of poly(amideimide)s were in the range 0.60-0.64 dL/g **(Table 5a.1)** indicating formation of reasonably high molecular weight polymers. Tough, transparent and flexible films of poly(amideimide)s could be cast from DMAc solutions of poly(amideimide)s.

5a.4.1.1 Structural Characterization

The formation of poly(amideimide)s was confirmed by FT-IR and ^{1}H-NMR spectroscopy.

A representative FTIR spectrum of poly(amideimide) based on 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and benzene-1,2,4,5-tetracarboxylic dianhydride (PMDA) is shown in **Figure 5a.1**.

FTIR spectrum of polymer exhibited characteristic absorption bands for the imide ring at 1779 and 1722 cm^{-1} due to asymmetrical and symmetrical stretching vibration of the imide carbonyl group.[53] Absorption bands at 1364 and 731 cm^{-1} correspond to the C–N–C stretching and bending vibrations of the imide. The absorption at 1122 cm^{-1} corresponds to imide ring deformation. The presence of bands around 3354 and 1650 cm^{-1} corresponds to the NH and C=O of amide linkage.

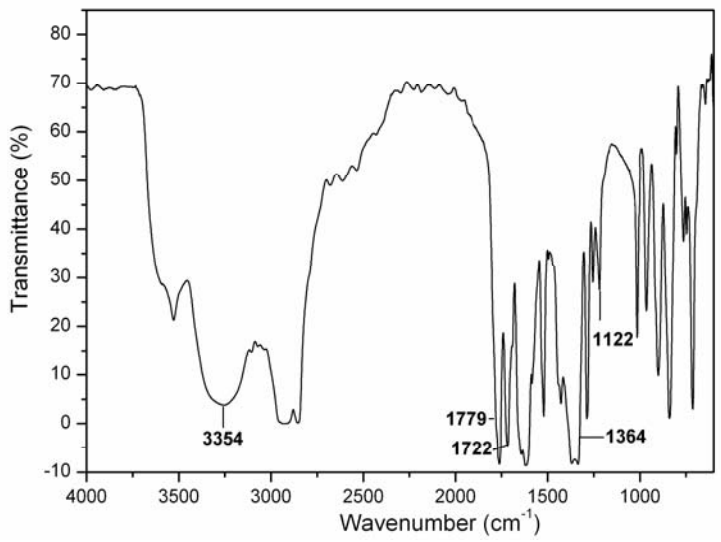


Figure 5a.1 FTIR spectrum of poly(amideimide) derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and benzene-1,2,4,5-tetracarboxylic dianhydride

^{1}H-NMR spectrum of poly(amideimide) derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and 4,4'-oxydiphthalic anhydride is shown in **Figure 5a.2.** Interestingly, two separate peaks were observed in ^{1}H-NMR spectrum for –NH of the amide linkage at 11.17 and 11.34 δ ppm. As has already been discussed in case of polyazomethines, constitutional isomerism could arise due to the use of unsymmetrical diacyl hydrazide monomer. The two aromatic protons next to imide carbonyl groups on ODPA ring and two protons *ortho* to amide functionality appeared as a multiplet in the range 8.01-8.13 δ ppm. Other four aromatic protons on ODPA ring and one proton *ortho* to amide carbonyl groups appeared as a multiplet in the range 7.58-7.78 δ

ppm, while the four aromatic protons *ortho* to ether linkage from diacyl hydrazide component exhibited a multiplet over the range 7.04-7.25 δ ppm.

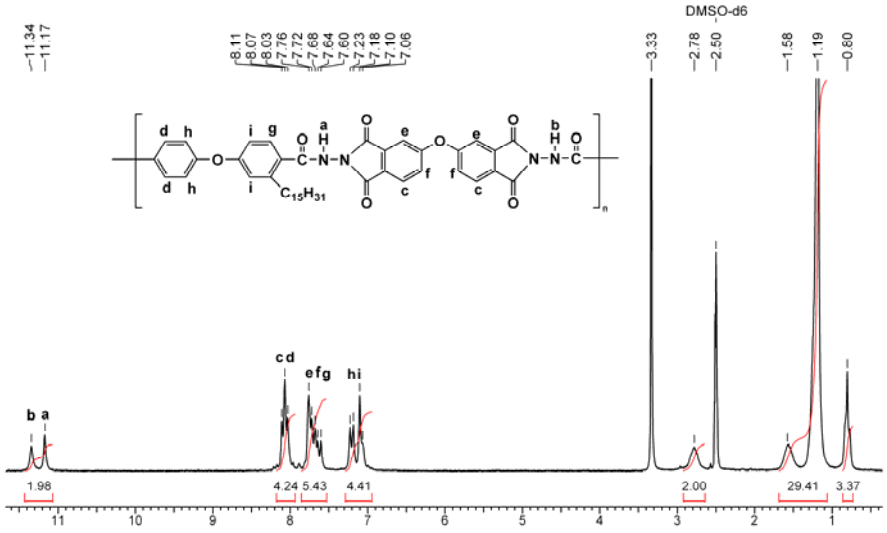


Figure 5a.2 ^{1}H-NMR spectrum of poly(amideimide) derived from 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecylbenzohydrazide and 4,4'-oxydiphthalic anhydride in DMSO-d_6

In diacyl hydrazide component, the benzylic –CH_2 appeared as a triplet at 2.78 δ ppm. The methylene protons β to aromatic ring exhibited a triplet at 1.58 δ ppm. The other methylene protons displayed a multiplet over the range 1.17-1.21 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.80 δ ppm.

5a.4.1.2 Solubility measurements

Solubility of poly(amideimide)s was tested in various organic solvents at a 3 wt % concentration and data is summarized in **Table 5a.2.**

Table 5a.2 Solubility data of poly(amideimide)s derived from 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

Polymer	Diacylhydrazide	Dianhydride	$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
PAI-I	HPPB	PMDA	--	--	++	++	++	++	++	++	+-
PAI-II	HPPB	BPDA	--	--	++	++	++	++	++	++	+-
PAI-III	HPPB	BTDA	--	--	--	--	++	+-	++	+-	--
PAI-IV	HPPB	ODPA	--	--	++	++	++	++	++	++	+-
PAI-V	HPPB	6-FDA	--	--	++	++	++	++	++	++	+-

++ : soluble at room temperature; +- : soluble on heating; + : partially soluble on heating; -- : insoluble

These pentadecyl chain- containing poly(amideimide)s exhibited excellent solubility in organic solvents. They are soluble in polar solvents such as DMAc, NMP, DMF, *m*-cresol and pyridine. With the exception of poly(amideimide) based on BTDA, poly(amideimide)s were also found to be soluble in common low boiling organic solvent such as THF. The improved solubility of these poly(amideimide)s results from the presence of pendant pentadecyl chains which limits tight chain packing and leads to reduced intermolecular interactions.

5a.4.1.3 X-Ray diffraction studies

X-Ray diffractograms of poly(amideimide)s derived from 4-[4'-(hydrazino carbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides are shown in **Figure 5a.3**.

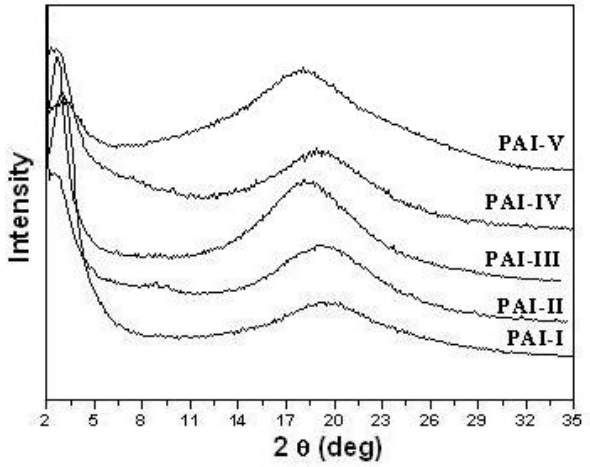


Figure 5a.3 X-Ray diffraction patterns of poly(amideimide)s derived from 4-[4'-(hydrazino carbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

WAXD patterns of poly(amideimide)s showed broad halo at around $2\theta = \sim 19^{o}$ in the wide-angle region suggesting that all polymers were amorphous. The presence of pentadecyl chain in the polymer backbone disrupts the hydrogen bond formation between the amide groups of the polymer thereby reducing the intra- as well as inter-molecular interactions resulting in loose polymer packing. In the small-angle region at $2\theta = \sim 3^{o}$, poly(amideimide)s exhibited reflections. The observed reflections in the small angle region, could arise from the formation of layered structures from packing of pentadecyl side chains.

5a.4.1.4 Thermal properties

In the present study, thermal stability of poly(amideimide)s was determined by thermogravimetric analysis (TGA) at a heating rate of 15^{o}C /minute under nitrogen. TG curves of poly(amideimide)s are shown in **Figure 5a.4**. The initial decomposition temperature (IDT), the

temperature at 10% weight loss (T_{10}) and the weight residues at 900°C for poly(amideimide)s are given in **Table 5a.3**.

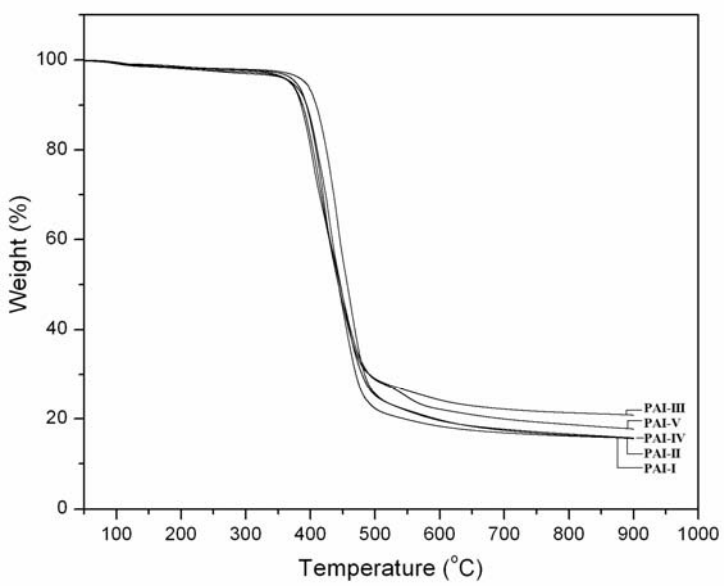


Figure 5a.4 TG curves of poly(amideimide)s derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

TGA data indicate that the polymers exhibited one-step decomposition pattern with no significant weight loss below 340°C in nitrogen. T_{10} values obtained from TG curves were in the range of 388-410°C for poly(amideimide)s indicating their good thermal stability. The weight residue of polymers at 900 °C were in the range 15-21%.

Table 5a.3 Thermal properties of poly(amideimide)s derived from 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

Polymer	Diacylhydrazide	Diamine	T_0[a] (°C)	T_{10}[b] (°C)	Weight residue at 900°C (%)	T_g (°C)
PAI-I	HPPB	PMDA	351	388	16	168
PAI-II	HPPB	BPDA	356	410	15	198
PAI-III	HPPB	BTDA	340	389	21	162
PAI-IV	HPPB	ODPA	347	398	16	164
PAI-V	HPPB	6-FDA	349	394	18	178

a : Initial decomposition temperature, *b* : temperature at which 10% weight loss is observed

Glass transition (T_g) temperature of poly(amideimide)s was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of poly(amideimide) samples at a heating rate of 10°C / minute. DSC curves are reproduced in **Figure 5a.5** and T_g values are given in **Table 5a.3**.

Glass transition temperatures of poly(amideimide)s containing pendant pentadecyl chains and ether linkages were in the range of 162-198°C. The highest observed T_g (198°C), in case of

polyamideimide derived from BPDA **PAI-II**, could be attributed to the rigid biphenyl moiety present in BPDA.

A large difference between glass transition (162-198^{o}C) and initial decomposition temperature (340-356^{o}C) was observed. This offers poly(amideimide)s a wide processing window.

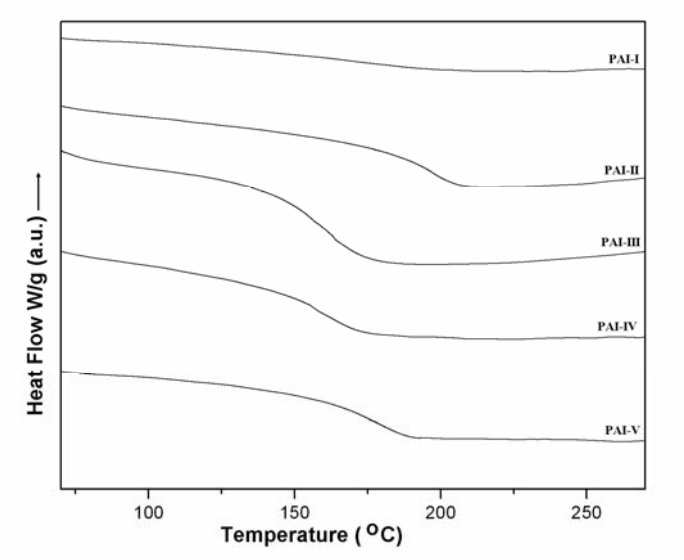


Figure 5a.5 DSC curves of poly(amideimide)s derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides

5a.5 Conclusions

1. A new series of poly(amideimide)s containing pendant pentadecyl chains and ether linkages was synthesized from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide and aromatic dianhydrides by a two-step solution polycondensation in DMAc *via* the poly(hydrazide acid) intermediate.
2. Inherent viscosities of the poly(amideimide)s were in the range 0.60-0.64 dL/g indicating formation of reasonably high molecular weight polymers.
3. Most of the poly(amideimide)s were found to be soluble in aprotic polar solvents such as NMP, DMAc and DMF. Rigid dianhydrides such as PMDA and BPDA also gave soluble poly(amideimide)s. This indicates that the incorporation of pendant flexible pentadecyl chains leads to a significant improvement in solubility of poly(amideimide)s.
4. Tough, transparent and flexible films could be cast from the solution of poly(amideimide)s in DMAc.
5. WAXD patterns showed that poly(amideimide)s containing pendant pentadecyl chains were amorphous in nature. Layered structure formation was observed due to the packing of pentadecyl chains in the polymer backbone.
6. T_{10} values for poly(amideimide)s were in the range 388-410°C indicating the good thermal stability of polymers.
7. Thermal analysis showed that the attached pentadecyl side chain induced the depression of T_g (162-198 ^oC).

References

1. Ghosh, M. K.; Mittal, K. L. *Polyimides: Fundamentals and Applications* (New York: Dekker) **1996**.
2. Abadie, M. J.; Sillion, B. *Polyimides and Other High-Temperature Polymers* (Amsterdam: Elsevier) **1991**.
3. Mittal, K.L. *Polyimides:Ssynthesis, Characterization and Applications*. Plenum, New York, **1985.**
4. Lee, H.; Stoffey, D.; Neville, K. *NewLinear Polymers*. McGraw-Hill, New York **1967**.
5. Edwards, W.M.; Robinson, I.M. US Pat 2,710,853, **1955**.
6. Sroog, C.E. *J. Polym. Sci*. **1967**, 16, 1191.
7. Critchley, J.P. ; Grattan, P.A.; White, M.A.; Pippett, J.S. *J. Polym. Sci. Polym. Chem*. **1972**, 10, 1789.
8. a) Harris, F. W. *Polym. Prep.* **1992**, 33, 449. b) Acevedo, M, Harris F.W. *Polymer* **1994**, 35, 4456.
9. Kricheldorf, H.R.; Linzer, V. *Polymer* **1995**, 36, 1893.
10. Padmanaban, M.; Toriumi, M.; Kakimoto, M.; Imai, Y. *Makromol. Chem. Rapid Commun*. **1990**, 11, 15.
11. Rogers, M.E.; Glass, T.E.; Mechan, S.J.; Rodriguez, D.; Wilkes, G.L.; McGrath, J.E. *J. Polym. Sci. Polym. Chem*. **1994**, 32, 2663.
12. Moon, Y.D.; Lee, Y.M. *J. Appl. Polym. Sci*. **1993**, 50, 1461.
13. Adrova, N.; Bessonov, M.; Laius, L.A.; Rudakov, A.P. *Polyimides: A New Cclass of Heat-Resistant Polymers*. IPST Press, Jerusalem **1969**.
14. Dine-Hart, R.A.; Wright, W.W. *Makromol. Chem*. **1972**, 153, 237.
15. Gibbs, H.H.; Breder, C.V. *Polym. Prep*. **1974**, 15, 775.
16. St. Clair, T.L.; St. Clair A.K.; Smith, E.N. *Polym. Prep.* **1976**, 17, 359.
17. Takekoshi, T.; Wirth, J.G.; Heath, D.R.; Kochanowski, J.E.; Manello, J.S.; Webber, M.J. *J. Polym. Sci. Polym. Chem.* **1980**, 18, 3069.
18. Davies, M.; Hay, J.N.; Woodfine, B. *High Perform. Polym*. **1992**. 5, 37.
19. Connel, J.W.; Croall, C.I.; Hergenrother, P.W. *Polym. Prep*. **1992**, 33, 1101.
20. Abadie, M.J.M.; Sillion, B. *Polyimides and Other High-Temperature Polymers*. Elsevier, Amsterdam **1991**.
21. Young, P,R.; Davis, J.R.J.; Chang, A.H.; Richardson, J.N. *J. Polym. Sci. Polym. Chem*. **1990**, 28, 3107.
23. Zoia, G.; Stern, S.A.; St Clair, A.K. ; Pratt, J.A. *J. Polym. Sci. Polym. Phys*. **1994**, 32, 53.
24. Bell, V.L.; Kilzer, L.; Hett, E.M.; Stokes, G.M. *J. Appl. Polym. Sci*. **1981**, 26, 3805.
25. Havens, S.J.; Hergenrother, P.M. *J. Polym. Sci. Polym. Chem*. **1990**, 28, 2427.
26. Muellerleile, J.T.; Risch, B.G.; Rodriguez, D.E.; Wilkes, G.L. *Polymer* **1993**, 34, 789.
27. Asanuma, T.A.; Oikawa, H.; Ookawa, Y.; Yamasita, W.; Matsuo, M.; Yamaguchi, A. *J. Polym. Sci. Polym. Chem*. **1994**, 32, 2111.
28. Liou, G.S.; Maruyama, M.; Kakimoto, M.A.; Imai, Y. *J. Polym. Sci. Polym. Chem*. **1993**, 31, 3273.
29. Kumar, D.; Gupta, A.D. *Polym. Prep*. **1995**, 36, 49.
30. Harris, F.W.; Hsu, S.L.C. *High Perform. Polym*. **1989**, 1, 3.
31. Giesa, R.; Keller, U.; Eiselt, P.; Schmidt, H.W. *J. Polym. Sci. Polym. Chem*. **1993**, 31, 141.

32. Imai, Y.; Maldar, N.N.; Kakimoto, M.A. *J. Polym. Sci. Polym. Chem*. **1984**, 22, 2189.
33. Akutsu, F.; Kataoka, T.; Shimizu, H.; Naruchi, K.; Miura, M. *Macromol. Chem. Rapid Commun*. **1994**, 15, 411.
34. Spiliopoulos, I.K.; Mikroyannidis, J.A. *Macromolecules* **1996**, 29, 5313.
35. Lozano, A.E.; de la Campa, J.G. ; de Abajo, J.; Preston, J. *J. Polym. Sci. Polym. Chem*. **1993**, 31, 138.
36. Lozano, A.E.; de la Campa, J.G.; de Abajo, J.; Preston, J. *Polymer* **1994**, 35, 873.
37. Kricheldorf, H.R.; Schwarz, G. *Makromol. Chem. Rapid Commun*. **1989**, 10, 243.
38. Tsai, T.; Arnold, F.E. *Polym. Prep.* **1986**, 27, 221.
39. Becker, K.H.; Schmidt, H.W. *Macromolecules* **1992**, 25, 6784.
40. Yang, C. P.; Hsiao, S. H.; Yang, H. W. Mater. Chem. Phys. **2000**, 64, 116.
41. Avadhani, C.V.; Wadgaonkar, P.P.; Vernekar, S.P. J. Appl. Polym. Sci. **1990**, 40, 1325.
42. Hsiao, S. H.; Chang, L.M. *J. Polym. Sci. Polym. Chem.* 2000, 38, 1599.
43. Bhuvana, S.; Sarojadevi, M. *J. Polym. Res*. **2007**, 14, 261.
44. Bhuvana, S.; Sarojadevi, M, *Polym. Int.* **2007**, 56, 957.
45. Behniafar, H.; Haghighat, S. *Eur. Polym. J*. **2006**, 42, 3236.
46. Tsay, S.Y.; Tsai, M.F.; Chen, B.K. *J. Appl. Polym. Sci*. **2005,** 95, 321.
47. Behniafar, H.; Banihashemi, A. *Eur. Polym. J*. **2004**, 40, 1409.
48. Behniafar, H.; Habibian, S. *Polym. Int*. **2005**, 54, 1134.
49. Behniafar, H.; Haghighat, S.; Farzaneh, S. *Polymer* **2005**, 46, 4627.
50. Behniafar, H.; *J. Appl. Polym. Sci*. **2006**, 101, 869.
51. Behniafar, H. *J. Macromol. Sci. Pur. Appl. Chem*. **2006**, 43, 813.
52. Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; Pergamon Press: NewYork, **1989**.
53. Yang, C.P.; Hsiao, S.H. *J. Appl. Polym. Sci.* **1985**, 30, 2883.
54. Sarkar, A; More, A.S.; Wadgaonkar, P.P.; Shin, G.J.; Jung, J.C. *J. Appl. Polym. Sci*., **2007**, 105, 1793.

Chapter 5b

Synthesis and Characterization of Polyhydrazides and Polyoxadiazoles Based on 4-[4'-(Hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide

5b.1 Introduction

Polyhydrazides and polyoxadiazoles have been the focus of considerable interest particularly owing to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring which from the spectral and electronic point of view is similar to a *p*-phenylene structure.[1-4] The exploration of polyoxadiazoles has led to a host of new materials favorable for opto-electronics by offering not only improved balance of charge mobility but enhanced thermal and photostability as well.[5-14] Unfortunately, aromatic polyoxadiazoles are difficult to process due to their infusible and insoluble nature and their tendency to be brittle. Many efforts have been made to improve the solubility, e.g. by incorporating flexible linkages in the polymer backbone or by introduction of bulky pendant groups on the aromatic rings.[15-28]

It is generally recognized that the introduction of long and flexible side chains improves the solubility of the polymer in common organic solvents.

As a part of our continuing efforts to obtain soluble high performance polymers, a series of polyhydrazides containing pendant pentadecyl chains and ether linkages in the polymer backbone was synthesized by polycondensation of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides. Further, a series of polyoxadiazoles was synthesized by cyclodehydration reaction of derived polyhydrazides.

The polymers were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, gel permeation chromatography, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

5b.2 Experimental

5b.2.1 Materials

4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide (HPPB) was synthesized as described in **Chapter 3**. Terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) were synthesized from terephthalic acid and isophthalic acid (both, received from Aldrich, USA), respectively using excess thionyl chloride in the presence of DMF as a catalyst and were purified by distillation under reduced pressure. Anhydrous lithium chloride, received from Aldrich, USA, was dried at 180^{o}C for 8 h under reduced pressure. N,N-Dimethylacetamide (DMAc) received from Merck, India, was dried over calcium hydride and distilled under reduced pressure. Phosphorus oxychloride ($POCl_3$) was distilled under reduced pressure. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[28]

5b.2.2 Measurements

Inherent viscosities of polyhydrazides and polyoxadiazoles were measured with 0.5 % (w/v) solution of polymer in DMAc and $CHCl_3$, respectively at 30±0.1^{o}C using an Ubbelhode suspended

level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

Molecular weights of polyoxadiazoles were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter.

FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker 200 MHz spectrometer at resonance frequency of 200 MHz for ^{1}H measurements using DMSO-d_6 or $CDCl_3$ as a solvent.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 15 °C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

The solubility of polyhydrazides and polyoxadiazoles was determined at 3 wt.% concentration in various solvents at room temperature or upon heating.

5b.3 Synthesis of polyhydrazides and polyoxadiazoles

5b.3.1 Synthesis of polyhydrazides

A representative procedure for the synthesis of polyhydrazides is given below:

Into a 50 mL two necked round bottom flask equipped with a calcium chloride guard tube, a nitrogen inlet tube and a magnetic stirring bar were placed 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide (600 mg, 1.209 mmol) and N,N-dimethylacetamide (10 mL) containing LiCl (5 wt%). The reaction mixture was cooled to 0^{o}C. Thereafter, terephthalic acid chloride (240 mg, 1.209 mmol) was added to the reaction mixture. The reaction was carried out at 0^{o}C for 2 h and at room temperature for 12 h. At the end of the reaction time, the viscous solution formed was poured into aqueous methanol and the precipitated polymer was filtered and washed several times with water and then with methanol. The polymer was dried at 60^{o}C under reduced pressure.

A similar procedure was followed for the synthesis of other polyhydrazides.

5b.3.2 Synthesis of polyoxadiazoles

Polyoxadiazoles were synthesized by cyclodehydration of polyhydrazides

Into a 50 mL two necked round bottom flask equipped with a reflux condenser, a nitrogen inlet and a magnetic stirring bar were placed polyhydrazide (derived from 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide and terephthalic acid chloride) (500 g) and $POCl_3$ (25 mL). The reaction mixture was refluxed for 12 h under nitrogen atmosphere. The clear solution was slowly poured into aqueous methanol. The precipitated polymer was filtered, washed several times with water and then with methanol. Finally, the polymer was dried under reduced pressure at 50°C for 3 h.

