DIFUNCTIONAL MONOMERS STARTING FROM CASHEW NUT SHELL LIQUID (CNSL) AND HIGH PERFORMANCE POLYMERS THEREFROM

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by

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December 2012

Dedicated to

My Parents

Certificate of the Guide

Certified that the work incorporated in the thesis entitled: **"Difunctional Monomers Starting from Cashew Nut Shell Liquid (CNSL) and High Performance Polymers Therefrom"**, submitted by **Nilakshi V. Sadavarte** was carried out under my supervision/ guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

December 2012
Pune

Prakash P. Wadgaonkar
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Declaration

I hereby declare that all the experiments embodied in this thesis entitled **"Difunctional Monomers Starting from Cashew Nut Shell Liquid (CNSL) and High Performance Polymers Therefrom"**, submitted for the degree of Doctor of Philosophy in Chemistry, to the University of Pune has been carried out by me at the Polymers and Advanced Materials Laboratory, 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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December, 2012   *Nilakshi Sadavarte*

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Abstract

The use of materials from renewable resources is becoming increasingly important as the world's leading industries and manufacturers seek to replace dwindling petrochemical-based feedstocks with agricultural-based materials. The quest for materials from renewable resources supports global sustainability and comes at a time when there is an excess capacity in the agricultural industry. Thus, the diversification of utilization of renewable resources into non-food uses, addresses both an important global environmental issue and lends stability for an important segment of our economy. The material utilization of agricultural products has to overcome many technical barriers that often resulted in products, which were either non-competitive in price or properties compared to petroleum-based products. In this respect, cashew nut shell liquid (CNSL) represents a renewable, widely available and relatively low cost organic natural raw material.

The main objective of the present research was to synthesize difunctional condensation monomers for high performance polymers starting from CNSL. 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 of *meta*-linkages in the polymer structure to decrease the rigidity of the polymer backbone and to inhibit chain packing by introducing "kinks" to the main chain, thus reducing the interchain interactions leading to enhanced solubility ii) the presence of pendent pentadecyl chain along the polymer backbone reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect and consecutively aid in improved solubility and processability, iii) the presence of pendent pentadecyl chain along the polymer backbone offers asymmetry leading to constitutional isomerism, which could impart interesting properties to the derived polymers. A series of difunctional condensation monomers *viz.,* aromatic diamines, diacid, diisocyanate, diol and dinitrile containing pendent flexible pentadecyl chain were designed and synthesized starting from CNSL. The synthesized difunctional monomers were utilized to synthesize step-growth polymers *viz.,* polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and polyesters containing pendent flexible pentadecyl chains. The effect of incorporation of pentadecyl chains on the solubility and thermal properties of the polymers was studied.

The thesis has been divided into the following eight chapters:

Chapter 1 presents a brief review of literature on CNSL chemistry, monomers and polymers starting from CNSL, additives based on CNSL, etc. A comprehensive review of literature on high performance polymers, *viz.*, polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and aromatic polyesters covering methods of synthesis, structure-property relationship, etc., is also presented.

Chapter 2 discusses scope and objectives of the present thesis.

Chapter 3 describes synthesis of difunctional monomers containing pendent pentadecyl chain starting from CNSL *viz,,*

  a. 4-Pentadecylbenzene-1,3-diamine,

  b. *N,N'*-(4-Pentadecyl-1,3-phenylene) bis(4-aminobenzamide),

  c. *N,N'*-(4-Pentadecyl-1,3-phenylene) bis(3-aminobenzamide),

  d. 2,4-Diisocyanato-1-pentadecylbenzene,

  e. 3,5-Diamino-4'-pentadecyl benzophenone,

  f. 3,5-Diamino-*N*-(4-pentadecylphenyl)benzamide,

  g. 2,2'(4-Pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid),

  h. 2-Pentadecylbenzene-1,4-diol, and

  i. 4-Methoxy-6-pentadecylisophthalonitrile.