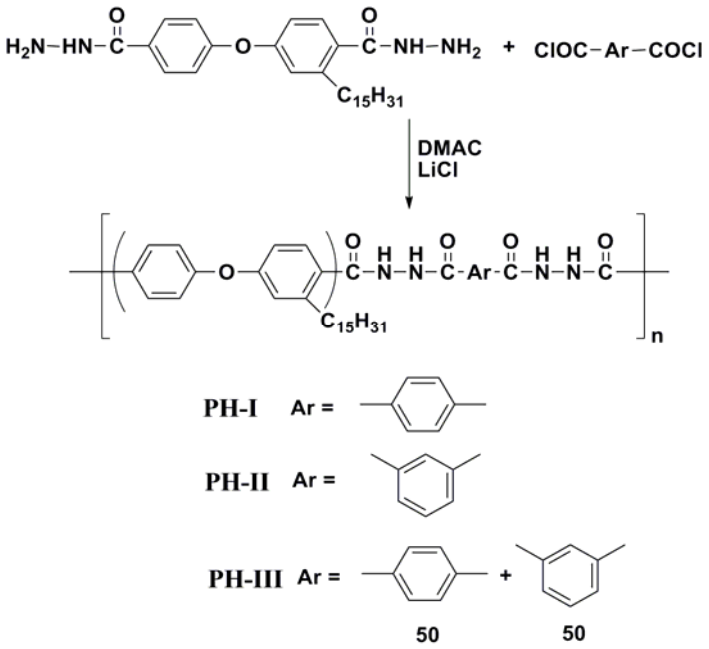
A similar procedure was followed for the synthesis of other polyoxadiazoles.

5b.4 Results and discussion

5b.4.1 Synthesis and characterization of polyhydrazides and polyoxadiazoles

Scheme 5b.1 depict synthesis of polyhydrazides by polycondensation of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides and polyoxadiazoles **(Scheme 5b.2)** by cyclodehydration reaction of corresponding polyhydrazides.

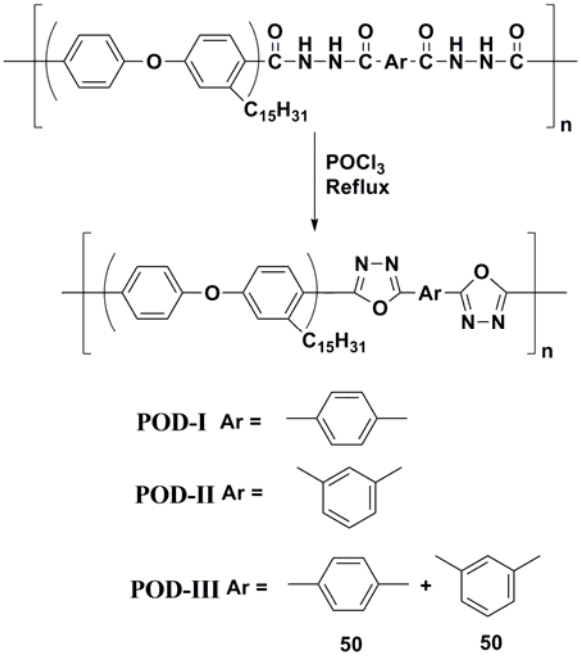
In the present study, 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide was polycondensed with equimolar quantities of aromatic diacid chlorides in DMAc containing anhydrous lithium chloride **(Scheme 5b.1)**. Polyhydrazides were obtained as white fibrous materials.



Scheme 5b.1 Synthesis of polyhydrazides from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides

Polyhydrazides are generally prepared by reacting diacyl hydrazide with diacid or diacid chloride.[29-35] Frazer[36-39] first synthesized fully aromatic polyhydrazides by low temperature solution polycondensation in NMP or HMPA containing LiCl. In these reactions, LiCl contributes to solubilize the obtained polymers probably by breaking bonds between chloride ions and hydrazide protons, as in the case of polyamides. Moreover, LiCl, a strong hydrophilic agent, prevents the hydrolysis of the diacid chlorides. Further, Dobinson and Pelezo[40-42] observed that the dissolution of polymerization products could be greatly enhanced by use of a DMAc/LiCl solvent system. Instability to rapid hydrolysis of diacid chlorides and insolubility of terephthaloyl dihydrazide in the polymerization medium are the greatest problems in obtaining high molecular weights of the prepared polymers. In literature, high temperature polycondensations are reported,[43,44] but low temperature polycondensation in DMAc/ LiCl is the best method for the synthesis of the polyhydrazides in the laboratory.

A series of polyoxadiazoles was synthesized by cyclodehydration of polyhydrazides (**Scheme 5b.2**).



Scheme 5b.2 Synthesis of polyoxadiazoles

Aromatic polyoxadiazoles can be prepared by the "one-step" method, starting from aromatic diacids (or the corresponding nitrile, amide or ester) and hydrazine sulfate in oleum or polyphosphoric acid.[45-46] Alternatively, they can be synthesized by cyclodehydration of polyhydrazide precursors; such reaction can be thermally ($T > 300^{o}C$) or chemically (using dehydrating agents like polyphosphoric acid or $POCl_3$) activated ("two-step" method).[47-49] In the present work, polyoxadiazoles were prepared using $POCl_3$ according to the route depicted in **Scheme 5b.2.**

The results of synthesis of polyhydrazides and polyoxadiazoles are summarized in **Table 5b.1**.

Table 5b.1 Synthesis of polyhydrazides and polyoxadiazoles from 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides

Polymer	Diacylhydrazide	Diacid Chloride		Yield (%)	η_{inh} (dL/g)
		TPC	IPC		
PH-I	HPPB	100	0	96	0.64[a]
PH-II	HPPB	0	100	93	0.53[a]
PH-III	HPPB	50	50	95	0.66[a]
POD-I	HPPB	100	0	96	0.49[b]
POD-II	HPPB	0	100	94	0.50[b]
POD-III	HPPB	50	50	93	0.53[b]

a: η_{inh} was measured with 0.5% (w/v) solution of polyhydrazide in DMAc at 30 ± 0.1°C.;
b: η_{inh} was measured with 0.5 (w/v) solution of polyoxadiazole in $CHCl_3$ at 30 ± 0.1°C

Inherent viscosities of polyhydrazides containing pendant pentadecyl chains were in the range 0.53-0.66 dL/g **(Table 5b.1)** indicating formation of medium to reasonably high molecular weight polymers. Inherent viscosities of corresponding polyoxadiazoles (0.49-0.53 dL/g) determined in chloroform, were found to be reduced in comparison with the parent polyhydrazides. This could be attributed partly to the different solvent used for inherent viscosity measurements and partly to the compactness of the chain structure while going from polyhydrazides to polyoxadiazoles. Tough, transparent and flexible films of polyhydrazides and polyoxadiazoles could be cast from DMAc and $CHCl_3$ solutions, respectively.

Polyoxadiazoles derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides were soluble in chloroform and the results of GPC measurements on polyoxadiazoles are presented in **Table 5b.2.**

Table 5b.2 GPC data for polyoxadiazoles derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides

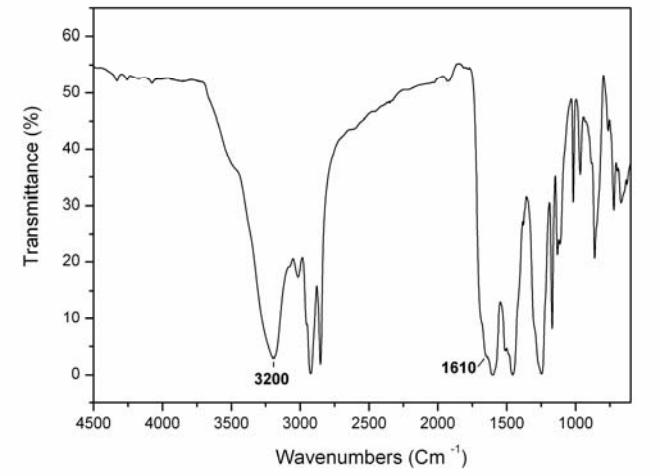
Polymer	Diacylhydrazide	Diacid Chloride		Molecular weight[a]		Polydispersity Index M_w/M_n
		TPC	IPC	M_n	M_w	
POD-I	HPPB	100	0	14,660	36,860	2.5
POD-II	HPPB	0	100	15,210	34,230	2.2
POD-III	HPPB	50	50	21,370	47,390	2.2

a: measured by GPC in chloroform, polystyrene was used as a calibration standard

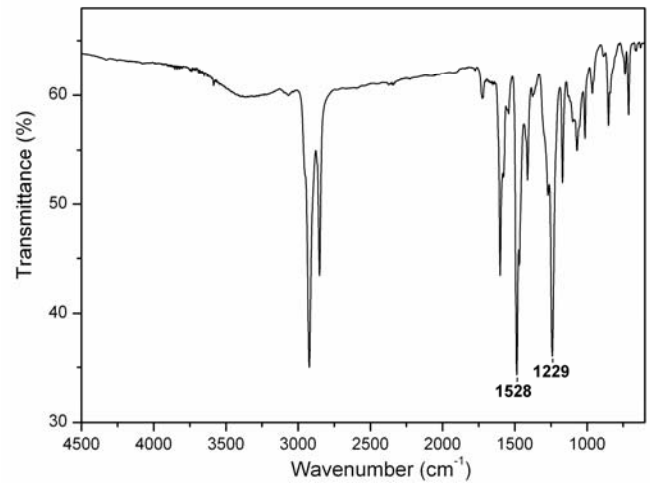
Inherent viscosity and GPC data indicated the formation of reasonably high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards.

5b.4.1.1 Structural Characterization

The chemical structures of polyhydrazides and polyoxadiazoles was confirmed by FT-IR and ^{1}H-NMR spectroscopy.



(a) FTIR spectrum of polyhydrazide (PH-I)

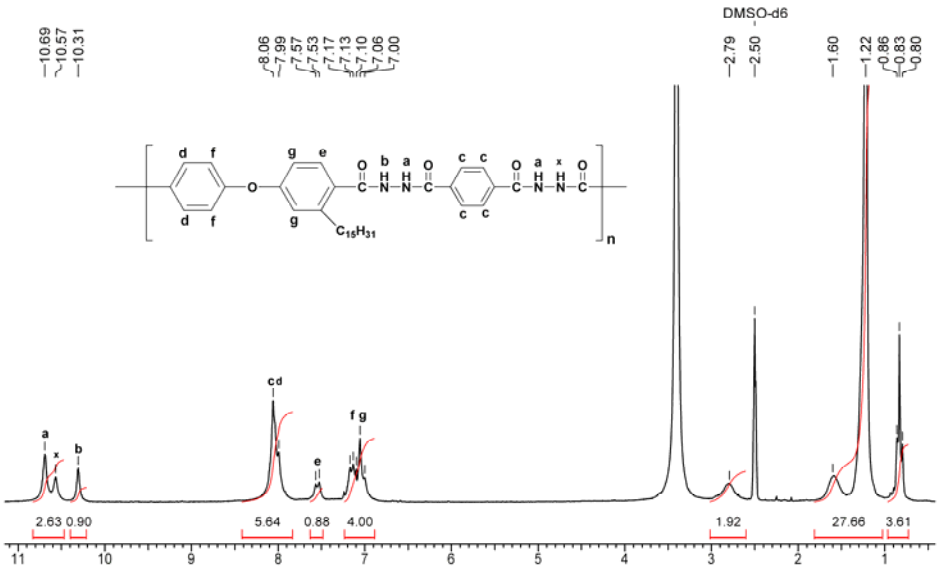


(b) FTIR spectrum of polyoxadiazole (POD-I)

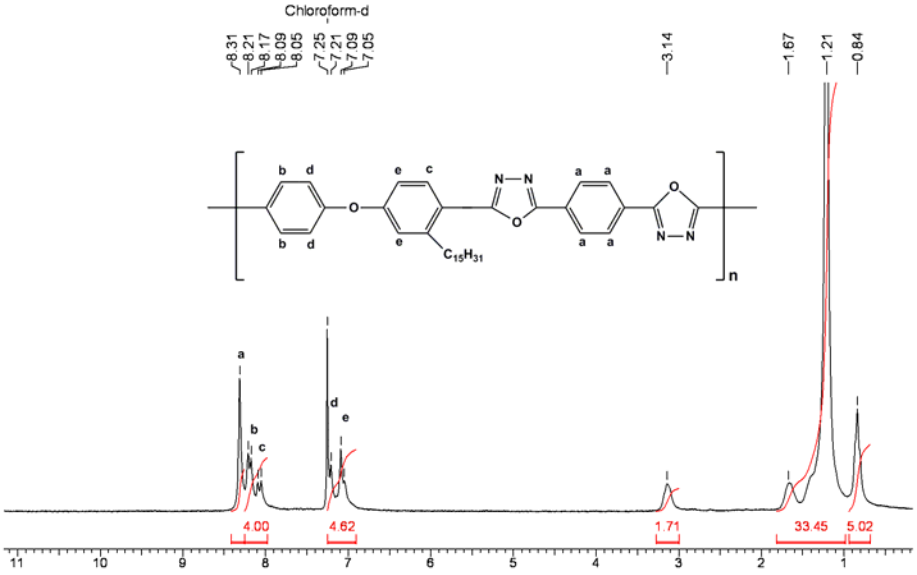
Figure 5b.1 FTIR spectrum of (a) polyhydrazide (PH-I) and (b) polyoxadiazole (POD-I)

In **Figure 5b.1,** a comparison between FTIR spectra of polyhydrazide **(PH-I)** and polyoxadiazole **(POD-I)** is shown as an example. After the treatment of $POCl_3$, the intense strong absorption band at around 1610 arising from carbonyl groups of polyhydrazide and those at 3200-3300 cm^{-1} due to N-H stretching disappeared. Meanwhile, the characteristic bands of the oxadiazole ring at 1528 cm^{-1} (C=N stretching) appeared, which confirmed the complete cyclization of polyhydrazide into polyoxadiazole.

^{1}H-NMR spectra of polyhydrazides **(PH-I)** and polyoxadiazole **(POD-I)** derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and terephthaloyl chloride are shown in **Figure 5b.2** as an example**.**



(a) ^{1}H-NMR spectrum of polyhydrazide (PH-I) in DMSO-d_6



(b) ^{1}H-NMR spectrum of polyoxadiazole (POD-I) in $CDCl_3$

Figure 5b.2 ^{1}H-NMR spectra of (a) polyhydrazide (PH-I) and (b) polyoxadiazole (POD-I) in DMSO-d_6 and $CDCl_3$, respectively

In ^{1}H-NMR spectrum of polyhydrazide **(PH-I)**, hydrazide protons, flanked by two carbonyl groups (-CO-NH-NH-CO-) appeared as three distinct singlets at 10.31, 10.57 and 10.69 δ ppm. The appearance of three distinct peaks could be explained on the basis of formation of constitutional isomers due to the use of unsymmetrical diacyl hydrazide monomer. The four protons on terephthalic acid ring and two protons 'd' *ortho* to carbonyl appeared as a multiplet in the range 7.97-8.08 δ ppm. The proton *ortho* to carbonyl group on pentadecyl-substituted aromatic ring appeared as a doublet at 7.55 δ ppm, while four protons *ortho* to ether linkage of diacyl hydrazide

component exhibited a multiplet in the range 6.98-7.19 δ ppm. The benzylic –CH_2 appeared as a triplet at 2.79 δ ppm. The methylene protons β to aromatic ring exhibited a triplet at 1.60 δ ppm. The other methylene protons displayed a multiplet over the range 1.20-1.24 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.83 δ ppm.

In ^{1}H-NMR spectrum of polyoxadiazole **(POD-I)**, the absence of signals corresponding to hydrazide protons in the range 10.29-10.71 δ ppm confirmed the complete cyclodehydration of polyhydrazides to polyoxadiazole. The four protons of terephthalic acid unit appeared as a singlet at 8.31 δ ppm. Aromatic protons 'b' *meta* to ether linkage and aromatic proton 'c' *ortho* to oxadiazole ring appeared as a multiplet in the region 8.03-8.23 δ ppm. The four aromatic protons *ortho* to ether linkage exhibited a multiplet in the range 7.03-7.27 δ ppm. The benzylic –CH_2 appeared as a triplet at 3.14 δ ppm. The methylene protons β to aromatic ring exhibited a triplet at 1.67 δ ppm. The other methylene protons displayed a multiplet over the range 1.19-1.24 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.83 δ ppm.

5b.4.1.2 Solubility measurements

The solubility of polyhydrazides and polyoxadiazoles was tested in various organic solvents at 3 wt % concentration and data is summarized in **Table 5b.3.**

Table 5b.3 Solubility data of polyhydrazides and polyoxadiazoles derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide and aromatic diacid chlorides

Polymer	Diacylhydrazide	Diacid Chlorides		$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
		TPC	IPC									
PH-I	HPPB	100	0	--	--	--	+-	++	++	--	+0	+-
PH-II	HPPB	0	100	--	--	--	++	++	++	++	++	++
PH-III	HPPB	50	50	--	--	--	++	++	++	+-	+-	+-
POD-I	HPPB	100	0	+-	+-	+0	--	--	--	+-	++	--
POD-II	HPPB	0	100	++	++	++	+-	+-	+-	++	++	+0
POD-III	HPPB	50	50	++	++	+-	--	+-	+-	+-	++	--

++ : soluble at room temperature; +- : soluble on heating; +0 : partially soluble on heating; -- : insoluble

Polyhydrazides exhibited excellent solubility in polar aprotic solvents such as DMAc, NMP, DMF and were also found to be soluble in *m*-cresol at room temperature or upon heating. The enhanced solubility could be attributed to the flexible pentadecyl chains in the repeat unit which restricted the close packing of polymer chains and therefore allowed solvent molecules to penetrate into the polymer chains. In spite of having rigid oxadiazole moiety in the polymer backbone, polyoxadiazoles dissolved in solvents such as chloroform, DCM, THF, pyridine and *m*-cresol at room temperature or upon heating. Except for **POD-I**, polyoxadiazoles were also soluble in polar

aprotic solvents such as DMAc and NMP upon heating. The good solubility behavior of polyoxadiazoles is due to the presence of pendant pentadecyl chains. The presence of C_{15} alkyl chain in polyoxadiazoles disrupted the packing of polymer chains as well as provided the additional 'handle' for interaction with solvents.

5b.4.1.3 X-Ray diffraction studies

X-Ray diffractograms of polyhydrazides and poly(1,3,4-oxadiazole)s derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide are shown in **Figure 5b.3**.

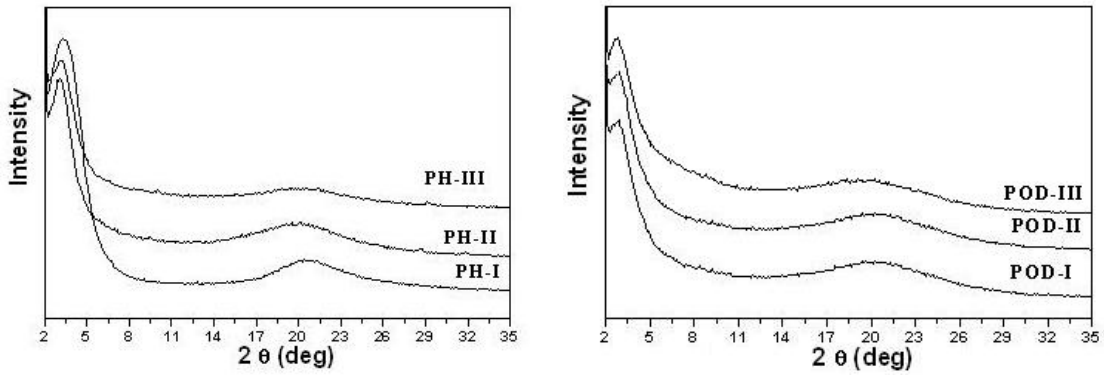


Figure 5b.3 X-Ray diffractograms of polyhydrazides and polyoxadiazoles derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides

Polyhydrazides and polyoxadiazoles exhibited broad halo at around $2\theta = \sim 20^{o}$ revealing an essentially amorphous nature. Obviously, the presence of pendant pentadecyl chain in the polymer backbone hindered chain packing and reduced the level of crystallinity. A strong reflection peak was observed in the small-angle region at around $2\theta = \sim 3^{o}$ both in polyhydrazides and polyoxadiazoles indicating the pentadecyl chains are present in a layered structure.[49,50]

5b.4.1.4 Thermal properties

In the present study, thermal stability of the polyhydrazides and polyoxadiazoles was determined by thermogravimetric analysis (TGA) at a heating rate of 15 ^{o}C /minute under nitrogen. Thermogravimetric (TG) curves of polyhydrazides and polyoxadiazoles are shown in **Figure 5b.4 and 5b.5,** respectively. The initial decomposition temperature (IDT), the temperature at 10% weight loss (T_{10}) and the weight residues at 900^{o}C for polyhydrazides and polyoxadiazoles are given in **Table 5b.4**.

Polyhydrazides showed a weight loss at around 300^{o}C **(Figure 5b.4)** which may be attributed to the loss of water due to the thermally activated cyclodehydration reaction leading to the *in-situ* formation of corresponding polyoxadiazole.[49-51]

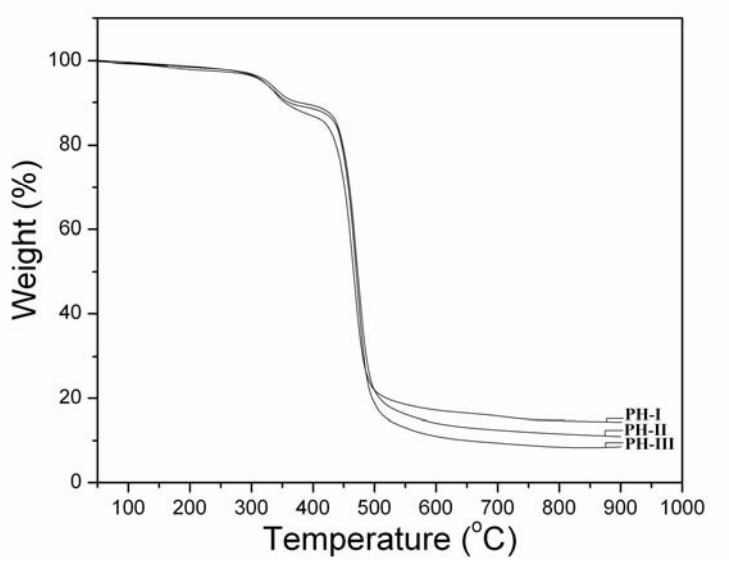


Figure 5b.4 TG curves of polyhydrazides derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides

Polyoxadiazoles showed degradation temperatures higher than corresponding polyhydrazides owing to the better thermal stability of 1,3,4-oxadiazole ring. T_{10} values obtained from TG curves for polyoxadiazoles were in the range of 433 to 449°C.

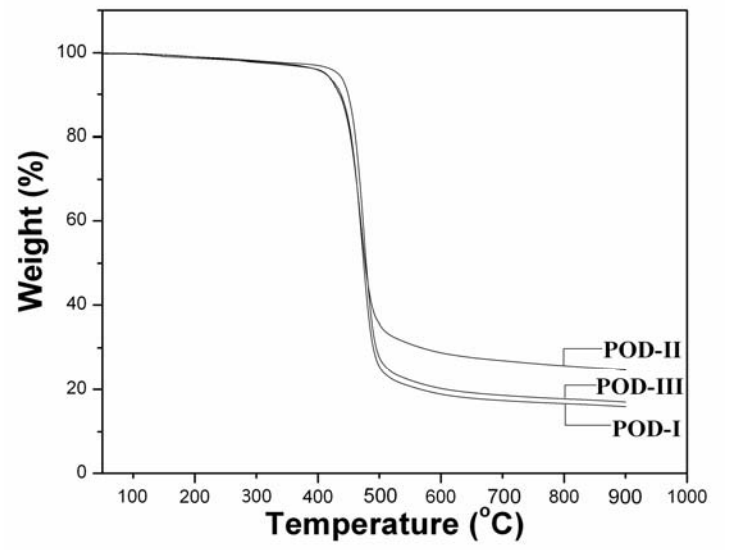


Figure 5b.5 TG curves of polyoxadiazoles

Glass transition (T_g) temperature of the polyhydrazides and polyoxadiazoles was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polymer samples at a heating rate of 10°C / minute. DSC curves for polyhydrazides and polyoxadiazoles are reproduced in **Figure 5b.6** and **5b.7** respectively, The glass transition temperature values are given in **Table 5b.4**.

Table 5b.4 Thermal properties of polyhydrazides and polyoxadiazoles derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide and aromatic diacid chlorides

Polymer	Diacylhydrazide	Diamine		T_0[a] (°C)	T_{10}[b] (°C)	Weight residue at 900°C (%)	T_g (°C)
		TPC	IPC				
PH-I	HPPB	100	0	300	-	15	166
PH-II	HPPB	0	100	298	-	09	143
PH-III	HPPB	50	50	303	-	11	148
POD-I	HPPB	100	0	395	435	16	102
POD-II	HPPB	0	100	383	433	25	90
POD-III	HPPB	50	50	404	449	17	100

a : Initial decomposition temperature,; *b* : temperature at which 10% weight loss is observed

DSC analysis revealed no melting transition for any samples, which agreed with the non-crystalline nature of the polymers. In all cases, it was possible to determine glass transition temperature. **(Table 5b.4**)

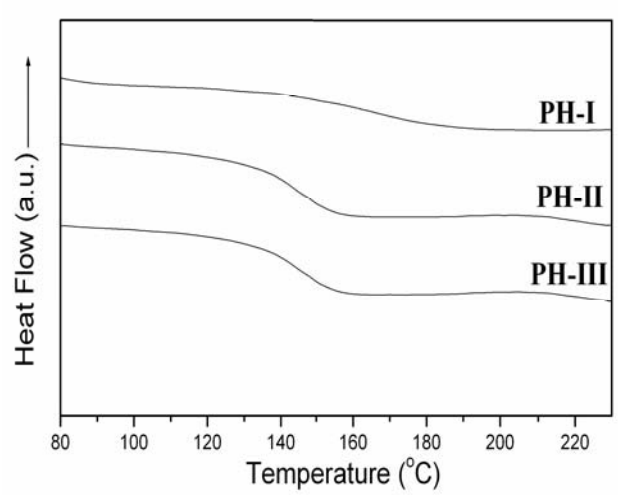


Figure 5b.6 DSC curves of polyhydrazides derived from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides

As shown in **Figure 5b.6**, the T_g's of polyhydrazides **PH-I, PH-II and PH-III** were 166, 143 and 148°C, respectively. It is well-known that T_g depends on the rigidity of the polymer main chain: the increase of the rigidity of the polymer increases the energy barriers for segmental motion, and hence T_g increases.[52] Polyhydrazide **PH-I** showed higher glass transition temperature among three polyhydrazides. This could be attributed to the rigid 1,4-phenylene unit in the polymer chain which induces rigidity in the polymer. While comparing the T_g data with those reported in literature, it was observed that, the polyhydrazide derived from 4,4'-oxybisbenzohydrazide and terephthalic acid chloride showed a glass transition at 196°C.[51] A drop in T_g values of polyhydrazides synthesized in the present study could be attributed to the internal plasticization effect of flexible pentadecyl

chains.