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

Chapter 4 describes synthesis of polyimides containing flexible pendent pentadecyl chains by one-step solution polycondensation of 4-pentadecylbenzene-1,3-diamine with commercially available aromatic dianhydrides, *viz.*, 4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride in *m*-cresol. Inherent viscosities of polyimides were in the range 0.33-0.67 dL/g indicating formation of medium to reasonably high molecular weight polymers. Polyimides were soluble at room temperature in polar solvents such as *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), *m*-cresol as well as in common organic solvent such as CHCl$_3$. The presence of C$_{15}$ alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. Tough, transparent and flexible films could be cast from the solution of polyimides in CHCl$_3$. Wide angle X-ray diffraction patterns showed that polyimides containing pendent pentadecyl chains were amorphous in nature. Layered structure formation was observed due to the packing of pentadecyl chains in the polymer backbone. T$_{10}$ values for polyimides were in the range 470-480 °C indicating the good thermal stability of polymers. DSC analysis showed that the attached pentadecyl side chain induced the depression of T$_g$ (158-206 ^{o}C). Overall, internal plasticization effect of the pentadecyl chain was shown to be effective in achieving processable polyimides.

Chapter 5 is divided into two sections:

Chapter 5a provides study on synthesis and characterization of polyamides containing pendent pentadecyl chains obtained by the direct polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic diacids *viz.*, biphenyl-4,4'dicarboxylic acid, 4,4'-oxybisbenzoic acid, terephthalic acid and isophthalic acid by Yamazaki-Higashi reaction (phosphorylation reaction). Inherent viscosities of polyamides were in the range 0.35-0.56 dL/g indicating formation of medium molecular weight polymers. Polyamides were found to be soluble in DMAc, *N,N*-dimethylformamide (DMF), NMP, pyridine and *m*-cresol at room temperature or upon heating. The presence of pendent flexible pentadecyl chains brought about significant improvement in solubility of polyamides. Tough, transparent and flexible films of polyamides could be cast from DMAc solution. Wide angle X-ray diffraction patterns of polyamides showed typical broad halo at around $2\theta \approx 20^{\circ}$ suggesting that polymers were amorphous. In the small-angle region ($2\theta \approx 3^{\circ}$), sharp reflections were observed for polyamides. These reflections are characteristics of a typical layered structure resulting from the packing of the pentadecyl side chains. T_{10} values for polyamides were in the range 430-460 °C indicating good thermal stability of polyamides. Polyamides showed glass transition temperatures in the range 169-215 $^{\circ}$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 (169-215 $^{\circ}$C) and initial decomposition temperature (410-445 $^{\circ}$C) was observed which offers these polyamides a broad processing window.

Chapter 5b deals with synthesis and characterization of poly(azomethines)s containing pendent pentadecyl chains obtained by solution polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic dialdehydes *viz.*, terephthaldehyde, isophthaldehyde and a 50:50 mol % mixture of terephthaldehyde and isophthaldehyde. Inherent viscosities of poly(azomethine)s were in the range 0.33-0.38 dL/g indicating formation of medium molecular weight polymers. Poly(azomethine)s containing pendent pentadecyl chains were found to be soluble in CHCl$_3$, *m*-cresol, THF and pyridine at room temperature or upon heating. Transparent, flexible and stretchable films of the poly(azomethine)s could be cast from CHCl$_3$ solution. Wide angle X-ray diffraction patterns indicated that poly(azomethine)s containing pendent pentadecyl chains were amorphous in nature. The formation of layered structure was observed due to the packing of pentadecyl chains. T_{10} values for poly(azomethine)s were in the range 425-440 °C indicating good thermal stability. T_g values of poly(azomethine)s were in the range 16-55 $^{\circ}$C. A large difference in T_g and decomposition temperature of poly(azomethine)s offers a broad processing window. Poly(azomethine)s were characterized by optical band gap values (E_g) and they were found to be in the range 2.82-3.10 eV, which indicates their potential application in photovoltaic devices.