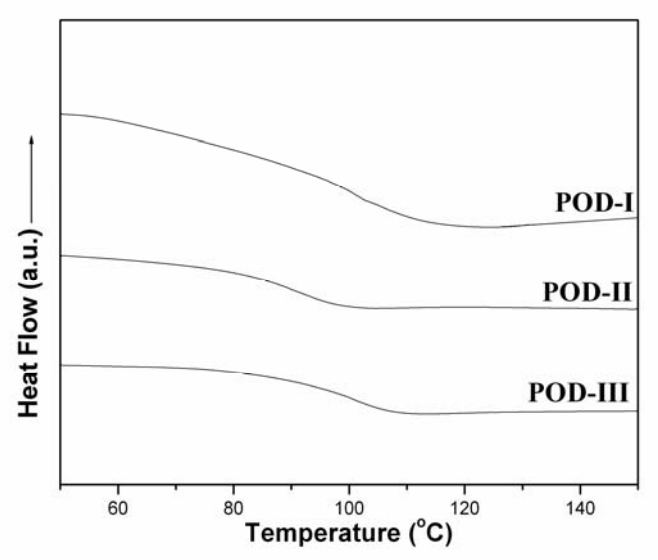


Figure 5b.7 DSC curves of polyoxadiazoles

The influence of the presence of 1,3,4-oxadiazole unit in the polymer backbone on thermal transitions was evaluated. **(Figure 5b.7)** It was observed that, the glass transition temperatures of derived polyoxadiazoles were lower than parent polyhydrazides. In spite of having rigid 1,3,4-oxadiazole repeat unit in the polymer chain, T_g values observed were in the range 90-102°C. These results revealed that the glass transition for polyoxadiazoles is strongly dependent on flexible pentadecyl chain present in the polymer backbone, and this conclusion is in agreement with data reported in literature.[49] A large difference between glass transition (90-102°C) and initial decomposition temperature (383-404°C) was observed. This offers polyoxadiazoles a wide processing window.

5b.5 Conclusions

1. A series of new polyhydrazides containing pendant pentadecyl chains and ether moieties was synthesized from 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide and aromatic diacid chlorides.
2. Poly(1,3,4-oxadiazole)s were synthesized by chemical cyclodehydration of corresponding polyhydrazides using $POCl_3$ as a dehydrating reagent.
3. Medium to high molecular weight polyhydrazides and polyoxadiazoles were obtained as indicated by their inherent viscosities, which were in the range 0.53-0.66 dL/g and 0.49-0.53 dL/g, respectively.
4. Polyhydrazides exhibited excellent solubility in polar aprotic solvents such as DMAc, NMP, DMF and were also found to be soluble in solvents such as *m*-cresol. Most of the polyoxadiazoles showed solubility in less polar solvents, such as $CHCl_3$, DCM, THF, pyridine and *m*-cresol and also soluble in polar aprotic solvents such as DMAc, NMP, DMF upon heating.
5. WAXD data showed that polyhydrazides and polyoxadiazoles containing pendant pentadecyl chains and ether linkages were amorphous in nature. In the small-angle region, a strong reflection was observed for both polyhydrazides and polyoxadiazoles indicating formation of layered structure due to ordered packing of pentadecyl chains.
6. The T_{10} for polyhydrazides and polyoxadiazoles were in the range 349-362°C and 433-449°C, respectively, indicating good thermal stability of polymers.
7. Both in polyhydrazides and polyoxadiazoles, a decrease in glass transition temperature was observed due to internal plasticization effect of pentadecyl chains.

References

1 Frazer, A.H.; Reed, T.A. *J. Polym. Sci. Part C.* **1967**, 19, 89.

2 Yang, H.H. *Aromatic High-strength Fibers*, Wiley, New York, **1989**.

3 Maglio, G.; Palumbo, R.; Tortora, M.; Trifuoggi, M.; Varricchio, G. *Polymer* **1998**, 39, 6407.

4 Fitch, J.W.; Cassidy, P.E.; Weikel, W.J.; Lewis, T.M.; Trial, T.; Burgess, L.; March, J.L.; Glowe, D.E.; Rolls, G.C. *Polymer* **1993**, 34, 4796.

5 Yu, W.L.; Meng, H.; Pei, J.; Huang, W.; Li, Y.; Hegger, A.J. *Macromolecules* **1998**, 31, 4838.

6 Huang, W.; Meng, H.; Yu, W.L.; Pei, J.; Chen, Z.K.;, Lai, Y.H. *Macromolecules* **1999**, 32, 118.

7 Song, S.Y.; Jang, M.S.; Shim, M.K.; Hwang, D.H.; Zyung, T. *Macromolecules* **1999**, 32, 1482.

8 Hwang, S.W.; Chen, Y. *Macromolecules* **2002**, 35, 5428.

9 Kim, S.C.; Park, S.M.; Park, J.S.; Lee, S.J.; Jin, S.H.; Gal, Y.S.; Lee, J.W. *J. Polym. Sci. Polym. Chem*. **2008**, 46, 1098.

10 Ding, J.; Day, M. *Macromolecules* **2006**, 39, 6054.

11 Kim, J.J.; Kim, K.S.; Baek, S.; Kim, H.C.; Ree, M. *J. Polym. Sci. Polym. Chem*. **2002**, 40, 1173.

12 Acierno, D.; Amendola, E.; Bellone, S.; Concilio, S.; Iannelli, P.; Neitzert, H. C.; Rubino, A.; Villani, F. *Macromolecules* **2003**, 36, 6410.

13 Udayakumar, D.; John Kiran, A.; Adhikari, A. V.; Chandrasekharan, K.; Shashikala, H. D. *J. Appl. Polym. Sci.* **2007**, 106, 3033.

14 Lee, K.; Kim, H. J.; Cho, J. C.; Kim, J. *Macromolecules* **2007**, 40, 6457.

15 Hedrich, J.L. *Polymer* **1992**, 33, 3375.

16 Thaemlitz, C.J.; Weikeil, W.J.; Cassidy, P.E. *Polymer* **1992**, 33, 3278.

17 Hensema, E.R.; Sena, M.E.R.; Mulder, M.H.V.; Smolders, C.A. *J. Polym. Sci. Polym.Chem.* **1994**, 32, 527.

18 Saegusa, Y.; Iwasaki, T.; Nakamura, S. *Macromol. Chem. Phys.* **1997**, 198, 1799.

19 Maglio, G.; Palumbo, R.; Tortora, M.; Trifuoggi, M.; Varricchio, G. *Polymer* **1998**, 25, 6407.

20 Hsiao, S.H.; Yu, C.H. *J. Polym. Sci. Polym. Chem* **1998**, 36, 1847.

21 Dai, L.R.; He, M.S. *J. Polym. Sci. Polym. Chem* **1999**, 37**,** 1169.

22 Hsiao, S.H.; He, M.H. *Macromol. Chem. Phys*, **2001**, 202, 3579.

23 Janietz, S.; Anlauf, S. *Macromol. Chem. Phys*. **2002**, 203, 427.

24 Stern, R.; Ballauf, M.; Lieser, G.; Wegner, G. *Polymer* **1991**, 11, 2096.

24 Huang, W.; Yu, W.L.; Meng, H.; Pei, J.; Li, S.F.Y. *Chem. Mater*. **1998**, 10, 3340.

25 Caruso, U.; Pragliola, S.; Roviello, A.; Sirigu, A.; Lannelli, P. *Macromolecules* **1995**, 28, 6089.

26 Centore, R.; Roviello, A.; Sirigu, A. *Macromol. Chem. Phys*. **1994**, 195, 3009.

27 Kricheldorf, H.R.; Engelhardt, *J. Macromol. Chem. Phys*. 1993, 191, 5281.

28 Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; Pergamon Press: NewYork, 1989.

29 Shukla J.S.; Dixit, S.K. *Macromol. Sci. Chem*. **1990**, A27, 381.

30 Joseph, K. A.; Srinivasan, M. *Polym. Int*. **1993**, 32, 257.

31 Nanjan, M. J.; Jayaprakash, D. *J. Polym. Sci. Polym. Chem*. **1983**, 21, 1227.

32 Preston, J. *J. Polym. Sci. Polym. Chem.* 1966, 4, 529.

33 Balasubramanian, M.; Nanjan, M. J.; Santappa, M. *J. Appl. Polym. Sci*. **1982**, 27, 1423.

34 Ubale, V.P.; Patil, A.S.; Maldar, N.N. *Eur. Polym. J*., **2007**, 43, 1038.

35 Mandal, R.; Maiti, S. *Polym. Int*. **1997**, 44, 428.

36 Frazer, A. H. (to E. I. du Pont de Nemours & Co., Inc.), U.S. Patent 3,130,183, **1964**.

37 Frazer, A. H. (to E. I. du Pont de Nemours & Co., Inc.), U.S. Patent 3,238,183, **1966**.

38 Frazer, A. H.; Wallenberger, F. T. *J. Polym. Sci. Polym. Chem*. **1964**, 2, 1147.

39 Frazer, A. H.; Wallenberger, F. T. *J. Polym. Sci. Polym. Chem*. **1964**, 2, 1137.

40 Dobinson, F.; Pelezo, C. A. (to Monsanto Co.), U.S. Patent 3,926,887, **1975**.

41 Dobinson, F.; Pelezo, C. A.; Black, W. B.; Lea, K. R.; Saunders, J. H. *J. Appl. Polym. Sci*. **1979**, 23, 2189.

42 Mahadevan, V.; Padma, S.; Srinivasan, M. *J. Polym. Sci. Polym. Chem*. **1981**, 19, 1409.

43 Yamakazi, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. Polym. Chem*. **1975**, 13, 1373.

44 Higashi, F.; Ishikawa, M. *J. Polym. Sci. Polym. Chem*, **1980**, 18, 2905.

45 Morton, A.A.; Leitsinger, R.L.; *J. Am.Chem. Soc*. **1945**, 67, 1537.

46 Iwakura, Y.; Uno, K.; Hara, S. *J. Polym. Sci. Polym. Chem.* **1965**, A3, 45.

47 Frazer, A. H.; Wallenberger, F. T. *J. Polym. Sci. Polym. Chem*. **1964**, 2, 1157.

48 Schulze, B.; Bruma, L. *Adv. Mater*. **1997**, 9, 601.

49 Gillo, M.; Iannelli, P.; Laurienzo, P.; Malinconico, M.; Roviello, A.; Mormile, P.; Petti, L.; *Chem. Mater*. **2002**, 14, 1539.

50 Capitani, D.; Laurienzo, P.; Malinconico, M.; Proietti, N.; Roviello, A. *J. Polym. Sci. Polym. Chem*. **2003**, 41, 3916.

51 Shige, Z.; Burkhard, S.; Maria B.; Ludwig B. *Polym. Adv. Technol*. **1996**, 7, 879.

Chapter 6

Synthesis and Characterization of Polyesters and Polyethers

Chapter 6a

Synthesis and Characterization of (Co) Polyesters Based on 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

6a.1 Introduction

Aromatic polyesters are an important class of high performance polymers. High thermal stability, solvent resistance and good mechanical properties of these polymers makes them possible to meet the demands of the modern industry in the areas of aviation, automobile, electronics, etc.[1,2] However, most aromatic polyesters encounter processing difficulties due to their high glass transition temperatures or melting temperatures coupled with insolubility in common organic solvents.[3,4] Therefore, development of aromatic polyesters for high temperature applications with improved processability is an important goal. Several approaches have been implemented[5-35] to improve solubility and processability of aromatic polyesters. These include:

1. Insertion of flexible spacers in the polymer backbone;
2. Incorporation of bent or 'crank-shaft' units along the backbone;
3. Appending of bulky side groups or flexible side chains.

The incorporation of bulky pendant groups along the polymer backbone has been demonstrated to improve solubility of polyesters. This is due to disturbance in dense chain packing of the polymer chains by bulky pendant groups which, in turn, increases the free volume. Another approach of interest is introduction of flexiblizing linkages either in the backbone or as pendant groups, both of which lead to improved solubility/processability.[36-38] When the flexiblizing group is appended to the polymer chains it is referred to as an "internal plasticizer" which can also acts as a bound solvent.[36] The pendant flexibilizing groups affect the polymer properties leading to reduction in melt viscosity, lowering the temperature of second order transition (T_g) and elastic modulus.

A series of (co)polyesters was synthesized by polycondensation of bisphenol containing pendant flexible pentadecyl chain *viz*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane with aromatic diacid chlorides, *viz*, terephthalic acid chloride and isophthalic acid chloride.

(Co) polyesters were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, gel permeation chromatography, X-ray diffraction analysis, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The effect of pentadecyl chains on the polymer properties was investigated

6a.2 Experimental

6a.2.1 Materials

1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane (BHPE) was synthesized as described in **Chapter 3**. Terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) were synthesized from terephthalic acid and isophthalic acid, (both, received from Aldrich, USA), respectively using excess thionyl chloride in the presence of DMF as a catalyst and were purified by distillation under reduced pressure. 2,2-Bis(4-hydroxyphenyl)propane or (bisphenol-A or BPA) and benzyltriethylammonium chloride (BTEAC), both received from Aldrich, USA were used as received. Dichloromethane, received from S. D. Fine Chem., India was dried and distilled according

to the reported procedure.[39] The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[39]

6a.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in chloroform at 30±0.1°C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

Molecular weights of (co) polyesters were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 ml chloroform and filtered through 0.2 µ SS-filter.

FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker 200 and 400 MHz spectrometer at resonance frequency of 200 MHz for ^{1}H and 100 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 15 °C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

The solubility of (co) polyesters was determined at 3 wt.% concentration in various solvents at room temperature or on heating.

6a.3 Synthesis of (co) polyesters

6a.3.1 Synthesis of polyesters from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic diacid chloride

A representative procedure for the synthesis of (co)polyesters is given below:

Into a 100 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel were placed 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane (500 mg, 1 mmol) and 1M NaOH (1.95 mL). Thereafter, BTEAC (30 mg) was added to the reaction mixture and the reaction mixture was cooled to 10°C. A solution of terephthalic acid chloride (200

mg, 1 mmol) dissolved in dichloromethane (10 mL) was added in one lot to the reaction mixture and the mixture was stirred vigorously at 2000 rpm for 1 h. The aqueous layer was decanted and the organic layer was diluted with additional 15 mL of dichloromethane. The polymer solution was precipitated in excess methanol and the precipitated polymer was filtered and washed several times with water and then with methanol. The polymer was dried at 60^{o}C under reduced pressure for 48 h.

A similar procedure was followed for the synthesis of other polyesters.

6a.3.2 Synthesis of copolyesters from a mixture of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and BPA with terephthalic acid chloride

A representative procedure for synthesis of copolyesters is described below.

Into a 100 mL two-necked round bottom flask equipped with a high-speed mechanical stirrer and an addition funnel, were placed BPA (500 mg, 2.21 mmol), 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane (120 mg, 0.246 mmol) and 1M NaOH (4.80 mL). Thereafter, BTEAC (40 mg) was added to the reaction mixture and the reaction mixture was cooled to 10^{o}C. A solution of terephthalic acid chloride (500 mg, 2.456 mmol) dissolved in dichloromethane (20 mL) was added in one lot to the reaction mixture and the mixture was stirred vigorously at 2000 rpm for 1 h. The aqueous layer was decanted and the organic layer was diluted with additional 15 mL of dichloromethane. The polymer solution was precipitated in excess methanol, the precipitated polymer was filtered and washed several times with water and then with methanol and dried at 60^{o}C under reduced pressure for 48 h.

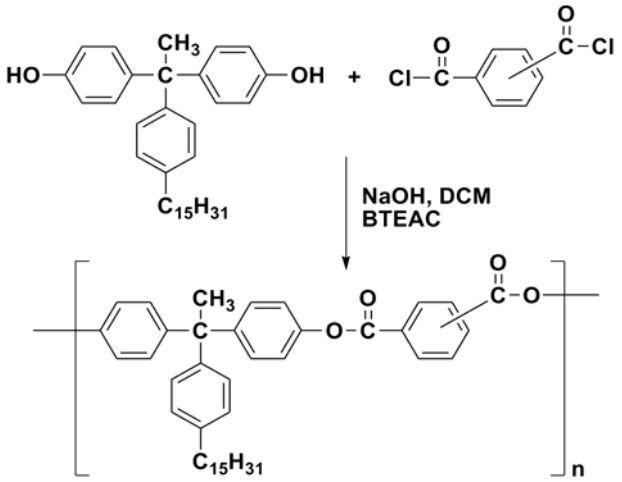
A similar procedure was followed for the synthesis of other copolyesters.

6a.4 Results and discussion

6a.4.1 Synthesis and characterization of (co) polyesters

Aromatic polyesters are well known for their high thermal stabilities and mechanical properties.[4,40-42] Different kinds of polyesters have been synthesized over the past decades from various diacid chlorides and diphenols.

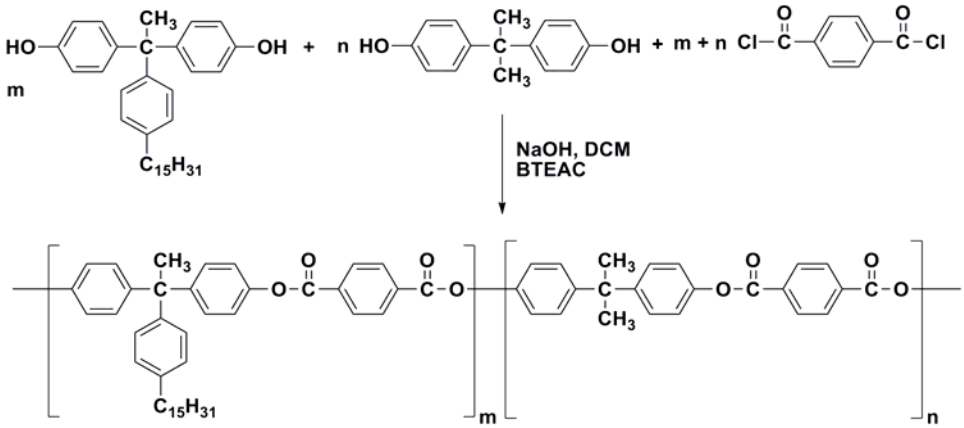
In the present study, polyesters and copolyesters containing pendant pentadecyl chains were synthesized in order to study the effect of incorporation of pentadecyl chains on the polymer properties. **Schemes 6a.1 and 6a.2** illustrate synthesis of (co) polyesters from bisphenols and aromatic diacid chlorides.



Scheme 6a.1 Synthesis of (co)polyesters from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl]ethane and terephthalic acid chloride and/ or isophthalic acid chloride

The interfacial polycondensation using phase transfer catalyst is a very effective method for the synthesis of aromatic polyesters.[43-47] In the present work, polyesters and copolyesters were synthesized by interfacial polycondensation with a solution of diacid chloride in dichloromethane and aqueous solution of sodium salt of bisphenols using BTEAC as the phase transfer catalyst.

Aromatic polyesters are difficult to process because of the rigid polymer backbone. Copolymerization is one of the most useful approaches for improving solubility and, in-turn, processability of polymers. Since bisphenol-A and TPC based polyester is insoluble in common organic solvents such as chloroform and dichloromethane, it was of interest to study the effect of incorporation of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane on the properties of polyester derived from bisphenol-A and TPC.



Scheme 6a.2 Synthesis of copolyesters from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and BPA with terephthalic acid chloride

Homopolymers from BPA-TPC and BPA-IPC as well as copolymer from BPA with TPC: IPC (50:50 mol %) were synthesized as reference materials. The results of polymerizations are

summarized in **Table 6a.1** and **6a.2.** Except to the polyesters **(PES-VII** and **PES-VIII)** rest of the polymerization reactions proceeded in a homogeneous manner and polyesters did not phase out of the reaction medium. Inherent viscosity (η_{inh}) of (co) polyesters was in the range 0.72-1.74 dL/g indicating formation of high molecular weight polymers.

Table 6a.1 Synthesis of (co) polyesters from bisphenol(s) and aromatic diacid chloride(s)

Polymer	Composition of Diols (mol%)		Diacid Chloride (mol%)		Yield (%)	η_{inh} (dL/g)[a]
	BHPE	BPA	TPC	IPC		
PES-I	100	0	100	0	95	0.91
PES-II	100	0	0	100	92	0.72
PES-III	100	0	50	50	94	0.75
PES-IV	15	85	100	0	92	1.65
PES-V	10	90	100	0	96	1.00
PES-VI	05	95	100	0	91	1.74
PES-VII	0	100	100	0	95	1.23[b]
PES-VIII	0	100	0	100	94	0.90[b]
PES-IX	0	100	50	50	95	1.46

a: η_{inh} was measured with 0.5% (w/v) solution of polyester in $CHCl_3$ at 30 ± 0.1°C.;
b: η_{inh} of polyester was measured with 0.5% (w/v) solution of polyester in phenol/ tetrachloroethane (60/40,w/w) at 30 ± 0.1°C

The results of GPC measurements on (co) polyesters are presented in **Table 6a.2.** Number average molecular weights (Mn) of (co) polyesters with flexible pentadecyl chains were in the range 64,390 to 186,520 with polydispersity index in the range 1.6 to 4.6.

Table 6a.2 GPC data for (co) polyesters derived from bisphenol (s) and aromatic diacid chloride (s)

Polymer	Composition of Diol		Diacid Chloride		Molecular weight[a]		Polydispersity Index
	BHPE	BPA	TPC	IPC	M_n	M_w	M_w/M_n
PES-I	100	0	100	0	48,450	1,07,830	2.2
PES-II	100	0	0	100	38,590	91,750	2.3
PES-III	100	0	50	50	18,170	62,680	3.4
PES-IV	15	85	100	0	40,360	1,86,520	4.6
PES-V	10	90	100	0	23,130	64,390	2.7
PES-VI	05	95	100	0	87,220	1,48,230	1.6
PES-IX	0	100	50	50	1,33,810	2,17,490	1.6

a: measured by GPC in chloroform, polystyrene was used as a calibration standard

Inherent viscosity and GPC data indicated the formation of high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards.

Tough, transparent and flexible films of (co) polyesters **(PES-I to PES-VI and PES-IX)** could be cast from their solutions in chloroform.

6a.4.1.1 Structural Characterization

(Co) polyesters were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride is reproduced in **Figure 6a.1**. Ester carbonyl band was observed at 1741 cm^{-1}

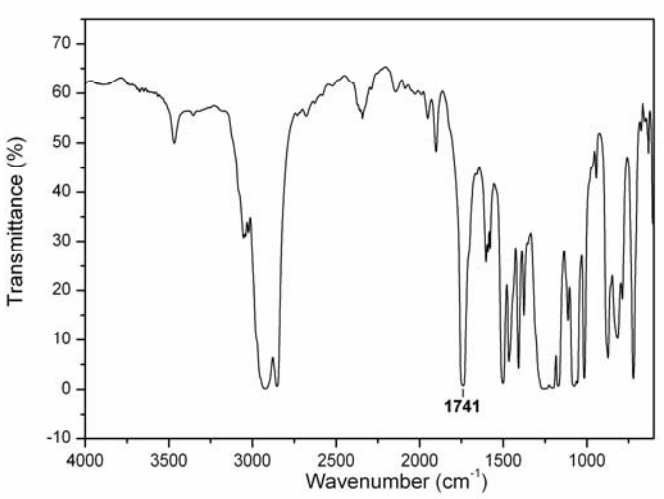


Figure 6a.1 FTIR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl]ethane and terephthalic acid chloride

^{1}H and ^{13}C-NMR spectra of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride along with assignments are shown in **Figure 6a.2** and **6a.3,** respectively.

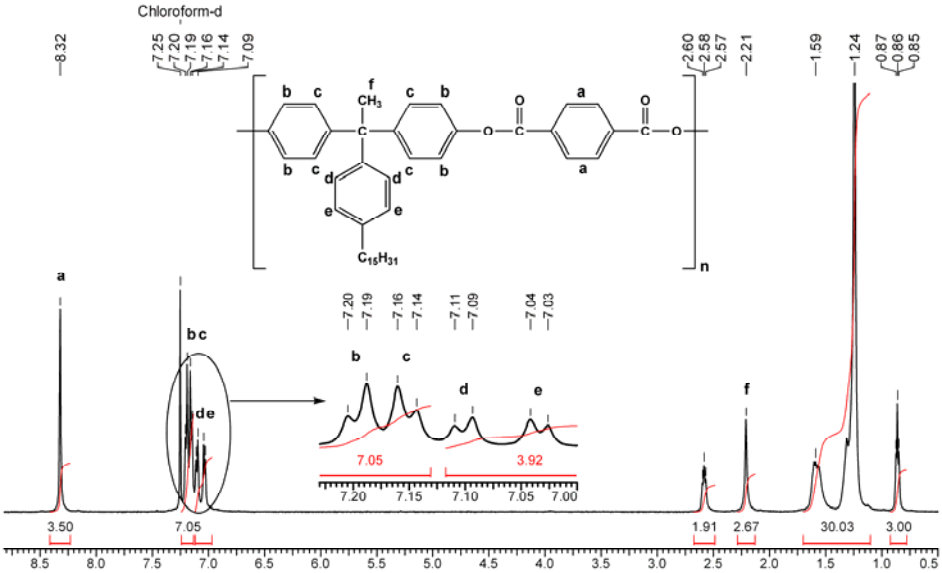


Figure 6a.2 ^{1}H-NMR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride in $CDCl_3$

^{1}H-NMR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride **(PES-I)** showed the presence of a singlet at 8.32 δ ppm for terephthalic acid ring protons indicating that all the four protons of terephthalic acid moiety are magnetically equivalent. Aromatic protons of bisphenol exhibited multiplet in the range 7.01-7.22 δ ppm. The methyl protons attached to the quaternary carbon of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane appeared as a singlet at 2.21 δ ppm. The benzylic $-CH_2$ appeared as a triplet at 2.58 δ ppm. The methylene protons β to aromatic ring exhibited a triplet at 1.59 δ ppm. The other methylene protons displayed a multiplet over the range 1.22-1.26 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.86 δ ppm.

^{13}C-NMR spectrum **(Figure 6a.3)** of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride **(PES-I)** exhibited a peak at 164.29 δ ppm corresponding to ester carbonyl carbon.

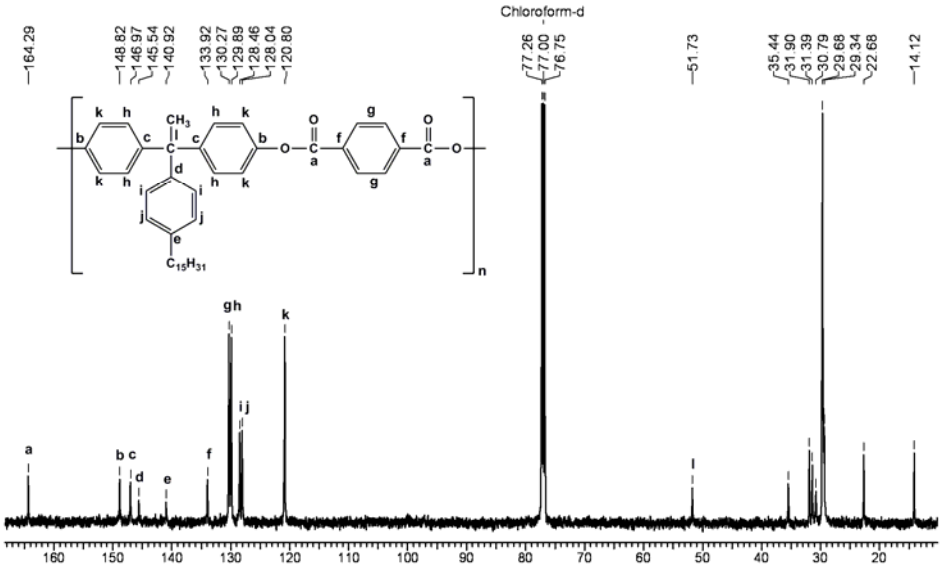


Figure 6a.3 ^{13}C-NMR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride in $CDCl_3$

^{1}H-NMR and ^{13}C-NMR spectra of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and isophthalic acid chloride **(PES-II)** along with assignments are reproduced in **Figure 6a.4 and 6a.5,** respectively.

Three different types of protons a, b and c can be distinguished for isophthalic moiety in ^{1}H-NMR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and isophthalic acid chloride. The most deshielded proton 'a' is located at 8.99 δ ppm as a singlet. The magnetically equivalent protons 'b' exhibited doublet at 8.43 δ ppm. Triplet at 7.66 δ ppm was observed for proton 'c'.

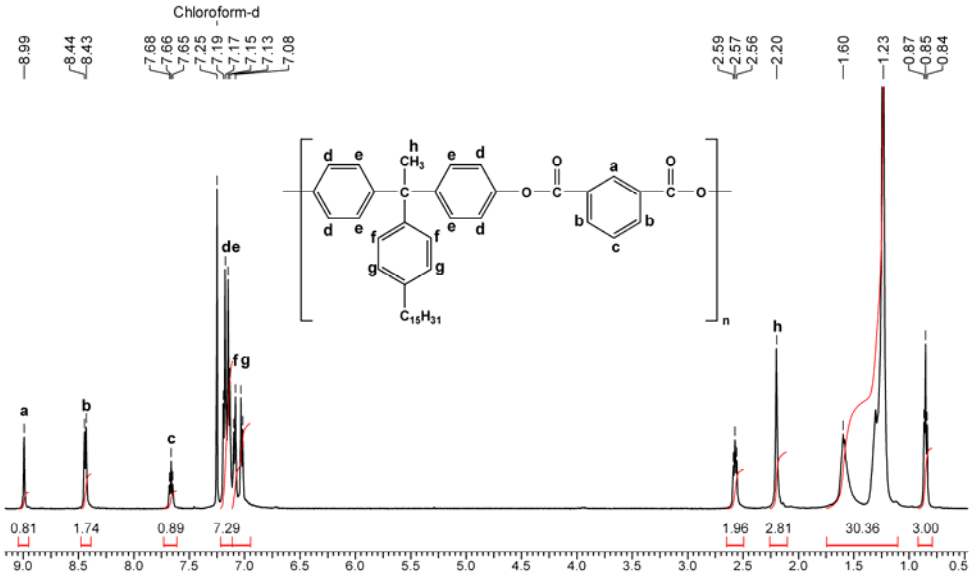


Figure 6a.4 ^{1}H-NMR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and isophthalic acid chloride in $CDCl_3$

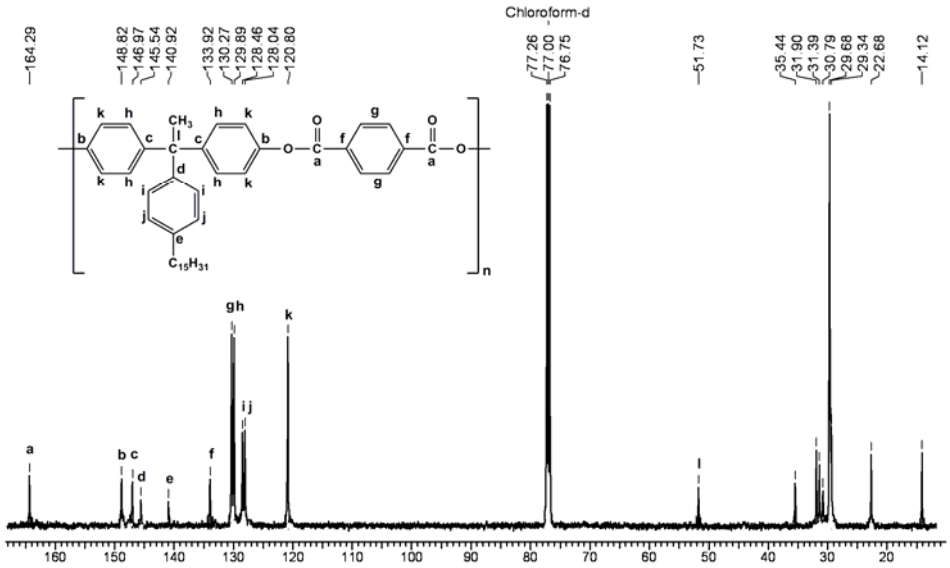


Figure 6a.5 ^{13}C-NMR spectrum of polyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and isophthalic acid chloride in $CDCl_3$

^{1}H-NMR and ^{13}C-NMR spectra of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and mixture of terephthalic acid chloride and isophthalic acid chloride **(PES-III)** alongwith assignments are shown in **Figure 6a.6** and **6a.7,** respectively.

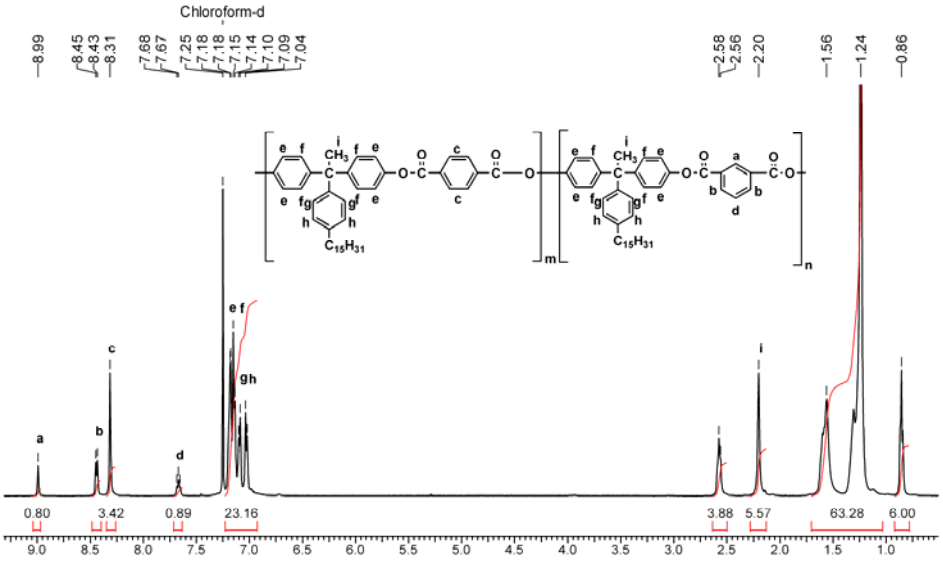


Figure 6a.6 ^{1}H-NMR spectrum of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and a mixture of terephthalic acid chloride and isophthalic acid chloride in $CDCl_3$

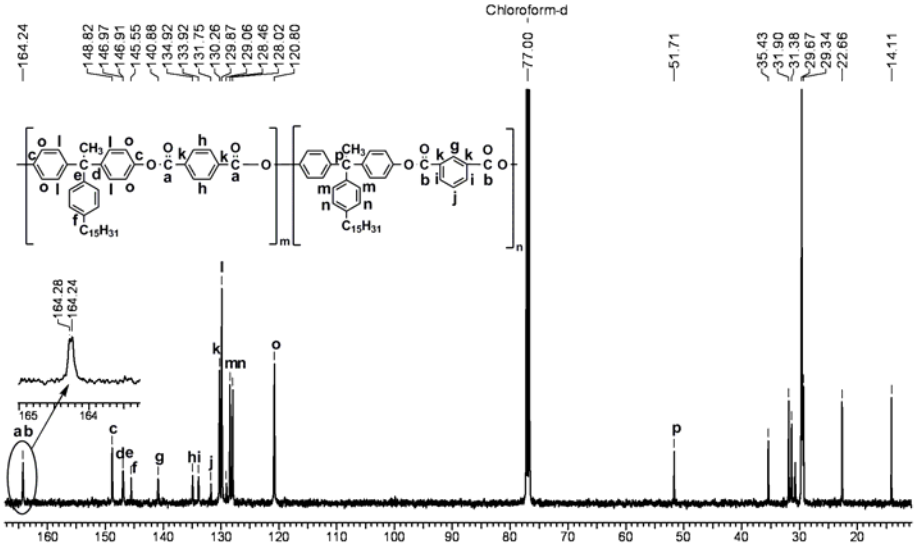


Figure 6a.7 ^{13}C-NMR spectrum of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and a mixture of terephthalic acid chloride and isophthalic acid chloride in $CDCl_3$

^{1}H-NMR and ^{13}C-NMR spectra of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and BPA with terephthalic acid chloride are shown in **Figure 6a.8** and **6a.9,** respectively. The compositions of copolyesters were determined by ^{1}H-NMR spectroscopy. **(Figure 6a.8)** For calculating the composition of copolyester, the integration of terephthalic ring protons were compared with that of the three methyl group protons present in the pentadecyl chain at δ 0.86 ppm. The integrated intensity ratio of these peaks was used to determine the amount of and

BPA present in copolyesters. There was reasonably good agreement between the observed incorporation of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and the amount taken for polymerization **(Table 6a.3).**

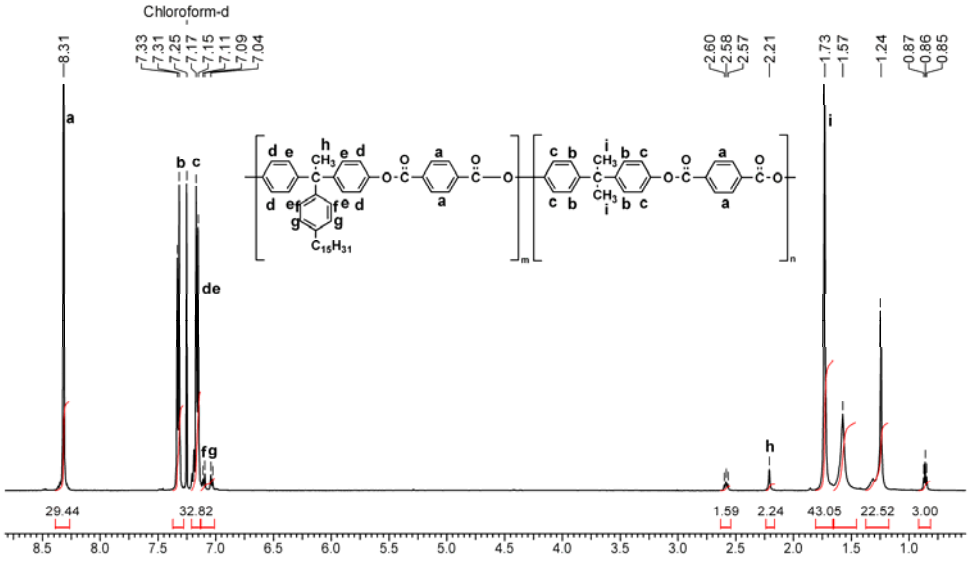


Figure 6a.8 ^{1}H-NMR spectrum of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and BPA with terephthalic acid chloride in $CDCl_3$ (PES-V)

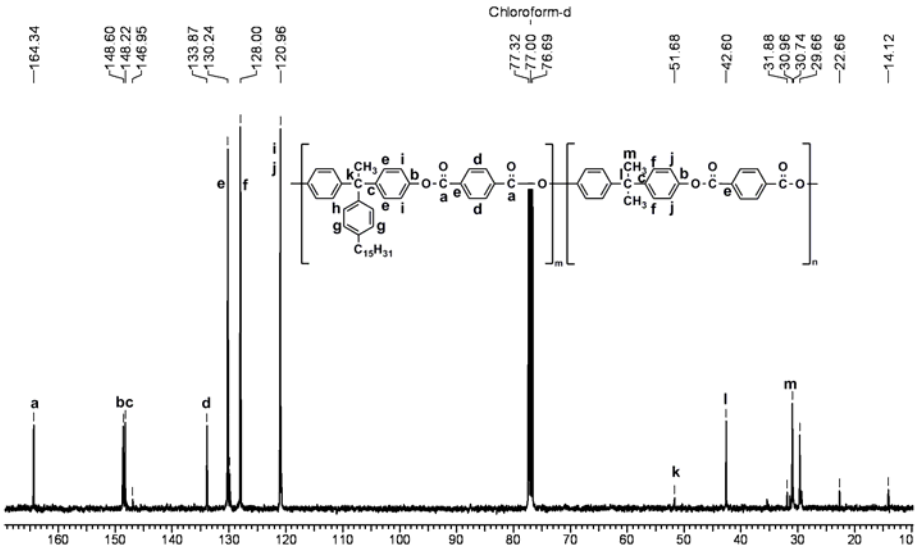


Figure 6a.9 ^{13}C-NMR spectrum of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and BPA with terephthalic acid chloride in $CDCl_3$ (PES-V)

Table 6a.3 Copolyester composition determined from ^{1}H-NMR spectra

Copolyester	Observed BHPE, mol%	Feed BHPE, mol%
PES-IV	12.2	15
PES-V	9.2	10
PES-VI	4.5	05

6a.4.1.2 Solubility measurements

Solubility of (co) polyesters was tested in various organic solvents at 3 wt % concentration and data is summarized in **Table 6a.4.**

Table 6a.4 Solubility data of (co)polyesters from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and/ or BPA and reference polyesters based on BPA

Polymer	Composition of diol		Diacid Chlorides										
	BHPE	BPA	TPC	IPC	$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
PES-I	100	0	100	0	++	++	++	+-	+-	+-	++	++	+0
PES-II	100	0	0	100	++	++	++	+-	+-	+-	++	++	+-
PES-III	100	0	50	50	++	++	++	+-	+-	+-	++	++	+-
PES-IV	15	85	100	0	++	++	+0	--	--	--	+-	++	--
PES-V	10	90	100	0	++	++	+0	--	--	--	+-	++	--
PES-VI	05	95	100	0	++	++	+0	--	--	--	+0	++	--
PES-VII	0	100	100	0	--	--	--	--	--	--	--	--	--
PES-VIII	0	100	0	100	--	--	--	--	--	--	--	--	--
PES-IX	0	100	50	50	++	++	++	--	++	++	++	++	--

++ : soluble at room temperature; +- : soluble on heating; +0 : partially soluble on heating; -- : insoluble

Polyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane with aromatic diacid chlorides were readily soluble in common organic solvents such as DCM, chloroform, tetrahydrofuran, *m*-cresol, pyridine and were also found to be soluble upon heating in aprotic polar solvents such as NMP, DMAc and DMF. In contrast, it was observed that polyesters based on BPA with TPC **(PES-VII)** and IPC **(PES-VIII)** showed insolubility in common organic solvents. This result indicates that the incorporation of pendant phenyl ring with pentadecyl chain in the polyester backbone enhanced the solubility of polyesters. This is due to the disturbance in the dense chain packing of the polymer by the pendent groups, which, in turn, facilitates the penetration of the solvent molecules resulting in improved solubility. Additionally, the presence of pentadecyl chains provided the 'handle' for interaction with solvents.

Copolyesters of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and BPA with terephthalic acid chloride were found to be soluble in common organic solvents such as, chloroform, DCM, *m*-cresol at room temperature or upon heating. The systematic incorporation study of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane showed that incorporation of even 5 mol% of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane was sufficient to impart solubility to copolyesters in common organic solvents.

6a.4.1.3 X-Ray diffraction studies

X-Ray diffraction patterns of (co) polyesters derived from bisphenols with aromatic diacid chlorides are shown in **Figure 6a.10.**

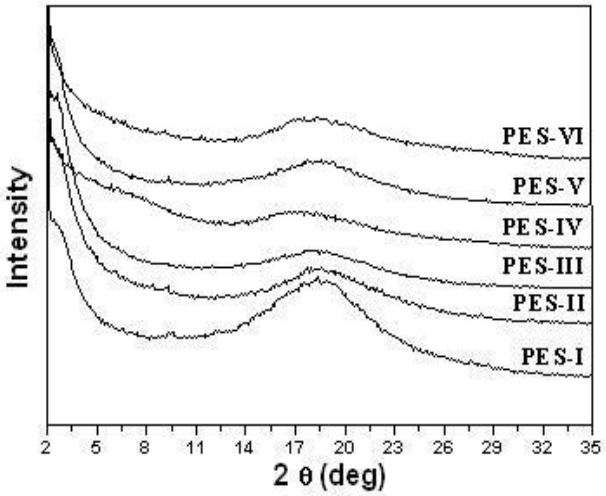


Figure 6a.10 X-Ray diffractograms of (co) polyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic diacid chlorides

X-Ray diffraction patterns **(Figure 6a.10)** for polyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and terephthalic acid chloride/ isophthalic acid chloride **(PES-I, PES-II** and **PES-III)** exhibited broad halo at around 2θ = ~ 19^{o} which could be mainly because of the presence of long pentadecyl chain, which hinders the packing of the polymer chains making them amorphous. This was reflected in their improved solubility in common organic solvents.

X-Ray diffraction patterns of copolyesters derived from BPA and 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane with terephthalic acid chloride **(PES-IV to PES-VI)** are shown in **Figure 6a.10**. It is known that, polyester derived from BPA and terephthalic acid chloride **(PES-VII)** is partially crystalline in nature. Copolyesters derived in the present study with varying mol % incorporation of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane showed broad halo at about 2θ = ~19^{o} in the wide angle region. This clearly indicates that the pendant phenyl ring with attached pentadecyl chain is responsible for disrupting chain regularity and packing in case of copolyesters.

In the small-angle region at around 2θ = ~ 3^{o}, a broad reflection was observed which could be attributed to formation of layered structure due to the packing of pentadecyl chains. Similar observations have been reported for other rigid rod polymers having long flexible side chains.[48-51]

6a.4.1.4 Thermal properties

In the present study, thermal stability of polyesters and copolyesters was determined by thermogravimetric analysis (TGA) at a heating rate of 15^{o}C /minute under nitrogen. Thermogravimetric (TG) curves of (co)polyesters are shown in **Figure 6a.11**. The initial decomposition temperature (IDT), the temperature at 10% weight loss (T_{10}) and the weight residues at 900^{o}C for (co) polyesters are given in **Table 6a.5**.

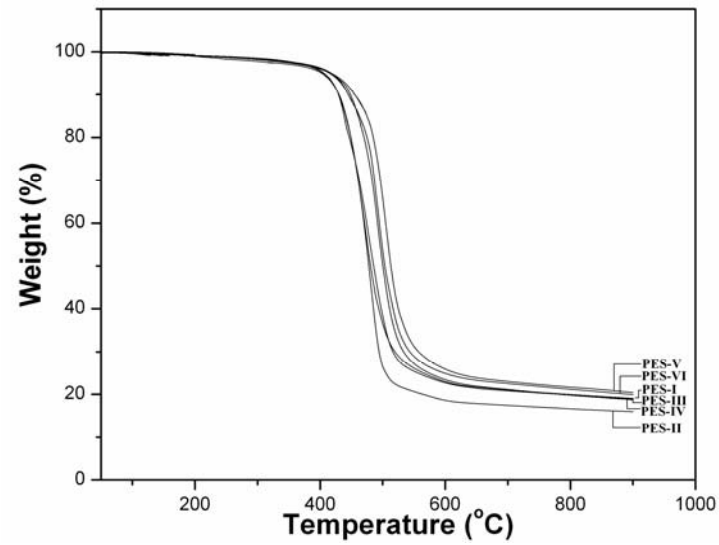


Figure 6a.11 TG curves (co) polyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic diacid chlorides

T_{10} values obtained from TG curves for homopolyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic diacid chlorides were in the range of 400 to 406°C indicating their good thermal stability. T_{10} values for copolyesters containing 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and BPA were in the range 443-460°C.

Table 6a.5 Thermal properties of (co) polyesters derived from bisphenols and aromatic diacid chlorides

Polymer	Composition of Diol		Diacid Chloride		T_0[a] (°C)	T_{10}[b] (°C)	Weight residue at 900°C (%)	T_g (°C)
	BHPE	BPA	TPC	IPC				
PES-I	100	0	100	0	370	406 (533)[c]	19	82 (244)[c]
PES-II	100	0	0	100	368	400 (525)[c]	16	63 (213)[c]
PES-III	100	0	50	50	373	401	19	65
PES-IV	15	85	100	0	393	443	18	177
PES-V	10	90	100	0	416	460	21	179
PES-VI	05	95	100	0	417	458	20	183
PES-VII	0	100	100	0	487	495	29	210
PES-VIII	0	100	0	100	475	490	29	181
PES-IX	0	100	50	50	491	501	-	197

a : Initial decomposition temperature; *b* : temperature at which 10% weight loss is observed, *c* : thermal values observed for 1,1-bis(4-hydroxyphenyl)-1-phenylethane- based polyesters.[52]

Glass transition (T_g) temperature of the (co) polyesters was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polymer samples at a heating rate of 10°C / minute. DSC curves for polyesters and copolyesters are reproduced in **Figure 6a.12** and **6a.13,** respectively. The glass transition temperature values are given in **Table 6a.5**.

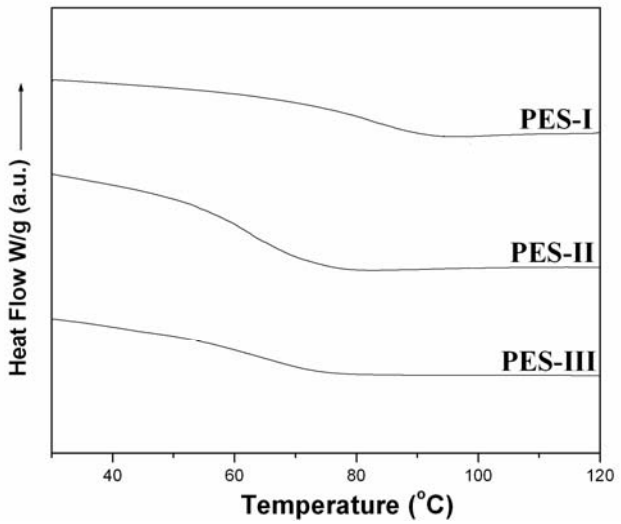


Figure 6a.12 DSC curves of (co)polyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic diacid chlorides

T_g values of polyesters derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl]ethane with terephthalic acid chloride and isophthalic acid chloride were 82 and 63°C, **(Figure 6a.12)** respectively. T_g value of copolyester derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane with mixture of terephthalic acid chloride and isophthalic acid chloride was 65°C **(Figure 6a.12).** A comparison of data with literature values of polyesters from acetophenone based bisphenol "1,1-bis(4-hydroxyphenyl)-1-phenylethane" (Bisphenol AP)[52] indicates that there is remarkable drop in glass transition temperature of polyesters by the incorporation of long pentadecyl chain. The incorporation of long pentadecyl chain as a pendant group could act as an "internal plasticizer" which is responsible for reduction of T_g of polyesters.