Chapter 6 describes synthesis and characterization of poly(amideimide)s containing pendent pentadecyl chains obtained by polycondensation of *N,N'*-(4-pentadecyl-1,3-phenylene)bis(4-aminobenzamide) and *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-aminobenzamide) with four commercially available aromatic dianhydrides, *viz.*, pyromellitic dianhydride, 4,4'-biphenyltetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride in DMAc employing conventional two step method *via* poly(amide amic acid) intermediate followed by thermal imidization. Reference poly(amideimide)s were synthesized by polycondensation of *N,N'*-(1,3-phenylene) bis(4-aminobenzamide) and *N,N'*-(1,3-phenylene) bis(3-aminobenzamide) with the same aromatic dianhydrides. Inherent viscosities of poly(amideimide)s containing pendent pentadecyl chains were in the range 0.37-1.23 dL/g in DMAc at 30 ± 0.1 ^{o}C indicating the formation of medium to high molecular weight polymers. Poly(amideimide)s containing pendent pentadecyl chains were found to be soluble in DMAc, DMF, NMP and pyridine and could be cast into transparent, flexible and tough films from their DMAc solution. Wide angle X-ray diffraction patterns exhibited broad halo indicating that the polymers were essentially amorphous in nature. X-Ray diffractograms also displayed sharp reflection in the small angle region ($2\theta \approx 3^{o}$) for poly(amideimide)s containing pentadecyl chains indicating the formation of layered structure arising from packing of flexible pentadecyl chains. The glass transition temperatures observed for reference poly(amideimide)s were in the range 331-275 ^{o}C and those for poly(amideimide)s containing pendent pentadecyl chains were in the range 185-286 ^{o}C indicating a large drop in T_g owing to the "internal plasticization" effect of pentadecyl chains. The temperature at 10 % weight loss (T_{10}), determined by TGA in nitrogen atmosphere, were in the range 460-480 ^{o}C indicating their good thermal stability.

Chapter 7 is divided into two sections:

Chapter 7a provides study on synthesis and characterization of poly(esterimide)s containing pendent pentadecyl chains obtained by direct polycondensation of 2,2'-(4-pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid) with five commercially available bisphenols, *viz.*, 4,4'-isopropylidenediphenol, 4,4'-(hexafluoroisopropylidene) diphenol, 4,4'-oxydiphenol, 4,4'-biphenol and 4,4'-(9-fluorenylidene) diphenol . Inherent viscosities of poly(esterimide)s were in the range 0.54-0.83 dL/g indicating formation of medium to reasonably high molecular weight polymers. Poly(esterimide)s containing pendent pentadecyl chains were soluble in polar solvents such as DMAC, NMP and *m*-cresol as well as in common organic solvent such as CHCl$_3$. Tough, transparent and flexible films of poly(esterimide)s could be cast from their CHCl$_3$ solutions. Wide angle X-ray diffraction patterns showed that poly(esterimide)s containing pendent pentadecyl chains were amorphous in nature. A loosely developed layered structure formation was observed due to the packing of pentadecyl chains. T_{10} values for poly(esterimide)s were in the range 450-470 °C indicating their good thermal stability. The glass

transition temperatures of poly(esterimide)s containing pentadecyl chains were in the range 145-198 ^{o}C.

Chapter 7b deals with synthesis of polyesters containing pendent pentadecyl chains obtained by direct polycondensation of 2-pentadecylbenzene-1,4-diol and aromatic diacids, *viz.,* isophthalic acid, a 50:50 mol % mixture of isophthalic acid terephthalic acid and terephthalic acid by the diphenylchlorophosphate-activated direct polycondensation. Inherent viscosities of polyesters were in the range 0.47- 0.53 dL/g indicating the formation of medium molecular weight polymers. Polyesters containing pendent pentadecyl chains were soluble at room temperature in organic solvents such as CHCl$_3$, THF, *m*-cresol, pyridine and nitrobenzene. Polyester derived from terephthalic acid was soluble in *m*-cresol, pyridine and nitrobenzene upon heating. Wide angle X-ray diffraction patterns showed that polyesters containing pendent pentadecyl chains were amorphous in nature. X-Ray diffractograms also displayed sharp reflection in the small angle region ($2\theta \approx 3^o$) indicating the formation of layered structure arising from packing of flexible pentadecyl chains. T$_{10}$ values for polyesters were in the range 430-450 °C indicating their good thermal stability. The glass transition temperature of polyesters containing pentadecyl chains were in the range 88-95 ^{o}C indicating a large drop in T$_g$.