Copolyesters obtained from a mixture of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl]ethane and BPA with terephthalic acid chloride **(Figure 6a.13)** showed glass transition temperature values in the range 177-183 °C. It was observed that, T_g of copolyesters decreases with the increase in the 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl]ethane content. This is mainly due to the presence of pentadecyl chain, which could act as an "internal plasticizer" and increases the chain mobility thus decreasing T_g of copolyesters.

A large difference between glass transition (63-183°C) and initial decomposition temperature (368-417°C) was observed. This offers (co)polyesters a wide processing window.

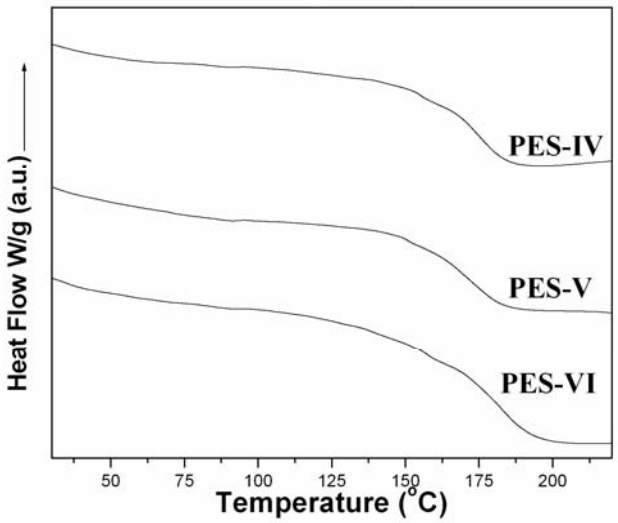


Figure 6a.13 DSC curves of copolyesters derived from varying mixture of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl]ethane and BPA with terephthalic acid chloride

6a.5 Conclusions

1. A series of (co) polyesters containing pendant pentadecyl chains was synthesized from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and aromatic diacid chlorides by phase-transfer catalysed interfacial polycondensation method.
2. A series of copolyesters was synthesized from a mixture of 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and BPA with terephthalic acid chloride.
3. Polyesters and copolyesters with inherent viscosities in the range 0.72-1.74 dL/g were obtained indicating formation of high molecular weight polymers.
4. (Co) polyesters were found to be soluble in chloroform, dichloromethane, pyridine, *m*-cresol, etc.
5. Tough, transparent and flexible films could be cast from solutions of polyesters and copolyesters in chloroform.
6. WAXD patterns showed that polyesters and copolyesters containing pendant pentadecyl chain were amorphous in nature. Layered structure formation was observed due to the packing of pentadecyl chains in the polymer backbone.
7. T_{10} values for polyesters and copolyesters were in the range 400-460^{o}C indicating their good thermal stability.
8. A drop in T_g values (63-183^{o}C) of polyesters and (co) polyesters was observed due to the internal plasticization effect of pentadecyl chains.

References

1. Arroyo. M. in *Handbook of Thermoplastics*, Olabisi,O., Ed., Marcel Dekker Inc.: New York, **1997,** pp 599.
2. Arroyo. M. in *Handbook of Thermoplastics*, Olabisi,O., Ed., Marcel Dekker Inc.: New York, **1997,** pp 599.
3. Vinogradova, S.V.; Vasnev, V.A.; Valetskii, P.M. *Russ. Chem. Rev.* **1994**, 63, 833.
4. Bier, G. *Polymer,* **1974**, 15, 127.
5. Korshak, V.V.; Vinogradova, S. V.; Vygodski, Y. S. *J. Macromol. Sci. Rev. Macromol. Chem.* **1974**, C11, 45.
6. Liaw, D.J.; Liaw, B.Y.; Hsu, J.J.; Chen, Y.C. *J. Polym. Sci. Polym. Chem.* **2000**, 38, 4451.
7. Hsiao, S. H.; Chiou, J. H. *Polym. J.* **2001**, 33, 95.
8. Chern, Y.T.; Huang, C.M. *Polymer* **1998**, 39, 2325.
9. Yerlikaya, Z.; Aksoy, S.; Bayramli, E. *J. Macromol. Sci. Pure Appl. Chem.* **2006**, 43, 433.
10. Bruma, M.; Fitch, J.W.; Cassidy, P.E. *J. Macromol. Sci.- Rev. Macromol. Chem. Phys.* **1996**, 36, 119.
11. Chern, Y.T. *Macromolecules* **1995**, 28, 5561.
12. Vibhute, S.S.; Joshi, M.D.; Wadgaonkar, P.P.; Patil, A.S.; Maldar, N.N. *J. Polym. Sci. Polym. Chem.* **1997**, 35, 3227.
13. Joshi, M.D.; Sarkar, A.; Yemul, O.S.; Wadgaonkar, P.P.; Lonikar, S.V.; Maldar, N.N. *J. Appl. Polym. Sci.* **1997**, 64, 1329.
14. Kane K.M.; Wels, L.A.; Cassidy, P.E. *High Perform. Polym.* **1991**, 3, 191.
15. Jeong, H. J.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci. Polym. Chem.* **1991**, 29, 1293.
16. Yang, C. P.; Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci. Polym. Chem.* **1990**, 28, 1353.
17. Imai, Y.; Tassavori, S.; *J. Polym. Sci. Polym. Chem.* **1984**, 22, 1319.
18. Naik, S.J.; Sarwade, B.D.; Wadgaonkar, P.P.; Mahajan, S.S. *Macromolecular Reports* **1995**, A 32, 1071.
19. Ehlers, G.F.L.; Evers, R.C.; Fisch, K.R. *J. Polym. Sci. Polym. Chem.* **1969**, 7, 3413.
20. Wang, H.; Shen, Z.; Cheng, S.Z.D.; Harris, F.W. *Polym. Prepr.* **1999**, 40, 88.
21. Kajiyama, M.; Kundo, J.; Mizumachi, H. *J. Polym. Sci. Polym. Chem.* **1999**, 37, 1135
22. Hsiao, S.H.; Chiang, H.W. *Eur. Polym. J.* **2004**, 40, 1691
23. Liu, B.; Dong, Y.; Hu, W.; Chen, C.; Wang, G.; Wu, Z. *Polym. Prepr*. **2000**, 41, 1268.
24. Tamami, B.; Yeganeh, H.; Kohmareh, G. *Eur. Polym. J.* **2004**, 40, 1651.
25. Liaw, D. J.; Liaw, B. Y.; Cheng, Y. C., Hsu, J. J. *J. Polym. Sci. Polym Chem*. **2000**, 38, 4451.
26. Jeong, H.J.; Iwasaki, K.; Kakimoto, M.; Imai, Y. *Polym. J.* **1994**, 26, 379.
27. Jeong, H. J.; Kakimoto, M.; Imai, Y. *J. Polym. Sci. Polym. Chem.* **1991**, 29, 1293.
28. Watanabe, S.; Murayama, H.; Murata, M.; Tanabe, M.; Imai, Y. *J. Polym. Sci. Polym. Chem*. **1998**, 36, 2229.
29. Watambe, S.; Kobayashi, A.; Kakimoto, M.; Imai.; Y. *J. Polym. Sci. Polym. Chem*. **1994**, 32, 909.
30. Morgan P. W. U. S. Patent 3546165, **1970.**
31. Nurmukhametov, F. N.; Askadskii, A. A.; Slonimskii, G. L.; Korshak, V. V.; Salazskin, S. N.; Vygodskii, Y. S, Vinogradova, S. V. *Polym. Sci. USSR* **1976**, 18, 922.
32. Shingate, R. D.; Thesis submitted to University of Pune, **2006.**
33. Jager, J.; Hendriks, A. J., *J. Appl. Polym. Sci*. **1995**, 58, 1465.
34. Loria-Bastarrachea, M.I.; Vazquez -Torres, H.; Aguilar–Vega, M.; de J. *J. Appl. Polym. Sci.* **2002**, 86, 2515.
35. a) Morgan, P. W. *Macromolecules* **1970**, *3*, 536. b) Morgan, P. W. U.S.Patent 3546165, **1970.**

36. Bicerano, J., *Prediction of Polymer Properties*; Marcel Dekker Inc.: New York, **1996**.
37. Mellan, I, *The Behavior of Plasticizers*; Pregamon Press: New York, **1961**.
38. Sears, J.K.; Darby, J.R. *The Technology of Plasticizers*; John Wiley and Sons: New York, **1981**.
39. Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, **1989**.
40. Rogers, M.E.; Long, T.E. *Synthetic Methods in Step Growth Polymers*, Eds. John Wiley and Sons : New York , **2003**.
41. Critchley, J. P.; Knight, G. J.; Wright,W. W. *Heat Resistant Polymers: Technologically Useful Materials*, Plenum Press: New York, **1983**.
42. Cassidy, P. A. *Thermally Stable Polymers*, New York: Dekker, **1980.**
43. Hsiao, S.H.; Chang, H.Y. *J. Polym. Res.* **1995**, 2, 99.
44. Imai, Y.; Tassavori, S.; *J. Polym. Sci. Polym. Chem.* **1984**, 22, 1319.
45. Morgan P. W., *Condensation Polymers by Interfacial and Solution Methods*, Wiley Interscience: New York, **1965**.
46. Hsiao, S.H.; Chang H.Y. *J. Polym. Res*. **1995**, 2, 99.
47. Villegas-Coss, I.; Ruiz-Trevino, F.A.; Hernandez-Lopez, S. *J. Polym. Sci. Polym. Phys*. **2006**, 44, 256.
48. Lee, S. J.; Jung, J. C.; Lee, S. W.; Ree, M. *J. Polym. Sci. Polym. Chem*. **2004**, 42, 3130.
49. Duran, R.; Ballauff, M.; Wenzel, M.; Wegner, G. *Macromolecules* **1988**, 21, 2897.
50. Chen, Y.; Wombacher, R.; Wendorff, J. H.; Greiner, A. *Polymer* **2003**, 44, 5513
51. Shi, H.; Zhao, Y.; Zhang, X.; Zhou, Y.; Xu, Y.; Zhou, S.; Wang, D.; Han, C. C.; Xu, D. *Polymer* **2004**, 45, 6299
52. Hsiao, S.H.; Chiang, H.W. *J. Polym. Res*. **2005**, 12, 211.

Chapter 6b

Synthesis and Characterization of Polyethers Based on

i) 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

ii) 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane

6b.1 Introduction

Poly(arylene ether)s are a class of high performance thermoplastics known for their unique combination of attractive chemical, physical and mechanical properties. High thermal stability, mechanical properties, resistance to mineral acids, solvents and oxidative degradation at elevated temperatures of these polymers makes them to be widely used in aerospace, automobile, medical devices, food processing, gas separation membranes, fuel cell, ultra filtration and electronic industries.[1-21]

Poly(arylene ether)s are usually prepared by nucleophilic displacement or Friedal-Crafts acylation.[2,3,22,23] The electrophilic route using Friedal-Crafts acylation has some limitations because of the mechanistic problems. The most common method used is the nucleophilic displacement of activated aromatic dihalides with alkali-metal bisphenoxides in polar aprotic solvents. The synthetic route involves generation of an ether linkage by nucleophilic aromatic substitution (S_NAr) as a polymer forming reaction and use of dihalide monomers. The best leaving group is fluorine but chlorine and nitro can be utilized as efficient leaving groups in some cases.[24-31]

In spite of their excellent performance, the processing and even the synthesis of poly(arylene ether)s especially PEEK has been restricted because of their low solubility in common organic solvents resulting from their high crystallinity. Many efforts have been expended towards the improvement of solubility and processibility of PEEK by the incorporation of *meta*-linkages, flexible linkages, or bulky groups.[32-46]

In continuation with our ongoing-efforts to synthesize processable high performance polymers, a series of poly(arylene ether)s viz; poly(ether ether ketone)s and poly(ether ether ketone ketone)s was synthesized by polycondensation of bisphenols *viz,*

1. 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane containing flexible pentadecyl chain, and
2. 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane containing cyclohexylidene moiety with flexible pentadecyl substituent.

with commercially available aromatic dihalide monomers *viz*; 4,4'-difluorobenzophenone and 1,3-bis(4–fluorobenzoyl)benzene.

In addition, a series of poly(ether ether sulfone)s was synthesized by polycondensation of above bisphenols with bis(4-fluorophenyl)sulfone.

Poly(arylene ether)s were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, gel permeation chromatography, X-ray diffraction, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

6b.2 Experimental

6b.2.1 Materials

1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane (BHPE) and 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane (BHPC) were synthesized as described in **Chapter 3**. 4,4'-Difluorobenzophenone (DFB) and 1,3-bis(4–fluorobenzoyl)benzene (BFB) (both received from Aldrich, USA) were recrystallised from toluene before use. Bis(4-fluorophenyl)sulfone (FPS) (Aldrich, USA) was used as received. Anhydrous potassium carbonate (S.D. Fine) was dried at 150°C for 24 h under reduced pressure. N,N-Dimethylacetamide (DMAc) was dried over calcium hydride and distilled under reduced pressure. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[47]

6b.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in chloroform at 30±0.1°C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

Molecular weights of poly(arylene ether)s were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column-polystyrene-divinylbenzene (10^5Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter.

FTIR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker 200 and 400 MHz spectrometer at resonance frequency of 200 MHz for ^{1}H and 100 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 15 °C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

X-Ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

The solubility of poly(arylene ether)s was determined at 3 wt.% concentration in various solvents at room temperature or on heating.

6b.3 Synthesis of poly(arylene ether)s

A representative procedure for the synthesis of poly(arylene ether)s is given below:

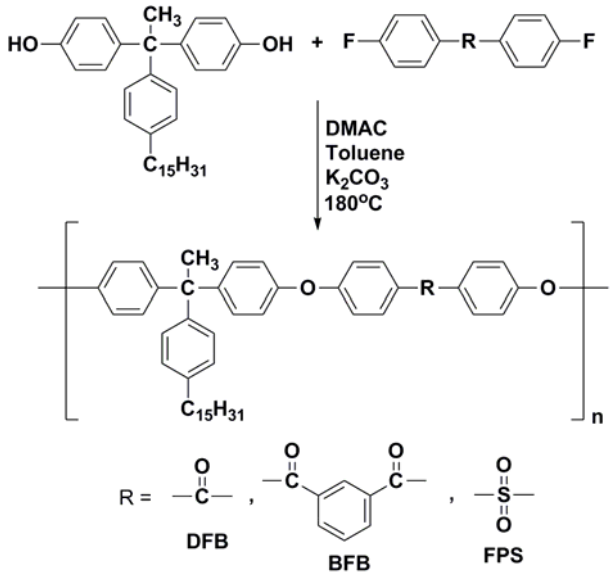
Into a 100 mL three necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube, a magnetic stirring bar and a Dean-Stark trap were charged 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane (500 mg, 1 mmol), 4,4'-difluorobenzophenone, (210 mg, 1 mmol), potassium carbonate (160 mg, 1.2 mmol), DMAc (10 mL) and toluene (10 mL). The reaction mixture was heated with stirring at 150°C for 3 h. Toluene was used to remove the water by azeotropic distillation. Toluene was removed after 3 h and temperature of the reaction mixture was raised to 180 °C and kept at that temperature for 3 h. The viscous reaction mixture was poured into methanol (100 mL); the precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and precipitated into methanol. The polymer was filtered, washed with methanol, and dried under reduced pressure at 80 ^{o}C for 24 h.

Similar procedure was followed for the synthesis of other poly(arylene ether)s.

6b.4 Results and discussion

6b.4.1 Synthesis and characterization of poly(arylene ether)s

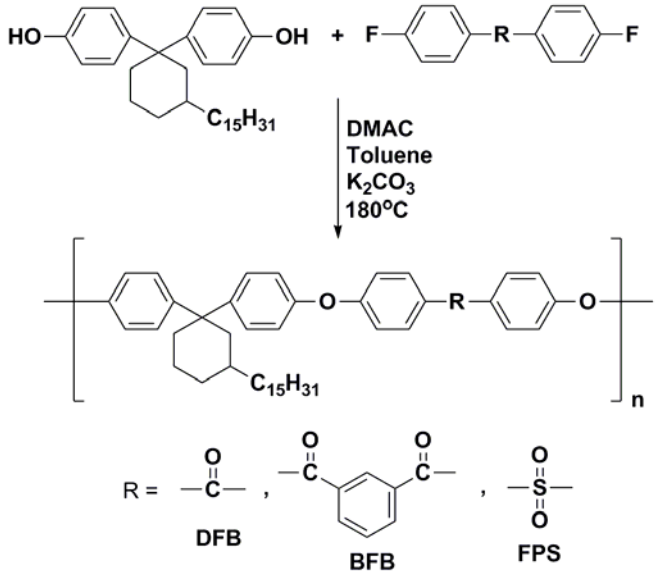
In the present study, two series of poly(arylene ether)s containing flexible pentadecyl chains **(Scheme 6b.1)** or cyclohexylidene moieties with pentadecyl chains **(Scheme 6b.2)** were synthesized. **Scheme 6b.1 and 6b.2** illustrates synthesis of poly(arylene ether)s.



Scheme 6b.1 Synthesis of poly(arylene ether)s from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecyl phenyl] ethane and aromatic dihalides

Poly(arylene ether)s are synthesized by nucleophilic substitution reaction of bisphenol and dihalide in the presence of potassium carbonate in a mixture of polar aprotic solvent and azeotropic

solvent such as toluene or chlorobenzene.[31]



Scheme 6b.2 Synthesis of poly(arylene ether)s from 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane and aromatic dihalides

The key factors playing important role in building molecular weight are monomer purity, removal of water formed during the reaction and type of the alkali ion used. It is very essential to remove the formed water during the polycondensation. The water formed as a result of polycondensation could potentially hydrolyze the fluoro groups and prevent formation of high molecular weight polymers. The expensive difluoro monomer is required rather than the less expensive dichloro-analogue because the weakly electron-withdrawing carbonyl group does not strongly activate the halogen to nucleophilic displacement and consequently a good leaving group is necessary for efficient reaction. Another factor to consider for nucleophilic reactions of this type is the alkali metal ion and the manner in which the bis-phenate salts are produced and utilized. The use of sodium salts tend to decrease the rate of reaction and side-reactions leads to the formation of gel. In practice, either potassium salt or a mixture of potassium and sodium salts is used.

Polymerization reactions were carried out in the presence of potassium carbonate in DMAc and toluene under conditions described in **Experimental Section**. The by-product water was removed from the reaction mixture by azeotropic distillation with toluene. Polymers were isolated by precipitating viscous reaction mixture in excess methanol.

The results of polymerization are presented in **Table 6b.1**. Poly(arylene ether)s were isolated as white fibrous materials with inherent viscosities (η_{inh}) in the range 0.64-1.27 dL/g indicating formation high molecular weight polymers. Tough, transparent and flexible films of poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane could be cast from their solutions in chloroform.

Table 6b.1 Synthesis of poly(arylene ether)s from bisphenols and aromatic dihalides

Polymer	Bisphenol	Dihalide	Yield (%)	η_{inh} (dL/g)[a]
PE-I	BHPE	DFB	96	1.07
PE-II	BHPE	BFB	93	0.70
PE-III	BHPE	FPS	95	0.64
PE-IV	BHPC	DFB	95	1.27
PE-V	BHPC	BFB	96	1.0
PE-VI	BHPC	FPS	92	1.12

a: η_{inh} was measured with 0.5% (w/v) solution of polyarylene ether in $CHCl_3$ at 30 ± 0.1°C

The results of GPC measurements on poly(arylene ether)s are presented in **Table 6b.2.**

Table 6b.2 GPC data for poly(arylene ether)s derived from bisphenols and aromatic dihalides

Polymer	Bisphenol	Dihalide	Molecular Weight[a]		Polydispersity Index M_w/M_n
			M_n	M_w	
PE-I	BHPE	DFB	1,14,070	2,43,530	2.1
PE-II	BHPE	BFB	76,620	1,70,100	2.2
PE-III	BHPE	FPS	59,600	2,19,770	3.6
PE-IV	BHPC	DFB	1,25,130	3,33,230	2.6
PE-V	BHPC	BFB	1,36,720	3,33,870	2.4
PE-VI	BHPC	FPS	2,36,550	5,66,010	2.4

a: measured by GPC in chloroform, polystyrene was used as the calibration standard

The results of GPC measurements on poly(arylene ether)s are presented in **Table 6b.2.** Number average molecular weights (M_n) of poly(arylene ether)s with flexible pentadecyl chain were in the range 59,596 to 1,14,070 with polydispersity index in the range 2.1 to 3.6 and poly(arylene ether)s with cyclohexylidene moiety had number average molecular weights (M_n) in the range 2,36,550 to 1,25,130 with polydispersity index in the range 2.4 to 2.6.

Inherent viscosity and GPC data indicated the formation of high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards.

6b.4.1.1 Structural Characterization

The chemical structure of the poly(arylene ether)s was confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of poly(ether ether ketone) **(PE-I)** derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 4,4,-difluorobenzophenone is reproduced in **Figure 6b.1**. A characteristic band of the carbonyl group at around 1656 cm^{-1} was observed in the FTIR spectrum.

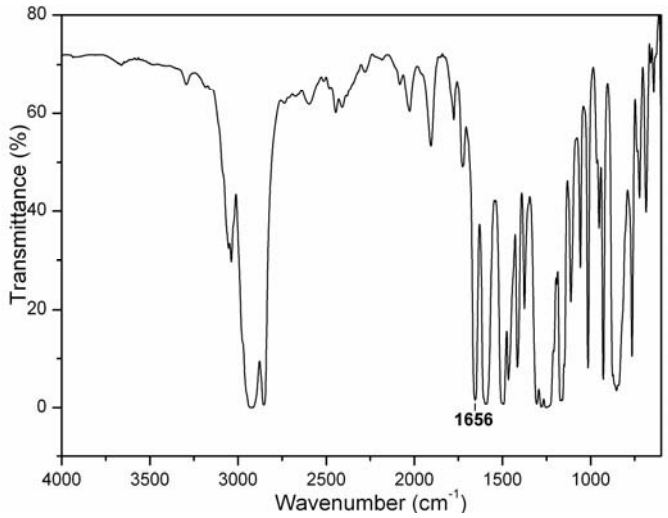


Figure 6b.1 FTIR spectrum of poly(ether ether ketone) derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 4,4'-difluorobenzophenone

FT-IR spectrum of poly(ether ether sulfone) obtained from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and bis(4-fluorophenyl)sulfone is reproduced in **Figure 6b.2.** The bands of the sulfone group appeared at 1327 cm^{-1} and 1156 cm^{-1} whereas band of the ether linkage appeared at 1247 cm^{-1}.

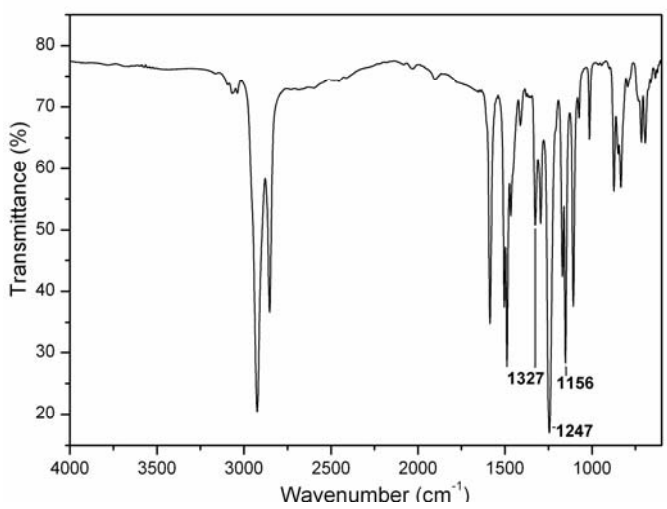


Figure 6b.2 FTIR spectrum of poly(ether ether sulfone) derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and bis(4-fluorophenyl)sulfone

^{1}H and ^{13}C-NMR spectra of poly(ether ether ketone) derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 4,4'-difluorobenzophenone along with assignments are shown in **Figure 6b.3** and **6b.4**.

A doublet at 7.78 δppm corresponds to four protons *ortho* to ketone group. Remaining sixteen aromatic protons appeared as a multiplet in the range 6.98-7.12 δ ppm. Methyl protons attached to a quaternary carbon appeared as a singlet at 2.18 δ ppm. The benzylic -CH_2 appeared as

a triplet at 2.57 δ ppm. The methylene protons β to aromatic ring exhibited a triplet at 1.61 δ ppm. The other methylene protons displayed a multiplet over the range 1.12-1.26 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.86 δ ppm.

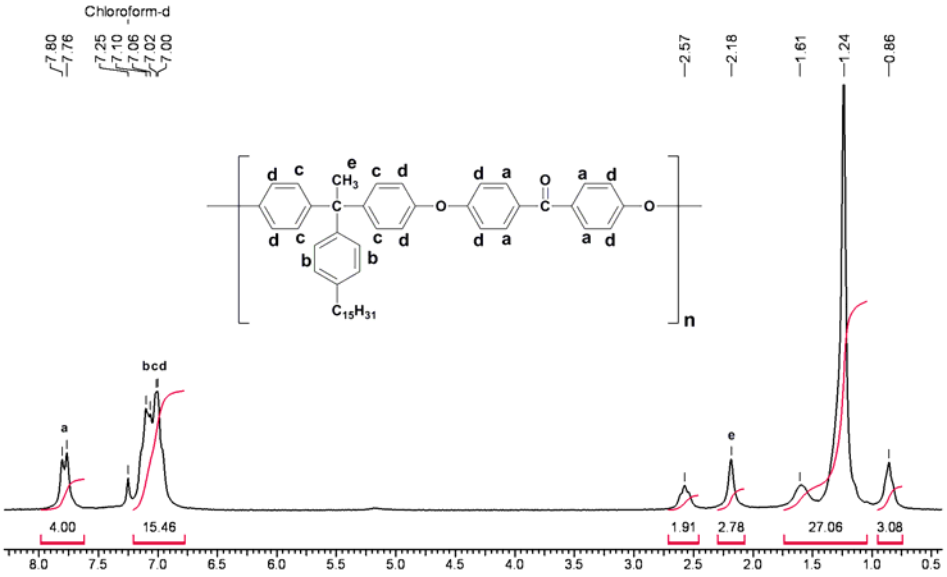


Figure 6b.3 ^{1}H-NMR spectrum of poly(ether ether ketone) derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 4,4'-difluorobenzophenone in $CDCl_3$

In ^{13}C-NMR spectrum of **PE-I (Figure 6b.4)**, carbonyl carbon shifted to most downfield region at δ 194.20 ppm.

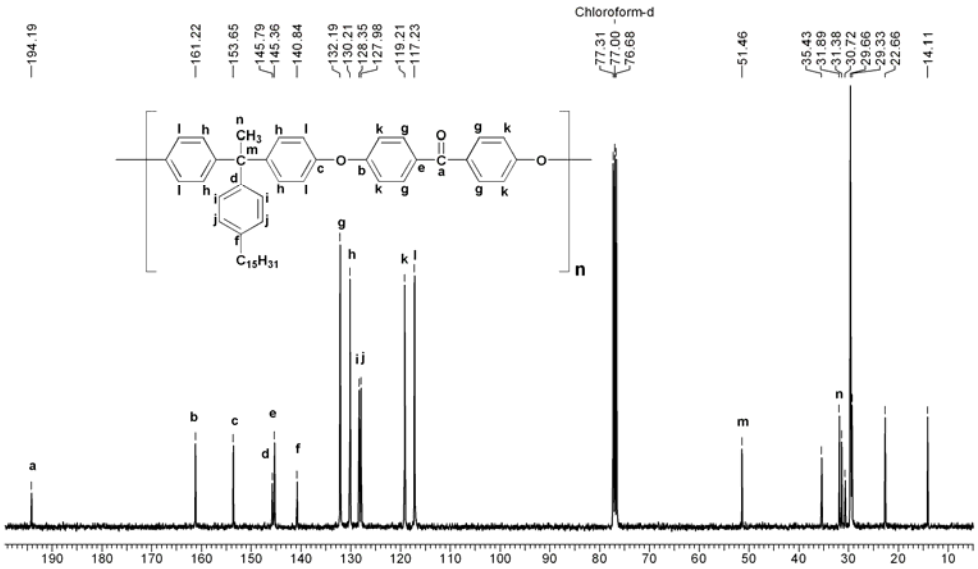


Figure 6b.4 ^{13}C-NMR spectrum of poly(ether ether ketone) derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 4,4'-difluorobenzophenone in $CDCl_3$

^{1}H and ^{13}C-NMR spectrum of poly(ether ether ketone ketone) **(PE-II)** derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 1,3-bis(4–fluorobenzoyl)benzene alongwith

assignments is shown in **Figure 6b.5** and **6b.6.**

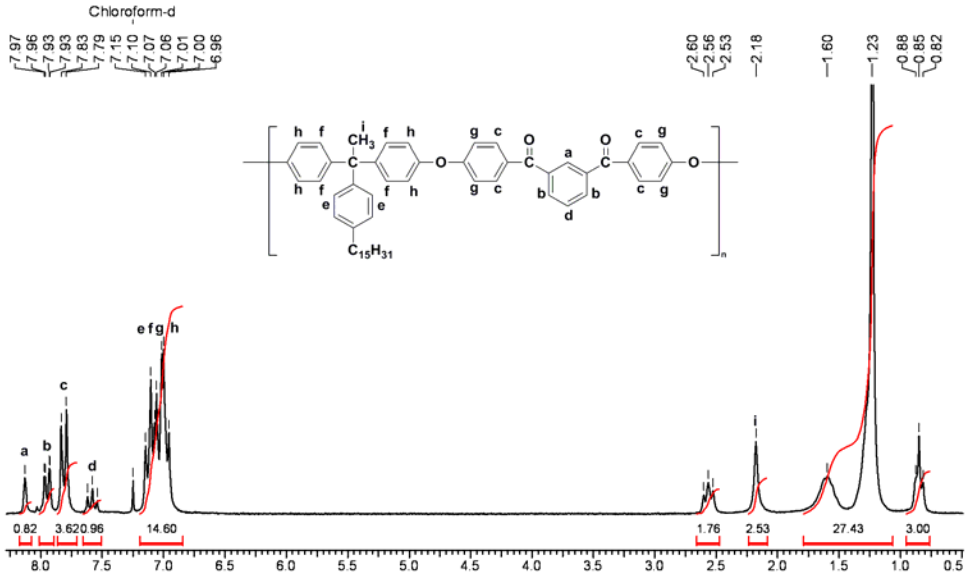


Figure 6b.5 ^{1}H-NMR spectrum of poly(ether ether ketone ketone) derived from 1,1,1-[bis(4-hydroxy phenyl)-4'-pentadecylphenyl]ethane and 1,3-bis(4–fluorobenzoyl)benzene in $CDCl_3$

A triplet at δ 7.96 ppm could be assigned to a proton 'a' flanked by two carbonyl groups. Protons 'b' appeared as doublet of doublet at 7.93 δ ppm, while proton 'd' exhibited a triplet at 7.55 δ ppm. The four aromatic protons 'c' *ortho* to carbonyl group appeared as a doublet at 7.81 δ ppm. Aromatic protons on bisphenol moiety appeared as a multiplet over the range 6.94-7.17 δ ppm.

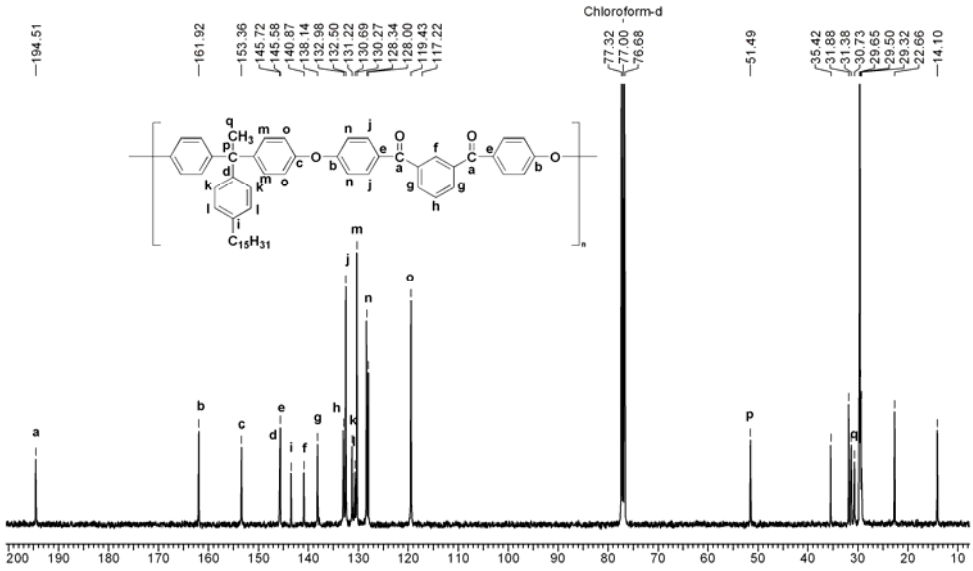


Figure 6b.6 ^{13}C-NMR spectrum of poly(ether ether ketone ketone) derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 1,3-bis(4–fluorobenzoyl)benzene in $CDCl_3$

^{1}H and ^{13}C-NMR spectra of poly(ether ether sulfone) **(PE-III)** derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and bis(4-fluorophenyl)sulfone alongwith assignments are shown in **Figure 6b.7** and **6b.8**.

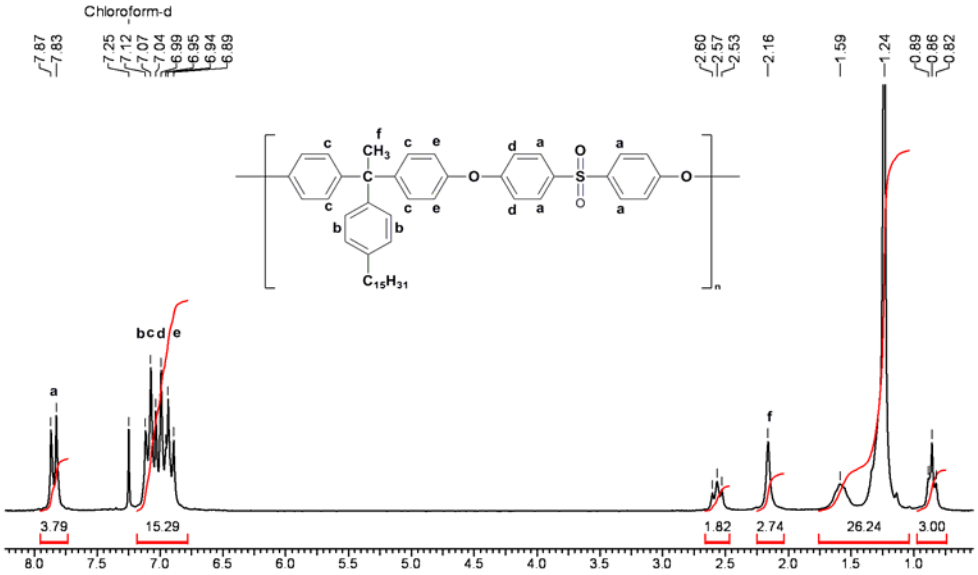


Figure 6b.7 ^{1}H-NMR spectrum of poly(ether ether sulfone) derived from 1,1,1-[bis(4-hydroxy phenyl)-4'-pentadecylphenyl]ethane and bis(4-fluorophenyl)sulfone in $CDCl_3$

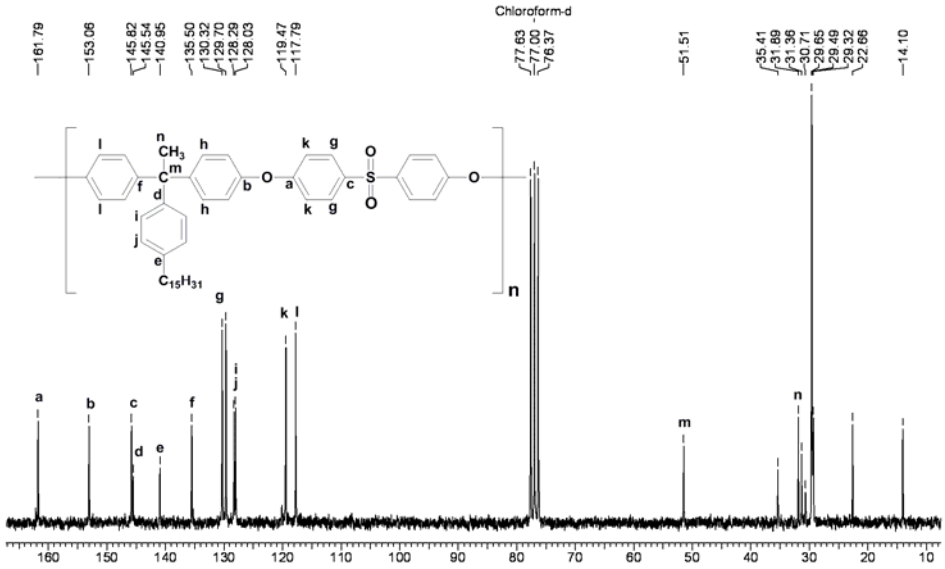


Figure 6b.8 ^{13}C-NMR spectrum of poly(ether ether sulfone) derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and bis(4-fluorophenyl)sulfone in $CDCl_3$

^{1}H and ^{13}C-NMR spectra of poly(ether ether ketone) **(PE-IV)** derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and 4,4'-difluorobenzophenone **(PE-IV)** alongwith assignments are shown in **Figure 6b.9** and **6b.10.**

^{1}H-NMR spectrum of **PE-IV** derived form 1,1-bis(4-hydroxy phenyl)-3-

pentadecylcyclohexane and 4,4'-difluorobenzophenone showed the presence of three peaks in the region 7.70-7.80 δ ppm for protons adjacent to carbonyl carbon.

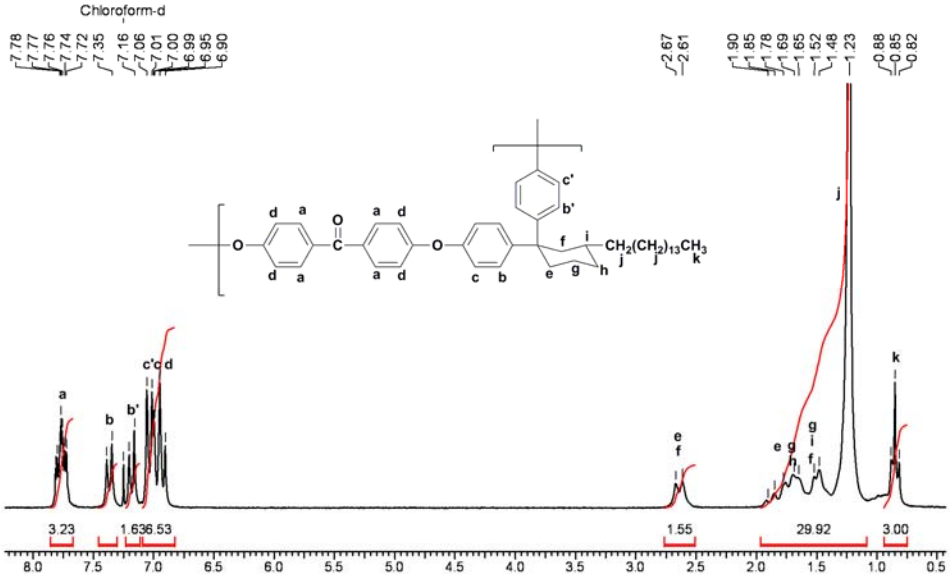


Figure 6b.9 ^{1}H-NMR spectrum of poly(ether ether ketone) derived from 1,1-bis(4-hydroxy phenyl) -3-pentadecylcyclohexane and 4,4'-difluorobenzophenone in $CDCl_3$

In case of symmetrical diols these protons gives a single peak as a doublet. It was observed that the protons next to carbonyl carbon experiences different environments based on the way 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane has condensed with 4,4'-difluorobenzophenone. It can be predicted that axial and equatorial phenyl rings in the bisphenol molecule can enchain with 4,4'-difluorobenzophenone in the following manner resulting in the observed NMR splitting patterns. There is a possibility of four types of constitutional isomerism

Axial-------Dihalide-------Axial

Axial-------Dihalide-------Equatorial

Equatorial-----Dihalide-----Axial

Equatorial-----Dihalide-----Equatorial.

As there is not much change in chemical shift difference between axial-equatorial and equatorial-axial isomers the protons of these 4,4'-difluorobenzophenone ring are undistinguishable under the recording conditions. At higher magnetic field strengths these protons might give separate signals.

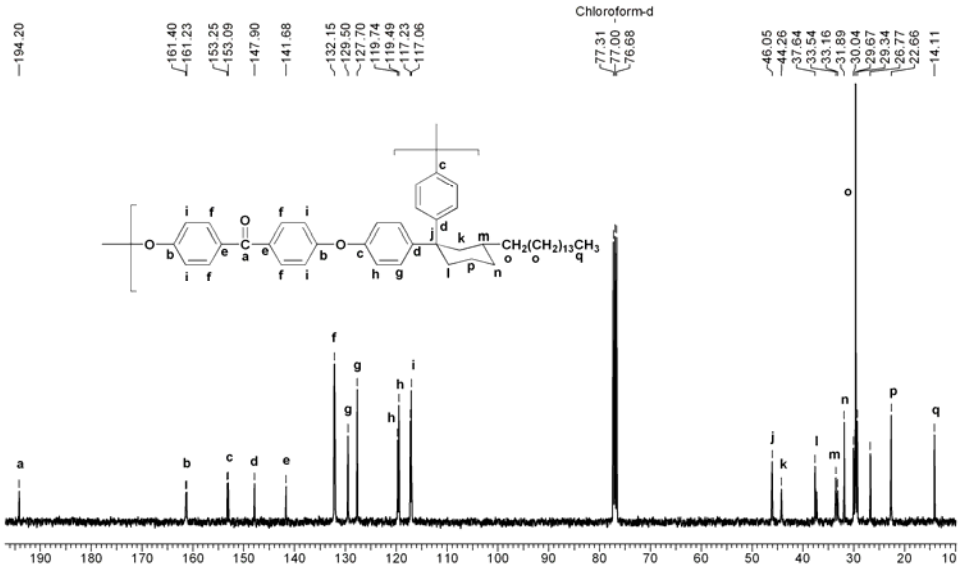


Figure 6b.10 ^{13}C-NMR spectrum of poly(ether ether ketone) derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and 4,4'-difluorobenzophenone in $CDCl_3$

^{1}H and ^{13}C-NMR spectra for **PE-V** and **PE-VI**, alongwith assignments are reproduced in **Figure 6b.11, 6b.12** and **Figure 6b.13, 6b.14** respectively, and are in good agreement with the proposed structure.

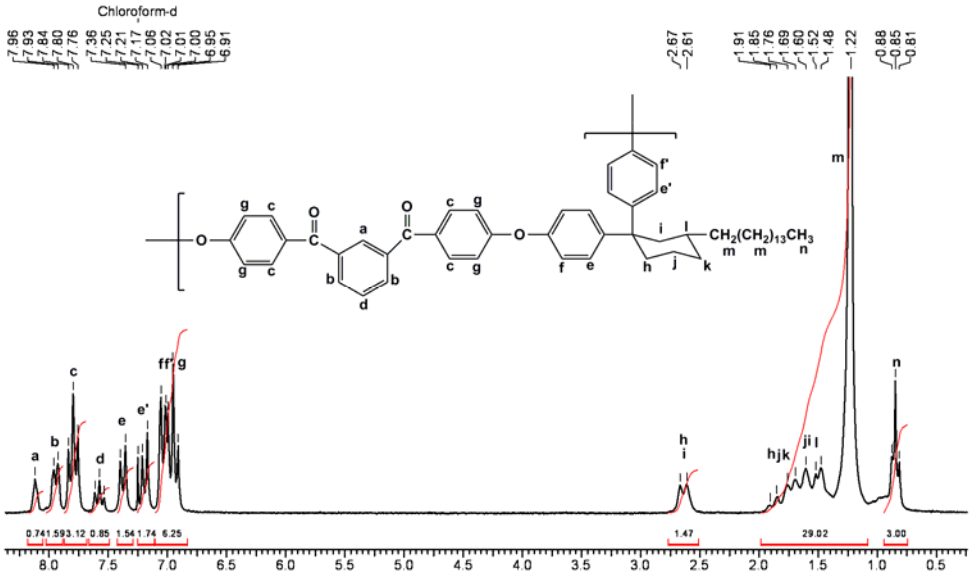


Figure 6b.11 ^{1}H-NMR spectrum of poly(ether ether ketone ketone) derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and 1,3-bis(4–fluorobenzoyl)benzene in $CDCl_3$

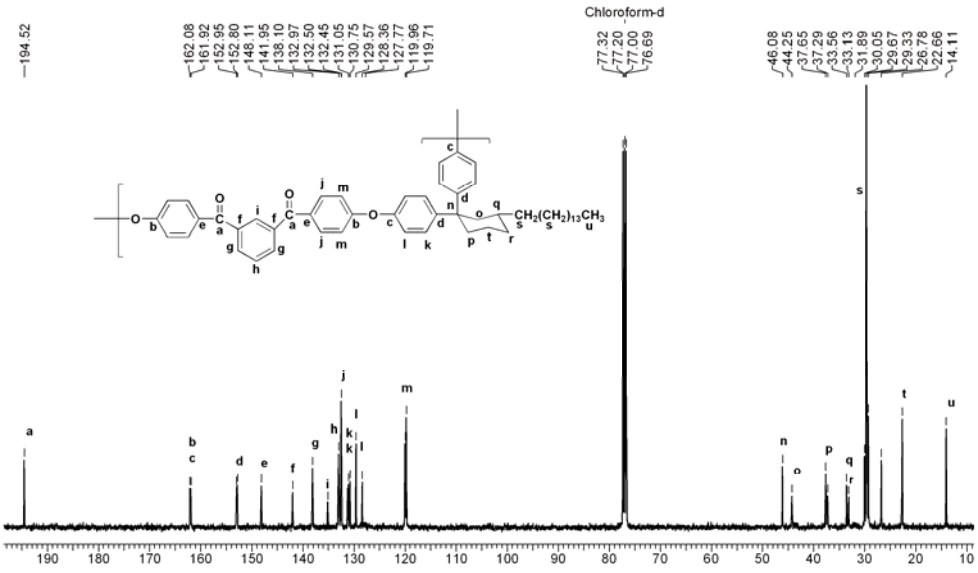


Figure 6b.12 ^{13}C-NMR spectrum of poly(ether ether ketone ketone) derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and 1,3-bis(4–fluorobenzoyl)benzene in $CDCl_3$

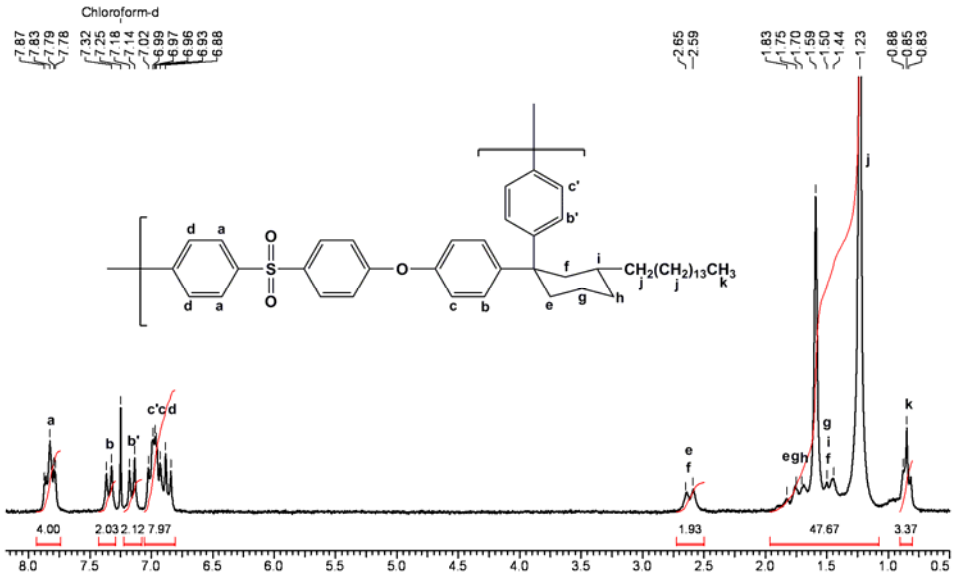


Figure 6b.13 ^{1}H-NMR spectrum of poly(ether ether sulfone) derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and bis(4-fluorophenyl)sulfone in $CDCl_3$

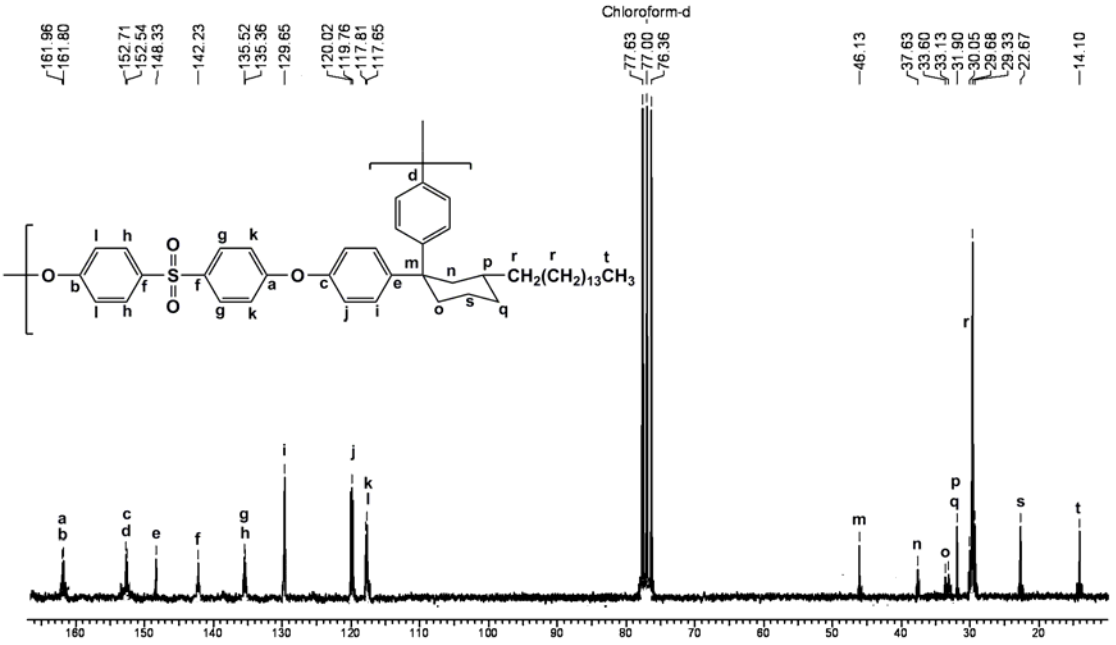


Figure 6b.14 ^{13}C-NMR spectrum of poly(ether ether sulfone) derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and bis(4-fluorophenyl)sulfone in $CDCl_3$

6b.4.1.2 Solubility measurements

Solubility of poly(arylene ether)s was tested in various organic solvents at 3 wt % concentration and data is summarized in **Table 6b.3.**

Table 6b.3 Solubility data of poly(arylene ether)s derived from bisphenol and aromatic dihalide

Polymer	Bisphenol	Dihalide	$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
PE-I	BHPE	DFB	++	++	++	+-	+-	+-	++	++	--
PE-II	BHPE	BFB	++	++	++	+-	+-	+-	++	++	--
PE-III	BHPE	FPS	++	++	++	+-	++	+-	++	++	+0
PE-IV	BHPC	DFB	++	++	++	+0	+0	+0	++	+-	--
PE-V	BHPC	BFB	++	++	++	+0	+-	+-	++	+-	--
PE-VI	BHPC	FPS	++	++	++	+-	+-	+-	++	+-	--

++: soluble at room temperature; +- : soluble on heating; +0: partially soluble on heating; -- : insoluble

It is well known that conventional PEEK derived from BPA and 4,4'-difluorobenzophenone can not be dissolved in most known organic solvents. In sharp contrast, the polymers reported in the current study were soluble in common organic solvents such as chloroform, DCM, THF, pyridine and *m*-cresol at room temperature or upon heating. Solubility in common organic solvent allows unique fabrication opportunities to PEEK. These PEEKs could be considered as good candidates for

applications such as gas separation and microelectronic devices where the combination of solubility plus excellent mechanical and thermal properties is desired. All polymers except **PE-IV**, were soluble on heating in polar aprotic solvents like NMP, DMAc and DMF upon heating.