Chapter 8 summarizes the results and describes salient conclusions of the investigations reported in this thesis.

Glossary

CNSL	Cashew nut shell liquid
HPP	High performance polymer
PI	Polyimide
PA	Polyamide
PAZ	Poly(azomethine)
PAI	Poly(amideimide)
PEI	Poly(esterimide)
PES	Polyester
m-**PDA**	1,3-Phenylenediamine
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
PAA	Poly(amic acid)
TPA	Terephthalic acid
TPAld	Terephthaldehyde
IPA	Isophthalic acid
IPAld	Isophthaldehyde
HMPA	Hexamethylphosphoramide
NMP	1-Methyl-2-pyrrolidinone
TPP	Triphenyl phosphite
TMA	Trimellitic anhydride
PTC	Phase transfer catalyst
PVC	Poly(vinyl chloride)
DPCP	Diphenyl chlorophosphate
BPA	2,2-Bis(4-hydroxyphenyl)propane or bisphenol-A
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

Organic chemicals play significant roles in our everyday lives. Since the middle of the 20th century, fossil oil and natural gas have served as the main raw material resources for production of chemicals.[1] Currently, almost all organic compounds can be derived from seven basic building blocks, including syngas from methane, ethylene, propylene, butanes, butylenes, butadiene, and BTX (which is a mixture of benzene, toluene, and xylene). These building blocks are obtained from natural gas, petroleum and coal.[2] There is a growing interest in the replacement of fossil-based chemicals with bio-based chemicals. Bio-based chemicals refer to the chemicals produced from biomass. Several factors including awareness of finite petroleum resources, availability of renewable resources, environmental imperatives and recent advances in processing technologies, are driving chemical industries to shift their feedstocks from petroleum to renewable counterparts for production of organic chemicals.[2]

It is well known that the reserves of oil, natural gas and coal are vast but still limited. Fossil energy sources will be depleted with their continuous exploitation. As a naturally abundant resource, biomass is a desirable alternative to petroleum for production of chemicals because of its sustainability and often low cost.[3] Supplementing petroleum consumption with renewable biomass resources is of critical importance in sustaining the growth of the chemical industry. The advantages of using biomass rather than petroleum to manufacture chemicals include opportunities for less pollution, no net CO_2 contribution to the atmosphere, and sustainable products and, in some cases, lower cost.[4] It has been found that many biomass-derived chemicals have economical advantages, particularly for some functionalized chemicals.[5] In addition, recent advances in process technologies, especially in fermentation technologies such as enzymatic engineering, metabolic engineering and genetic manipulation, provide new opportunities for producing a wide variety of industrial products from renewable plant resources.[6,7] The implementation of biorefinary concept in chemical manufacturing industries has led to a gradual shift towards the use of renewable biomass resources.[8] Similar to a petroleum refinery, a biorefinery integrates a variety of processing technologies to produce multiple bio-products from various biomasses.

Renewable resources, generally known as biomass, refer to any material having recent biological origin, including plant materials, agricultural crops, and even animal manure.[9] The most widely used renewable raw materials include: wood, proteins, cellulose, lignin, tannins, starch, oleochemicals such as vegetable oils, animal resources like chitin and chitosan.[10] A variety of chemicals have been prepared from these biomass-derived materials. For instance, bio-oil and syngas (mainly CO and H_2) are obtained by the pyrolysis of wood and agricultural wastes.[12] Bio-oil can be upgraded for applications as transportation fuels[11] while syngas can be converted to methanol,[13] both of which can be used in chemical industry. Currently, the annual worldwide production of biomass is estimated to exceed 100 trillion kilograms. In the United

States, the 250 billion kilograms of wasted plant biomass produced each year far exceeds the current total consumption of 100 billion kilograms for organic chemicals, plastic resins, and fibers.[6] However, presently, only 5 % of chemicals are derived from renewable resources.[14] Therefore, there is a huge potential for bio-based chemicals to share markets with their fossil-based counterparts.