Poly(ether sulfone)s exhibited excellent solubility pattern and were found to be soluble in solvents such as chloroform, DCM, THF, DMF, DMAc, NMP, pyridine and *m*-cresol at room temperature or on heating.

The good solubility of the polymers could be attributed to the introduction of the pendant pentadecyl chains and pendant cyclohexylidene moiety with pentadecyl chain, which disturbed the close packing of the polymer chains and led to the increase in free volume. Therefore, it was easy for the solvent to solubilize the polymers and this is necessary for the industrial processing of the polymers. The presence of C_{15} alkyl chain disrupted the packing of polymer chains, as well as provided additional 'handle' for interaction with solvents.

6b.4.1.3 X-Ray diffraction studies

X-Ray diffraction patterns of poly(arylene ether)s derived from bisphenols with aromatic dihalides are shown in **Figure 6b.15.**

In the X-ray diffraction patterns **(Figure 6b.15)** for poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic dihalides **(PE-I to PE-III)** broad halo at around $2\theta = \sim 19^{o}$ was observed. The introduction of pendant flexible pentadecyl chain into the polymer backbone hinders the chain packing resulting in amorphous nature of these poly(arylene ether)s, which is also reflected in their enhanced solubility.

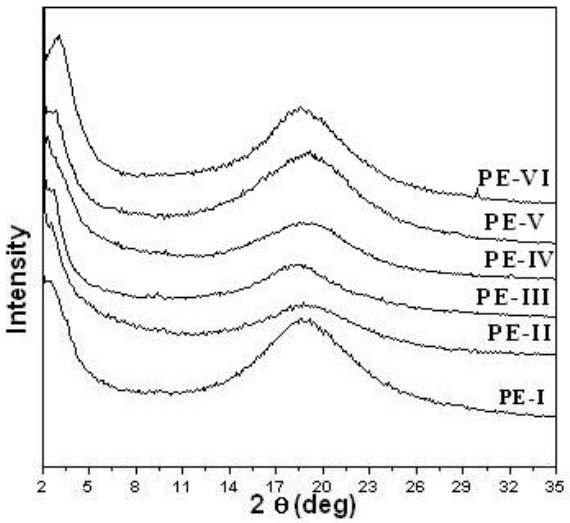


Figure 6b.15 X-Ray diffractograms of poly(arylene ether)s derived from bisphenol and aromatic dihalide

X-Ray diffraction patterns of poly(arylene ether)s derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane aromatic dihalides **(PE-IV to PE-VI)** are shown in **Figure 6b.15**. All poly(arylene ether)s were amorphous in nature. The presence of pentadecyl chain along with cyclohexyl "cardo" group hindered the packing of the polymer chains.

In the small-angle region at around 2θ = ~ 2-3°, a broad reflection is observed for all poly(arylene ether)s. This indicates the presence of layered structure in poly(arylene ether)s. These layered structures developed due to the packing of pentadecyl chains. [48]

6b.4.1.4 Thermal properties

In the present study, thermal stability of the poly(arylene ether)s was determined by thermogravimetric analysis (TGA) at a heating rate of 15°C /minute under nitrogen. The initial decomposition temperature (IDT), the temperature at 10% weight loss (T_{10}) and the weight residues at 900°C for polymers are given in **Table 6b.4**.

Thermogravimetric (TG) curves of poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic dihalides are shown in **Figure 6b.16**.

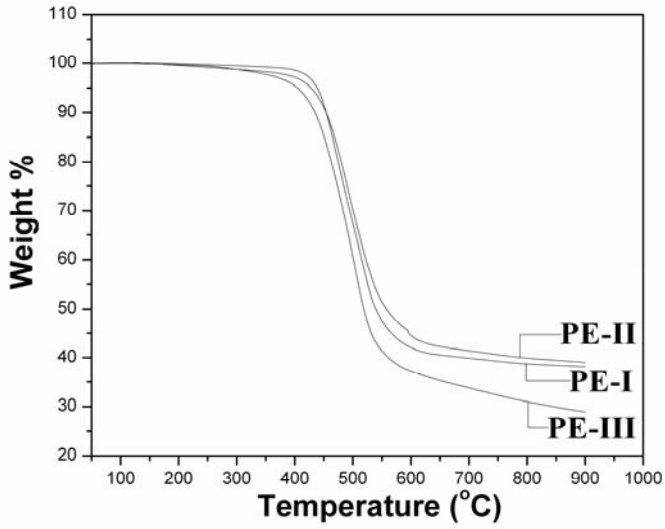


Figure 6b.16 TG curves poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic dihalides

T_{10} values obtained from TG curves for poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane were in the range of 416-440°C indicating good thermal stability of poly(arylene ether)s .

TG curves for poly(arylene ether)s derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane are shown in **Figure 6b.17.**

T_{10} values obtained from TG curves for poly(arylene ether)s derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane were in the range of 416-459°C, indicating their good thermal

stability.

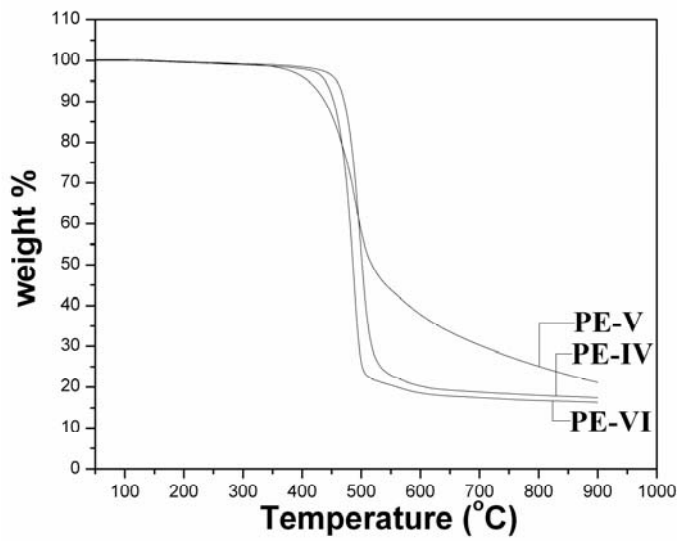


Figure 6b.17 TG curves poly(arylene ether)s derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and aromatic dihalides

Table 6b.4 Thermal properties of poly(arylene ether)s derived from bisphenol and aromatic dihalide

Polymer	Bisphenol	Dihalide	T_0[a] (°C)	T_{10}[b] (°C)	Weight residue at 900°C (%)	T_g (°C)
PE-I	BHPE	DFB	413	440	38	68
PE-II	BHPE	BFB	392	429	39	75
PE-III	BHPE	FPS	380	416	28	93
PE-IV	BHPC	DFB	417	459	17	69
PE-V	BHPC	BFB	378	416	21	78
PE-VI	BHPC	FPS	413	443	16	95

a : Initial decomposition temperature; *b* : temperature at which 10% weight loss is observed;

Glass transition (T_g) temperature of the poly(arylene ether)s was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polymer samples at a heating rate of 10°C / minute. DSC curves for poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and 1,1-bis(4-hydroxy phenyl)-3-pentadecyl cyclohexane are reproduced in **Figure 6b.18** and **Figure 6b.19,** respectively, The glass transition temperature values are given in **Table 6b.4**.

Poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic dihalides exhibited glass transition temperature in the range 68-93°C **(Figure 6b.18)**. Like in case of polyesters **(Chapter 6a)**, presence of long pentadecyl chain is responsible for the reduction of glass transition temperature of poly(arylene ether)s substantially. Pentadecyl chain acts as an "internal plasticizer" which results in depression in T_g of the poly(arylene ether)s.

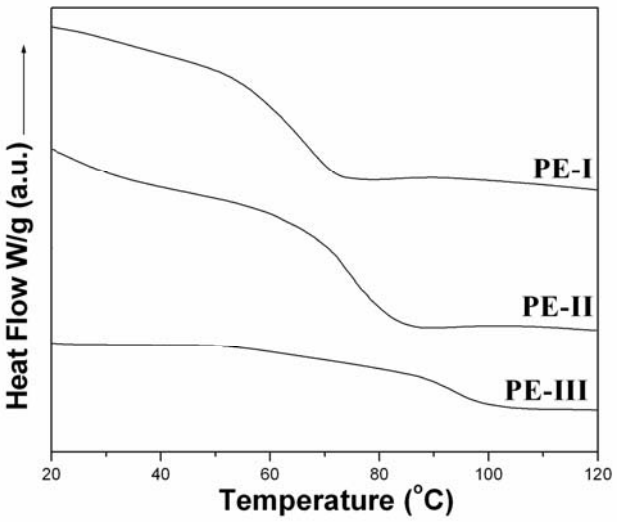


Figure 6b.18 DSC curves of poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic dihalides

A similar drop in T_g values of poly(arylene ether)s derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane was observed. The T_g values were in the range 69-95°C.

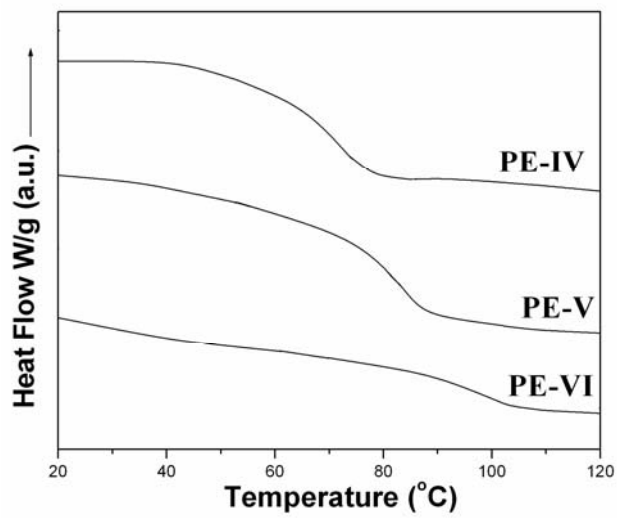


Figure 6b.19 DSC curves of poly(arylene ether)s derived from 1,1-bis(4-hydroxy phenyl)-3-pentadecylcyclohexane and aromatic dihalides

Lower glass transition temperatures of polymers demonstrated the plasticization effect of the pentadecyl chain. It has been reported that as the plasticizer content increases the free volume of the polymer increases which eventually decreases the glass transition temperature.[49] This has resulted in substantial decrease in the glass transition temperature as seen in **Figure 6b.19**.

A large difference between glass transition (68-95°C) and initial decomposition temperature (378-417°C) was observed. This offers poly(arylene ether)s a wide processing window.

6a.5 Conclusions

1. A series of poly(arylene ether)s was synthesized by polycondensation of bisphenols *viz*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane containing pendant flexible pentadecyl chain and 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane containing cyclohexylidene moiety with flexible pentadecyl substitutent with activated aromatic dihalides.
2. Inherent viscosities of poly(arylene ether)s were in the range 0.64-1.27 dL/g indicating formation of high molecular weight polymers.
3. Poly(arylene ether)s with improved solubility in organic solvents such as chloroform, dichloromethane, THF, pyridine and *m*-cresol were obtained.
4. Tough, transparent and flexible films could be cast from solutions of poly(arylene ether)s in chloroform.
5. WAXD patterns exhibited that all poly(arylene ether)s containing pendant pentadecyl chain were amorphous in nature. The formation of layered structure was observed due to the packing of pentadecyl chains.
6. T_{10} values for poly(arylene ether)s were in the range 416-459 ^{o}C, indicating their good thermal stability.
7. Glass transition temperature (75-95 ^{o}C) of poly(arylene ether)s was lowered substantially due to internal plasticization effect of pentadecyl chain in polymer backbone.

References

1. Mathias, L. J.; Lewis, C. M.; Wiegel, K. N. *Macromolecules* **1997**, 30, 5970
2. Liu, F. T.; Ding, J. F.; Li, M.; Day, M.; Robertson, G.; Zou, M. *Macromol. Rapid. Commun*. **2002**, 23, 844.
3. Maes, C.; Devaux, J.; Legras, R.; McGrail, P. T. *Polymer* **1995**, 36, 3159.
4. Gao, C. P.; Hay, A. S. *J. Polym. Sci. Polym. Chem*. **1995**, 33, 2731.
5. Ueda, M.; Toyota, H. ; Ouchi, T.; Sugiyma, J.; Yonetake, K.; Masuko, T.; Teramoto, T. *J. Polym. Sci. Polym. Chem*. **1993**, 31, 853
6. Cotter, R. J. *Engineering Plastics: A Hand Book of Polyarylethers*, Gordon and Breach Publisher, Amsterdam **1995.**
7. Ge, X.C.; Xu, Y.; Xiao, M.; Meng, Y.Z.; Hay, A.S. Eur. Polym. J. **2006**, 42, 1206.
8. Hergenrother, P.M.; Connell, J.W.; Labadie, J.W.; Hedrick, J.L. *Poly(arylether)s containing heteeocyclic units*. Berlin, Germany: Springer Verlag, **1994.**
9. Cassidy, P.E. *Thermally stable Polymers, Synthesis and Properties*; New York: Dekker, **1986**.
10. Hedrick, J.L.; Yilgor, I.; Wilkes, G.L.; McGrath, J.E. *Polym. Bull*. **1985**, 13, 201.
11. Hedrick, J.L.; Yilgor, I.; Jurek, M.; Hedrick, J.C.; Wilkes, G.L.; McGrath, J.E.; *Polymer* **1991**, 32, 2020.
12. Aguilar-Vega, M.; Paul, D. R. *J. Polym. Sci. Polym. Phys*. **1993**, 31, 1599.
13. Liu, B.; Hu, W.; Rao, X.; Wang, G.; Jiang, Z.; Wu, Z.; Matsumoto, T. *Polym. Bull***. 2004**, 52, 235.
14. Strukelj, M.; Hay, A. H *Macromlecules* **1991**, 24, 6870.
15. Jeong, H. J.; Iwasaki, K.; Kakimoto, M.; Imai, Y. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, A31, 1975.
16. Watambe, S.; Kobayashi, A.; Kakimoto, M.; Imai, Y. *J. Polym. Sci. Polym. Chem*. **1994**, 32, 909.
17. Aitken .C.L.; Koros, W.J.; Paul, D. R. *Macromolecules* **1992**, 25, 3424.
18. Pixton, M. R.; Paul, D. R. *Polymer* **1995**, 36, 3165.
19. Mathias L. J.; Lewis, C. M.; Wiegel, K. N. *Macromolecules* **1997**, 30, 5970.
20. Wang, Z. Y.; Hay, A. S. *J. Polym. Sci. Polym. Chem*. **1991**, 29, 1045.
21. Reuter, K.; Weymans, G.; Freitag, D.; Dehin, R.; Meier, E.; Muller, G. EP 0362603 A1, **1990.**
22. Tullos, G.L.; Cassidy, P.E.; *Macromolecules* **1991**, 24, 6059.
23. Bonner, W.H.; US Patent US 3,062,205, **1962**.
24. Kim, Y. J.; Chung, I. S.; Kim, S. Y. *Macromolecules* **2003**, 36, 3809.
25. Chung, I. S.; Kim, S. Y. *Macromolecules* **2000**, 33, 9474.
26. Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, 29, 58.
27. Chung, I. S.; Kim, S. Y. *J. Am. Chem. Soc*. **2001**, 123, 11071.
28. Park. S.K. Kim, S. Y. *Macromolecules* **1998**, 31, 3385.
29. Jennings, B. E.; Jones, M. E. and Rose, J. B. *J. Poly. Sci. Part C*, **1967**, 16, 715.
30. Barr, D. A.; Rose, J. B. ICI, GB 1153035, **1965**.
31. Johnson, R. N. et.al. *J. Polym. Sci. Polym. Chem***. 1967**, 5, 2375.
32. Mathias, L. J.; Lewis, C. M.; Wiegel, K. N. *Macromolecules* **1997**, 30, 5970.
33. Liu, B.; Hu, W.; Jin Y.; Chen, C.; Jiang, Z.; Wu, Z.; Matsumoto, T.; Matsumura, A. *Macromol. Chem. Phys*. **2004**, 205, 1677.
34. Liu, B.; Hu, W.; Chen, C.; Jiang, Z.; Zhang, W.; Wu, Z.; Matsumoto, T. , *Polymer* **2004**, 45, 3241.
35. Liu, B.; Wang, G.; Hu, W.; Jin, Y.; Chen, C.; Jiang, Z.; Zhang, W.; Wu, Z.; Wei, Y. *J. Polym. Sci. Polym. Chem*. **2002**, 40, 3392.

36. Strukelj, M.; Hay, A. H. *Macromolecules* **1991**, 24, 6870.

37. Jeong, H.J.; Iwasaki, K.; Kakimoto, M.; Imai, Y. *J. Macromol. Sci., Pure Appl. Chem*. **1994**, A31, 1975.

38. Watanabe, S.; Murayama, H.; Murata,M.; Tanabe, M.; Imai, Y. *J. Polym. Sci. Polym. Chem*. **1998**, 36, 2229.

39. Mathias L. J.; Lewis, C. M.; Wiegel, K. N. *Macromolecules* **1997**, 30, 5970.

40. Wang, Z. Y.; Hay, A. S. *J. Polym. Sci. Polym. Chem*. **1991**, 29, 1045.

41. Wang, Z.; Chen, T.; Xu, J. *Macromolecules* **2000**, 33, 5672.

42. Reuter, K.; Weymans, G.; Freitag, D.; Dehin, R.; Meier, E.; Muller, G. EP 0364741 B1, **1990**.

43. Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, 20, 1204.

44. Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, 22, 1096.

45. Attwood, T. E.; King, T.; Leslie, V. J.; Rose, J. B. *Polymer*, **1982**, 18, 369.

46. Rose, J. B. Staniland, P. A. ICI, EP 0001879, **1977.**

47. Armargeo,W.L.F.; Perrin, D. D. '*Purification of Laboratory Chemicals"* Butterworth-Heinemann, Oxford, 4th Edition **1996**.

48. Sarkar, A.; Halhalli, M.R.; Kulkarni, A.D.; Wadgaonkar, P.P. *J. Appl. Polym. Sci*. **2009**, 112, 461.

49. Sasthav, J.R.; Harris, F.W. *Polymer*, **1995**, 26, 4911

Chapter 7

Summary and Conclusions

7.1 Summary and Conclusions

The progressive dwindling of fossil resources coupled with the increase in oil prices has sparked an intense activity in search for alternatives based on renewable resources for the production of energy. Given the predominance of petroleum- and carbon-based chemistry for the manufacture of organic chemical commodities, a similar preoccupation has recently generated numerous initiatives aimed at replacing these fossil sources with renewable counterparts. In particular, major efforts are being conducted in the field of polymer science and technology to prepare macromolecular materials based on renewable resources.

The aim of the present thesis was to provide a humble contribution to the ongoing research throughout the scientific community in the view of diminishing petroleum resources. Broadly, the current research work was based on the four objectives: i) making use of a renewable resource material *viz;* cashew nut shell liquid (CNSL) for the synthesis of monomers and polymers, ii) design and synthesis of monomers that disturb structural regularity and chain packing of the polymer backbone, iii) synthesis of processable high performance polymers, and iv) to study structure-property relationship.

Hence, the combination of phenolic character and flexible pentadecyl chain of 3-pentadecyl phenol, which in turn was obtained from CNSL-a renewable resource material- inspired a series of difunctional monomers, *viz*;

1. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene,
2. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid,
3. 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide,
4. 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine,
5. 4-(2'-Aminophenoxy)-2-pentadecylbenzenamine,
6. 1-Isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene,
7. 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, and
8. 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane.

The most important aspect in designing of monomers was the presence of flexible linear pentadecyl chain. The existence of long alkyl chain along the polymer backbone aids in improvement in the polymer processability/ solubility.

Thus, total eight difunctional monomers were designed and synthesized starting from CNSL *via* simple organic transformations. Of these, six monomers were synthesized for the first time.

All the monomers and intermediates involved in their synthesis were characterized by spectroscopic techniques such as FTIR and NMR spectroscopy.

These difunctional monomers were utilized for the synthesis of a variety of high performance polymers. In order to investigate the effect of incorporation of pendent pentadecyl chains on polymer properties, such as solubility, thermal transitions and heat resistance were

evaluated. For this study, polymers such as polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(ether ketone)s and poly(ether sulfone)s were synthesized and characterized.

4-(4'-Aminophenoxy)-2-pentadecylbenzenamine was polycondensed with commercially available aromatic dialdehydes to obtain a series of (co) polyazomethines containing pendant pentadecyl chains. Inherent viscosity of (co) polyazomethines was in the range 0.50-0.70 dL/g. Medium to reasonably high molecular weight (co) polyazomethines soluble in common organic solvents such as chloroform, DCM, THF, pyridine and *m*-cresol were obtained. The presence of C_{15} alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. Transparent and stretchable films of (co) polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with terephthaldehyde and / or isophthaldehyde could be cast from chloroform solutions. Encouraged by excellent solubility pattern of (co) polyazomethines bearing pendant pentadecyl chains, a series of copolymers by polycondensation of a mixture of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and 4,4'-oxydianiline with terephthaldehyde was prepared. However, the derived copolyazomethines were insoluble in common organic solvents. All (co) polyazomethines showed a broad halo in the wide angle region ($2\theta = \sim 19^{o}$). In the small-angle region ($2 = \sim 3^{o}$), a reflection was observed for all of the (co) polyazomethines. These peaks are characteristics of a typical layered structure resulting from packing of the pentadecyl side chains. T_{10} values obtained from TG curves for (co) polyazomethines were in the range 434-443 ^{o}C indicating their good thermal stability. Glass transition (T_g) temperature of (co) polyazomethines was evaluated by differential scanning calorimetery. All these polymers manifest a T_g value in the range 21-59 ^{o}C. The depression in glass transition temperature of (co) polyazomethines due to the presence of pendant pentadecyl chain demonstrated it's plasticizing ability. A large difference between glass transition (21-59 ^{o}C) and initial decomposition temperature (346-380^{o}C) was observed. This offers (co) polyazomethines a wide processing window.

New polyamides were synthesized from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines viz; 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenedianiline, 4,4'-(hexafluoroisopropylidene) dianiline and 4-(4'-aminophenoxy)-2-pentadecyl benzenamine by Yamazaki-Higashi reaction (phosphorylation reaction). The obtained polyamides had inherent viscosities in the range 0.45-0.66 dL/g and could be cast into films from DMAc solution. Most of the polyamides were soluble in polar aprotic solvents such as DMAc and NMP at room temperature or on heating. Wide angle X-ray diffraction patterns exhibited broad halo at around $2\theta = \sim 19^{o}$ indicating that the polymers were amorphous in nature. X-Ray diffractograms showed a reflection in the small-angle region ($2\theta = \sim 2\text{-}5^{o}$) for all polyamides characteristics of formation of layered structure arising from packing of pentadecyl chains. T_{10} values obtained from TG curves of polyamides were in the range 425-455 °C indicating good thermal stability of

polyamides. The derived polyamides showed glass transition temperatures in the range 148-189 ^{o}C. The lowering of T_g could be attributed to the fact that the long alkyl chains acts as a bound solvent or internal plasticizers and also increase the free volume, thereby increasing segmental mobility, thus resulting in a reduction in the T_g. A large difference between glass transition (148-189 ^{o}C) and initial decomposition temperature (335-376^{o}C) was observed which offers these polyamides a broad processing window.

A series of new poly(amideimide)s was synthesized by two-step polycondensation of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides viz, benzene-1,2,4,5-tetracarboxylic dianhydride or pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. Inherent viscosities of poly(amideimide)s were in the range 0.60-0.64 dL/g indicating formation of reasonably high molecular weight polymers. Tough, transparent and flexible films of poly(amideimide)s could be cast from DMAc solutions of poly(amideimide)s. Remarkably, most of the poly(amideimide)s were found to be soluble in DMAc, NMP, pyridine and *m*-cresol at room temperature or upon heating. The presence of pendent flexible pentadecyl chains brought about improvement in solubility of poly(amideimide)s. Wide angle X-ray diffraction patterns of poly(amideimide)s showed broad halo at around $2\theta = \sim 19^{o}$ suggesting that all polymers were amorphous. In the small-angle region ($2\theta = \sim 3^{o}$), a reflection was observed for poly(amideimide)s. These reflections were characteristics of a layered structure resulting from the packing of the pentadecyl side chains. T_{10} values obtained from TG curves were in the range of 388-410^{o}C for poly(amideimide)s indicating their good thermal stability. Glass transition temperatures of poly(amideimide)s containing pendant pentadecyl chains and ether linkages were in the range of 162-198^{o}C. It was observed that the plasticization effect of the attached pentadecyl side chains induced the depression of T_g. A large difference between glass transition (162-198^{o}C) and initial decomposition temperature (340-356^{o}C) was observed. This gives an opportunity for these poly(amideimide)s to be melt processed or compression molded.