Vegetable oils such as soybean, corn, tung, linseed, rapeseed, castor oil and cashew nut shell oil or cashew nut shell liquid (CNSL) have a wide variety of applications: fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers and construction materials.[15] Among these, CNSL, an agricultural by-product abundantly available in the country, is unique in that it contains a phenolic moiety with an unsaturated 15-carbon side chain.[16] CNSL can potentially replace phenol in many applications with equivalent or better results. Greater utilization of CNSL as a monomer for industrial polymer products can be an attractive proposal in view of its low cost, abundant availability (availability in the world: 1,25,000 tonnes per annum: availability in India: 15,000 tonnes per annum), and chemically reactive nature, amongst other attributes.[17]

The next section gives short overview regarding production, composition, chemistry, applications and various value added chemicals derived from CNSL.

1.2   Cashew Nut Shell Liquid

The liquid contained within the shell of the cashew nut is called as 'Cashew Nut Shell Liquid' (CNSL) which 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 nut. Cashew nut is a product of the cashew tree, *Anacardium occidentale* L.,[18] which is native to Brazil and is abundantly available in many parts of the world, such as Brazil, India, Bangladesh, Tanzania, Kenya, Mozambique, tropical regions of Africa, and South-East and Far-East Asia. In some of these regions, cashew is a popular plantation product, while some others import cashew nuts for processing. CNSL belongs to the family of long-chain hydrocarbon phenols which are phenolic lipids present in plants of families notably the *Anacardiacae*.[16] The plant may grow upto 12 m in height. Cashew nuts are the cash crop yielded by the tree, but it also produces cashew apple, wood suitable for boats, charcoal, etc., and a gum similar to gum arabic. The cashew apple is used in beverages, jams and jellies. The cashew apple juice has been reported to have antitumor and antimicrobial properties.[19] The cashew nut is greenish-gray in color and is attached to the cashew apple, which when ripe is either bright yellow or red. The pericarp of the nut consists of a coriaceous epicarp, spongy mesocarp and a stony endocarp (**Figure 1.1**).

| (a) | (b) | (c) |
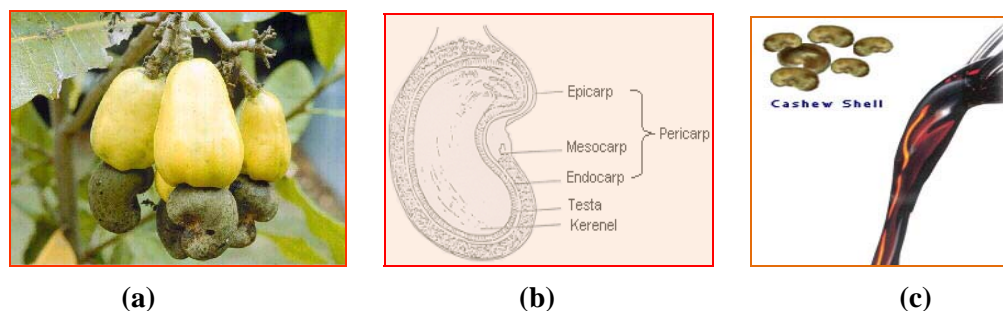
Figure 1.1 (a) Cashew fruit, (b) Cross section of cashew nut, (c) Cashew Nut Shell Liquid

The kernel is inside the shell and is covered with a brown skin known as testa. The nut has a kidney shape and may vary in size from 2.5 to 4 cm. CNSL constitutes 18-27 % of the total raw nut weight.[19]

1.2.1 Extraction of CNSL

Traditionally a number of methods have been employed to extract CNSL from the nuts. Two processes are used mainly in the extraction of CNSL: Hot oil process and roasting process in which CNSL oozes out from the shell.[20] Extraction of the oil by solvents such as benzene, toluene, petroleum hydrocarbon solvents or alcohols[21] or supercritical extraction of the oil using a mixture of CO_2 and isopropyl alcohol are the other reported techniques for extraction of CNSL.[22]

1.2.2 Refining of CNSL

Sulfides, nitrogenous materials and minerals contained in the crude CNSL directly affect the quality of the oil. Hence, CNSL is often subjected to chemical treatment with materials such as hydrocarbon sulfates and sulfuric acid before industrial use.[18] Several acid treatment processes have been found to reduce the poisoning or vesicant action.