A series of polyhydrazides was derived by polycondensation of 4-[4'-(hydrazinocarbonyl) phenoxy]-2-pentadecylbenzohydrazide and aromatic diacid chlorides *viz.*, terephthalic acid chloride and isophthalic acid chloride. A series of polyoxadiazoles were synthesized by cyclodehydration reaction of derived polyhydrazides. Inherent viscosities of polyhydrazides and polyoxadiazoles were in the range 0.53-0.66 dL/g and 0.49 to 0.53 dL/g, respectively indicating formation of medium to reasonably high molecular weight polymers. Polyhydrazides exhibited excellent solubility in polar aprotic solvent such as DMAc, NMP, DMF and were also found to be soluble in solvents such as *m*-cresol and pyridine at room temperature or upon heating. Polyoxadiazoles showed solubility in polar solvents such as DMAc, NMP and DMF upon heating and even in solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine and *m*-cresol. The enhanced solubility could be

attributed to the flexible pentadecyl chain in the repeat unit which restricted the close packing of polymer chains and therefore allowed solvent molecules to penetrate into the polymer chains. The presence of C_{15} alkyl chain in polyoxadiazoles provided the additional 'handle' for interaction with solvents. Wide angle X-ray diffraction patterns showed that polyhydrazides and polyoxadiazoles exhibited broad halo at around $2\theta = \sim 20^{o}$ revealing an essentially amorphous nature. A strong reflection peak was observed in small angle region ($2\theta = \sim 3^{o}$) both in polyhydrazides and polyoxadiazoles indicating formation of layered structure due to the ordered packing of pentadecyl chains. Polyhydrazides showed a weight loss at around 300°C which may be attributed to the loss of water due to the thermally activated cyclodehydration reaction leading to the formation of corresponding polyoxadiazoles. T_{10} values obtained from TG curves for polyoxadiazoles were in the range 433-449°C indicating their good thermal stability. A decrease in glass transition temperature was observed, both in polyhydrazides (143-166 °C) and polyoxadiazoles (90-102 °C) which could be ascribed to internal plasticization effect of pentadecyl chain.

A series of new aromatic polyesters was synthesized from bisphenol 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane and aromatic diacid chlorides viz; terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) by phase transfer catalysed interfacial polycondensation technique. Since the polyester obtained from bisphenol A (BPA) and TPC is insoluble in common organic solvents, efforts were made to obtain soluble copolyesters by incorporating 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane as a comonomer. Copolyesters were synthesized by interfacial polycondensation of BPA with TPC incorporating 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylphenyl]ethane as a co-monomer in different proportions. Inherent viscosities of (co)polyesters were in the range 0.72-1.65 dL/g indicating formation of high molecular weight polymers. Tough, transparent and flexible films of (co) polyesters could be cast from chloroform solutions. Homopolyesters and copolyesters obtained from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane exhibited good solubility in common organic solvents such as chloroform, dichloromethane, pyridine, *m*-cresol, etc. The presence of C_{15} alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. The broad halo at $2\theta = \sim 19^{o}$ was observed for all (co)polyesters in the wide angle X-ray diffraction patterns, which could be mainly because of the presence of long pentadecyl chain, which hinders the packing of the polymer chains making them amorphous. In the small-angle region ($2\theta = \sim 3^{o}$), a reflection was observed which could be attributed the formation of layered structures due to the packing of pentadecyl side chains. T_{10} values obtained from TG curves of (co) polyesters were in the range 400-460°C indicating their good thermal stability. The glass transition temperature for homopolyesters were in the range 63-82°C and for copolyesters were in the range 177-183°C. All these observations clearly indicate that there is remarkable drop in glass transition temperature of polyesters by the incorporation of long pentadecyl chain which is acting as an internal plasticizer. A

large difference between glass transition (63-183^{o}C) and initial decomposition temperature (368-417^{o}C) was observed. This offers (co)polyesters a wide processing window.

A series of poly(arylene ether)s *viz*, poly(ether ketone)s and poly(ether sulfone)s was synthesized by polycondensation of two bisphenol monomers *viz*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane containing pendant phenyl group with flexible pentadecyl chain and 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane bearing cyclohexylidene moiety with flexible pentadecyl substitutent with activated aromatic dihalides. Poly(arylene ether)s were isolated as white fibrous materials with inherent viscosities in the range 0.64-1.27 dL/g indicating formation of high molecular weight polymers. Tough, transparent and flexible films could be cast from solutions of poly(arylene ether)s in chloroform. It is well known that conventional PEEK and PEKK can not be dissolved in most known organic solvents. In sharp contrast, these polymers were soluble at room temperature in common organic solvents such as chloroform, DCM, THF, pyridine and *m*-cresol. Most of the poly(ether ketone)s were soluble upon heating in polar aprotic solvents such as NMP, DMAc and DMF. Poly(ether sulfone)s exhibited excellent solubility pattern and were found to be soluble solvents such as chloroform, DCM, THF, DMF, DMAc, NMP, pyridine and *m*-cresol at room temperature or upon heating. The good solubility of the polymers could be attributed to the introduction of the pendant phenyl group with pentadecyl chain and cyclohexylidene moiety, which disturbed the close packing of the polymer chains and led to the increased free volume. The presence of C_{15} alkyl chain provided the additional 'handle' for interaction with solvents. In wide angle X-ray diffractograms, all poly(arylene ether)s exhibited a broad halo at $2\theta = \sim 19^{o}$, indicating their amorphous nature. In the small-angle region (2θ = 2-3^{o}), a reflection is observed for all poly(arylene ether)s. This indicates the formation of layered structure in poly(arylene ether)s due to the packing of pentadecyl chains. T_{10} values obtained from TG curves for poly(arylene ether)s were in the range 416-459 ^{o}C, indicating their good thermal stability. Poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and aromatic dihalides exhibited glass transition temperature in the range 68-93^{o}C; while, those derived from 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane showed T_g values in the range 69-95 ^{o}C. This showed that, plasticization effect of long pentadecyl chain is responsible for the substantial reduction of glass transition temperatures of poly(arylene ether)s. A large difference between glass transition (68-95^{o}C) and polymer degradation temperature (378-417^{o}C) was observed. This offers poly(arylene ether)s a wide processing window.

In summary, CNSL- a renewable resource material- was exploited to derive a range of new difunctional monomers *via* simple organic transformations. The unique feature of CNSL, i.e. the presence of C_{15} alkyl chain has been utilized to reduce strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect and consecutively aid in improved solubility and processability. Overall, the polymer processability / solubility was improved by the

incorporation of pendant pentadecyl chains *via* internal "plasticization". The presence of C_{15} alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. A large window between glass transition and polymer degradation temperature was observed. This offers polymers a wide processing window. Thus improved solubility with reasonably good thermal stability of these polymers makes them attractive materials for high performance polymers applications.

7.2 Perspectives

The present work on design and synthesis of difunctional monomers starting from CNSL and processable high performance/ high temperature polymers has opened up many prospects for the future work.

- The present work on the synthesis of difunctional monomers starting from CNSL- an inexpensive and abundantly available renewable resource material- has expanded the range of condensation monomers available for the preparation of high performance polymers with improved processability.
- The dibromo compound *viz*, 1-bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene synthesized in the present work is a potentially useful monomer for synthesis of polyamides and polyesters by transition metal-catalyzed carbonylative coupling with diamines and diphenols, respectively.
- 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene could easily be converted into corresponding diphenol and diladehyde, which by themselves represent valuable monomers for synthesis of a host of high performance polymers.
- The difunctional monomers synthesized in the present work are unsymmetrical and the difference in reactivity of the two functional groups arises due to steric factors. It would be interesting to systematically investigate the constitutional isomerism in the polymers derived from such monomers and examine its influence on the polymer properties.
- It would now be interesting to synthesize other step-growth polymers based on synthesized difunctional monomers. For example, aromatic diisocyanate containing pendant pentadecyl chain is a potentially useful monomer for the synthesis of polyurethanes and polyureas.
- The primary focus of the present work was to illustrate the influence of pendant pentadecyl chains on the solubility behavior and thermal properties of polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters and poly(arylene ether)s. Detailed studies using variable temperature WAXD and ^{13}C solid-state NMR spectroscopy would yield useful information on the packing mode and conformational transitions of the pentadecyl side chains.

- High performance/ high temperature polymers synthesized in the present work could be cast into tough and flexible films from solution in organic solvents. It would be worthwhile to evaluate some selected polymers as membrane materials for gas separation studies.

Synopsis

Synopsis of the Thesis Entitled

"Synthesis of New Monomers Starting from Renewable Resource Materials and Polymers Derived Therefrom"

Introduction:

Presently, a wide range of industrial materials such as solvents, fuels, chemical products and synthetic fibers are being manufactured from petroleum resources. However, rapid depletion of fossil and petroleum resources is encouraging chemists to orient their research towards designing chemicals, products, and processes based on renewable feedstocks with an increased awareness of environmental and industrial impact.[1,2] Advances in genetics, biotechnology, process chemistry, and engineering are leading to new manufacturing concepts for converting renewable biomass to valuable fuels and products, generally known as "biorefinery" concept.[2-6] The swift integration of crop-based materials synthesis and "biorefinery" manufacturing technologies offers the potential for new advances in sustainable energy alternatives and biomaterials that will lead to a new manufacturing paradigm. In future research, developing bio-based materials will be a fascinating yet demanding practice which will have direct impact on industrial applications as an economically viable alternative.

Biomass constitutes a renewable source of natural products capable of being used as unfailing starting material for access to new compounds and able to substitute petroleum derivatives.[7] Nature offers an abundance of opportunities for shaping structural and functional materials in its wide variety of raw materials which include carbohydrates, proteins, oleochemicals, etc. Among them, vegetable oils (oleochemicals) are expected to be an ideal alternative chemical feedstock.[8-10] Oleochemicals are abundantly available throughout the world and offer an exceptional variety of chemical building blocks for the design of materials with a strong added value.

Cashew nut shell liquid (CNSL), obtained as a by-product of cashew processing industry, is unique in that it contains phenolic moiety with an unsaturated 15-carbon side chain. It's extraction, chemistry, and composition have been well documented.[11] Considerable attention from polymer scientists throughout the world is devoted to utilize its potential attributes as a substitute for petrochemical derivatives.[12,13] CNSL has already found use in phenolic resins in break lining, surface coatings and other miscellaneous applications.[11-19] Of late, it has been used in the preparation of many speciality materials such as liquid crystalline polyesters,[16,17] cross-linkable polyphenols,[18] polyurethanes[20-22] and a range of other speciality polymers and additives.[11]

The most attractive aspect of CNSL as a starting material is it's low cost and easy availability. The materials / products based on CNSL exhibit flexibility due to the presence of long alkyl chain resulting in improved processing characteristics of the polymers. Inspite of massive literature accumulated on CNSL, many areas remain which are yet to utilize this attractive raw

material. There are only a few reports[20-26] describing CNSL as a starting material for synthesis of difunctional monomers useful in the preparation of step-growth polymers. Therefore, design and synthesis of difunctional condensation monomers starting from CNSL is an attractive proposition.

Considerable efforts over the years have focused on development of monomers that yield processable high-performance polymers. Many approaches have been attempted to improve processability of high performance polymers such as introduction of kinks or flexible units in the main chain,[27,28] use of asymmetric monomers,[29-31] introduction of cardo groups[32] and replacing the conventional monomers with ones containing pendent groups.[33] Another interesting approach that has been tried to improve polymer processability is *via* internal plasticization. Plasticization normally involves the incorporation of a low molecular mass additive which improves polymer flow and processability.[34] In internal plasticization, the plasticizer is chemically attached to or incorporated in the polymer backbone. It is reported that the introduction of flexible side groups onto the polymer backbone leads to dramatic increase in solubility and decrease in the glass transition temperature.[35,36]

Thus, our synthetic research efforts were directed towards design and synthesis of difunctional monomers with features that disturb chain packing and structural regularity in polymer backbone. The approach involved making use of 3-pentadecyl phenol as a starting material which in turn is obtained from CNSL. The monomers were designed with a view to incorporate structural features such as: i) the presence aromatic ether linkage to provide lower energy of internal rotation, and ii) the presence of flexibilizing pentadecyl chain on only one phenyl ring to offer asymmetry to the polymer backbone and at the same time presence of pentadecyl chain in the polymer structure for improving processability *via* internal plasticization effect.

Another objective of the present work was to synthesize and characterize step-growth polymers containing pendant flexible pentadecyl chains and to investigate the effect of incorporation of pentadecyl chains on the solubility and thermal properties of the polymers.

With above objectives in mind, the following specific work was chosen for the thesis:

Objectives of the present thesis:

- Design and synthesis of difunctional monomers, *viz*, aromatic dibromide, diacid, diacylhydrazide, diamines and diisocyanate containing pendent flexible pentadecyl chain starting from CNSL.
- Synthesis of a bisphenol containing pendent pentadecyl chain utilizing CNSL as a starting material.
- Synthesis of a bisphenol containing cyclohexylidene moiety with flexible pentadecyl substituent starting from CNSL.

- Synthesis of polyazomethines, polyamides, poly(amideimide)s, polyhydrazides and polyoxadiazoles containing ether moiety and pendant pentadecyl chains.
- Synthesis of aromatic polyesters, poly(ether ketone)s and poly(ether sulfone)s based on bisphenols containing pentadecyl chains.
- To study the effect of the incorporation of pentadecyl chains on polymer properties such as solubility and thermal behavior.

The thesis has been divided into the following seven chapters.

Chapter 1: Introduction and Literature Survey

This chapter deals with brief overview of polymers derived from renewable resource materials, with emphasis on polymers derived from CNSL. A comprehensive review of literature on polymers, *viz*., polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(ether ketone)s and poly(ether sulfone)s covering methods of synthesis, structure-property relationship, etc., is presented.

Chapter 2: Scope and Objectives

This chapter discusses scope and objectives of the thesis

Chapter 3: Synthesis and Characterization of Condensation Monomers

This chapter describes:

I. Synthesis of difunctional monomers containing ether moiety and pendant pentadecyl chain, *viz*,
   a. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene,
   b. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid,
   c. 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide,
   d. 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine,
   e. 4-(2'-Aminophenoxy)-2-pentadecylbenzenamine,
   f. 1-Isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene.

II. Synthesis of bisphenol containing pendant pentadecyl chain., *viz.*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, and

III. Synthesis of bisphenol containing cyclohexylidene moiety with a flexible pentadecyl substituent., *viz.*, 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane.

The difunctional monomers and the intermediates involved in their synthesis were characterized by IR, ^{1}H-NMR, and ^{13}C–NMR spectroscopy.

Chapter 4: Synthesis and Characterization of Polyazomethines and Polyamides

This chapter is sub-divided into two sections:

Chapter 4 a: Synthesis and Characterization of Polyazomethines Based on 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine

This chapter describes:

i. Synthesis of (co) polyazomethines containing pendant flexible pentadecyl chain by polycondensation of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine with commercially available aromatic dialdehydes, *viz.,* terephthaldehyde, isophthaldehyde and a mixture of terephthaldehyde and isophthaldehyde in various molar proportions.

ii. Synthesis of (co) polyazomethines by polycondensation of a mixture of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and 4,4'-oxydianiline with terephthaldehyde.

iii. (Co) polyazomethines were characterized by inherent viscosity measurements, gel permeation chromatography (GPC), solubility tests, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and differential scanning calorimetry (DSC).

Chapter 4 b: Synthesis and Characterization of Polyamides Based on 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid

This chapter deals with synthesis of polyamides containing pendant pentadecyl chains by polycondensation of 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid with commercially available aromatic diamines, *viz.*, 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylene dianiline and 4,4'-(hexafluoroisopropylidene) dianiline.

Chapter 5: Synthesis and Characterization of Poly(amideimide)s, Polyhydrazides and Polyoxadiazoles

This chapter is divided into two sections:

Chapter 5 a: Synthesis and Characterization Poly(amideimide)s Based on 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

This section provides study on synthesis and characterization of poly(amideimide)s containing pendent pentadecyl chains obtained by polycondensation 4-[4'-(hydrazino carbonyl)phenoxy]-2-pentadcyl benzohydrazide with commercially available aromatic dianhydrides, *viz.*, benzene-1,2,4,5-tetracarboxylic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride.

Chapter 5 b: Synthesis and Characterization of Polyhydrazides and Polyoxadiazoles Based on 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide

This section deals with:

i. Synthesis of polyhydrazides by polycondensation of 4-[4'-(hydrazino carbonyl)phenoxy]-2-pentadecyl benzohydrazide with aromatic diacid chlorides, *viz.*, terephthaloyl chloride and isophthaloyl chloride.

ii. Synthesis of polyoxadiazoles through cyclodehydration of synthesized polyhydrazides.

Chapter 6: Synthesis and Characterization of Polyesters and Polyethers

This chapter is divided into two sections:

Chapter 6 a: Synthesis and Characterization of (Co) Polyesters Based on 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

This chapter describes:

i. Synthesis and characterization of polyesters containing pendent pentadecyl chain obtained by interfacial polycondensation of a bisphenol, *viz*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane with aromatic diacid chlorides, *viz*, terephthaloyl chloride and isophthaloyl chloride

ii. Synthesis of copolyesters by polycondensation of mixture of bisphenols, *viz.*, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and 4,4'-isopropylidene diphenol (bisphenol-A) with terephthaloyl chloride.

Chapter 6 b: Synthesis and Characterization of Polyethers Based on

i) 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane

ii) 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane

This chapter deals with:

i. Synthesis of poly(ether ether ketone)s and poly(ether ether ketone ketone)s containing pendent pentadecyl chain or cyclohexylidene moiety with flexible pentadecyl substitutent.

ii. Synthesis of poly(ether ether sulfone)s containing pendent pentadecyl chain or cyclohexylidene moiety with pentadecyl substituent.

Chapter 7: Summary and Conclusions

This chapter summarizes the results and describes salient conclusions of the investigations reported in this thesis.

References:

1. Van Wyk, J. P. H. Biotechnology and the Utilization of Biowaste as a Resource for Bioproduct Development. *Trends Biotechnol.*, **2001**, *19*, 172.
2. Ragauskas, A. J.; Wiliams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, L. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The Path Forward for Biofuels and Biomaterials. *Science,* **2006**, *311*, 484.
3. Kamn, B.; Gruber, P.R.; Kamn, M. (Eds.), Biorefineries, Industrial Processes and Products: Status Quo and Future Directions, Vol. 1 and 2, Wiley-VCH Verlag GmbH and Co. Germany, 2006.
4. Lichtenthaler, F. W.; Peters, S. Carbohydrates as Green Raw Materials for the Chemical Industry. *C. R. Chem.*, **2004,** *7*, 65.
5. Lorenz, P.; Zinke, H. White Biotechnology: Differences in US and EU Approaches. *Trends Biotechnol.*, **2005**, *23*, 570.
6. Bozell, J.J.; Feedstocks for the future, ed. Bozell, J.J. and Patel, M.K., ACS Symposium Ser 921, Oxford University Press, **2006**, p. 1.
7. Koopmans, R. J. R&D Challenges for the 21st Century. *Soft Matter*, **2006**, *2*, 537.
8. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. *Chem. Soc. Rev*., 2007**,** *36* 1788.
9. Smith, H.V., *J. Am. Oil Chem. Soc*., **1985**, *62*, 351.
10. Sharma, V.; Kundu, P.P.; *Prog. Polym. Sci*., **2008**, *33*, 1199.
11. Luby, M. C.; Thachil, E. T.; *Des. Monomers Polym.*, **2000**, *3* 123.
12. Tullo, A.H. *Chem. Eng. News*, **2008**, *86*, 26.
13. Mele, G.; Vasapollo, G. *Mini-Rev. Org. Chem*., **2008**, *5*, 243.
14. S. Ramanujam, *PaintIndia*., **1961**, *11*, 47.
16. http://www.cardolite.com/
17. Saminathan, M.; Pillai, C. K. S. *J. Polymer Mater*., **2001**, *18*, 83.
18. Saminathan, M.; Krishna, C.; Pillai, C.K.S. *Macromolecules*, **1993**, *26*, 7103.
19. Suresh, K.I.; Kishanprasad, V.S. *Ind. Eng. Chem. Res*., **2005**, *44*, 4504.
20. Nayak, R.R.; Ray, G.; Guru, B.; Lenka, S. *Polym. Plast. Techno. Eng.*, **2004**, *43*, 261.
21. Bhunia, H. P.; Nando, G. B.; Chaki, T. K.; Basak, A.; Lenka, S.; Nayak, P. L. *Eur. Polym. J*., **1999**, *35*, 1381.
22. Bhunia, H. P.; Jana, R. N.; Basak, A.; Lenka, S.; Nando, G. B., *J. Polym. Sci., Part A: Polym. Chem*., **1998**, *36*, 391.
23. Sadavarte, N.V.; Halhalli, M.R.; Avadhani, C.V.; Wadgaonkar, P.P. *Eur. Polym. J.*, **2009,** *45*, 582.
24. Shingte, R.D.; Wadgaonkar, P.P. U.S. Patent 6,790,993, **2004**.
25. Mathew, J.S., Ph. D. Dissertation, University of Pune, Pune, India, **2001**.
26. Shingate R.D., Ph D. Dissertation, University of Pune, Pune, India, **2006**.
27 Shifrina, Z.B.; Rusanov, A.L.; *Russ. Chem. Rev*., **1996**, *65*, 599.
28. Hergenrother, P.M.; Havens, S.J. *Macromolecules.* **1994**, *27*, 4659.
29. Yokota, R.; Yamamoto, S.; Yano, S.; Sawaguchi, T.; Hasegawa, M.; Yamaguchi, H.; Ozawa, H.; Sato, R., *High Perform. Polym.*, **2001,** *13*, 61.
30. Sillion, B.; Rabilloud, G. in New Methods in Polymer Synthesis, Vol. 2, Ebdon, J.R.; Eastmond, G.C. (Eds.), Blackie, London, **1995**.
31. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. (Eds.), Polyimides Blackie & Sons Ltd.: Glasgow and London, **1990**.

32. Korshak, V. V.; Vinogradova, S. V.; Vygodskii, Y. S. *J. Macromol .Sci. Rev. Macromol. Chem*., **1974**, *C11*, 45.

33. Shen, Z.; Guo, M.; Cheng, S.D.; Harris, F.W. *Macromolecules,* **2007,** *40*, 889.

34. Yazdani-Pedram, M.; Soto, E.; Tagle, L. H.; Diaz, F. R.; Gargallo, L.; Radic, D. *Thermochimica Acta*, **1986**, *105*, 149.

35. Kim, D.H.; Jung, J.C. *Polym. Bull*., **2003**, *50*, 311.

36. Jung, J.C.; Lee, K.H.; Sohn, B.S.; Lee, S.W.; Ree, M. *Macromol. Symp.*, **2001**, *164*, 227.

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Research Guide

List of Publications

1. Synthesis and liquid-crystal-aligning properties of novel aromatic poly(amideimide)s bearing *n*-alkyloxy side chains. Anjana Sarkar, **Arvind S. More,** Prakash P. Wadgaonkar, Gyo J. Shin, Jin C. Jung, *Journal of Applied Polymer Science* **105** (4) 1793 (2007).

2. High Performance poly(styrene-*b*-diene-*b*-styrene) triblock copolymers from a hydrocarbon-soluble and additive-free dicarbanionic initiator. Rachid Matmour, **Arvind S. More,** Prakash P. Wadgaonkar, Yves Gnanou. *Journal of the American Chemical Society* **128** (5) 8158 (2006).

3. Free-standing gold nanoparticle membrane by the spontaneous reduction of chloroaurate ions by oxyethylene-linkage-bearing diamines at a liquid-liquid interface. P.R. Selvakannan, P. Senthil Kumar, **Arvind S. More,** Rahul D. Shingte, Prakash P. Wadgaonkar and Murali Sastry. *Advanced Materials* **16**, 966 (2004)

4. One pot, spontaneous and simultaneous synthesis of gold nanoparticles in aqueous and non-polar organic solvents using diamines-containing oxyehylene linkage P.R. Selvakannan, P. Senthil Kumar, **Arvind S. More,** Rahul D. Shingte, Prakash P. Wadgaonkar and Murali Sastry. *Langmuir* **20**, 295 (2004)

5. Synthesis and characterization of processable (co) polyazomethines (*To be communicated*) **Arvind S. More,** Prakash P. Wadgaonkar

6. Synthesis and characterization of organo-soluble polyamides (*To be communicated*) **Arvind S. More,** Prakash P. Wadgaonkar

7. Synthesis and characterization of processable polyesters (*To be communicated*) **Arvind S. More,** Prakash P. Wadgaonkar

Patent

1. Bisphenol compound and process for preparation thereof. *USP 7,446,234 B2*. **Arvind S. More,** Prakash P. Wadgaonkar

2. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecylbenzene and preparation thereof. *USP 7,297,822 B2*. **Arvind S. More**, Prakash P. Wadgaonkar

3. Process for the preparation of free standing membranes. *USP 7,182,894 B.* Pandian Senthil Kumar, Periasamy Selvakannan, **Arvind More**, Rahul Shingte, Prakash Wadgaonkar, Murali Sastry

4. A novel dicarbanionic initiator, a process for the preparation and use thereof. *USP 2007/0197723 A.* Y. Gnanou, R. Matmour, **Arvind S. More**, Prakash P. Wadgaonkar