The refined CNSL can be readily distilled under reduced pressure or may be readily hydrogenated, both processes leading to products with good colour stability.

1.2.3 Composition of CNSL

The earliest work published concerning the composition of cashew nut oil was by Staedeler.[23] Since then, many researchers have investigated the components of the oil.[24] Naturally occurring CNSL contains mainly four components: anacardic acid, cardanol, cardol, and 2-methyl cardol. They are monohydric or dihydric phenols or phenolic acids with a hydrocarbon side-chain at the *meta*-position. **Figure 1.2** represents the chemical structures of these compounds. Commercial-grade CNSL contains hardly any anacardic acid because of decarboxylation during the roasting process, which converts anacardic acid to cardanol.[25] The components of CNSL are themselves mixtures of four constituents differing in the side chain unsaturation, (**Figure 1.2**), namely saturated (~5-8 %), monoene (~48-49 %), diene (l6-17 %) and triene (29-30 %).[26]
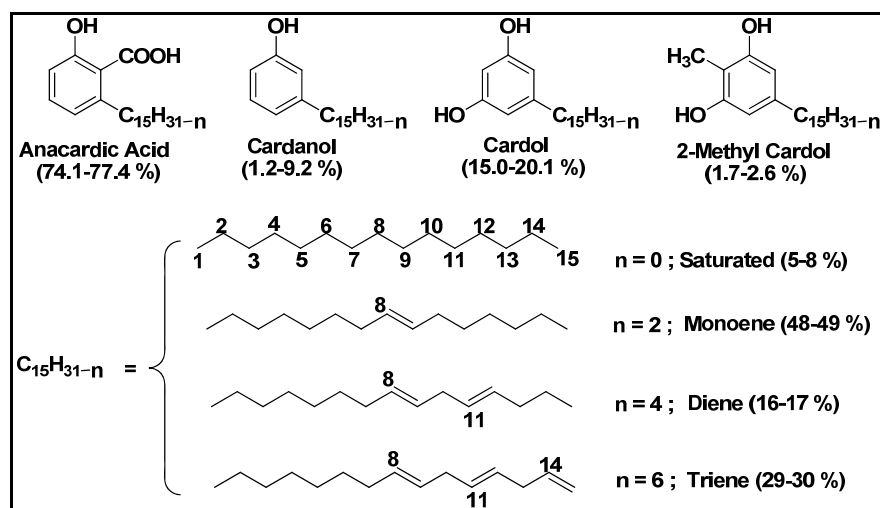
Figure 1.2 Components of CNSL

The composition of both natural and technical CNSL was studied by various workers[27] using mainly chromatographic techniques. Tyman and co-workers[28] have reported the presence of oligomeric and polymeric materials in significant amounts in natural and technical CNSL.

The phenolic composition of natural and technical CNSL[29] is given in **Tables 1.1**

Table 1.1 Phenolic composition of natural and technical CNSL (Values are in wt. %)

Component/ other material	Natural CNSL	Technical CNSL
Cardanol (%)	1.20	62.86
Cardol (%)	11.31	11.25
2-Methyl cardol (%)	2.04	2.08
Anacardic acid (%)	64.93	---
Polymer (and minor materials) by difference	20.3	23.8

1.2.4 Physical properties of CNSL

CNSL is a viscous oil with a characteristic smell, quite unlike other vegetable oils. It is opaque and when applied as a thin film, it is reddish-brown in color. It is immiscible with water but is miscible with most of the organic solvents. CNSL has germicidal and fungicidal properties. It is used traditionally as a cure for fungal attack of the feet in Kerala.[16]

1.2.5 Reactions of CNSL

CNSL constituents have been widely used as "synthon" for the preparation of many compounds with potential biological activities.[30] The chemical structure of CNSL is such that it can take part in a large number of reactions. CNSL components are of commercial importance since several useful industrial products can be produced from them. A few reviews have appeared summarizing the reactions of CNSL.[31] The reactions given in the following sections are based on cardanol, and are summarized in **Scheme 1.1**
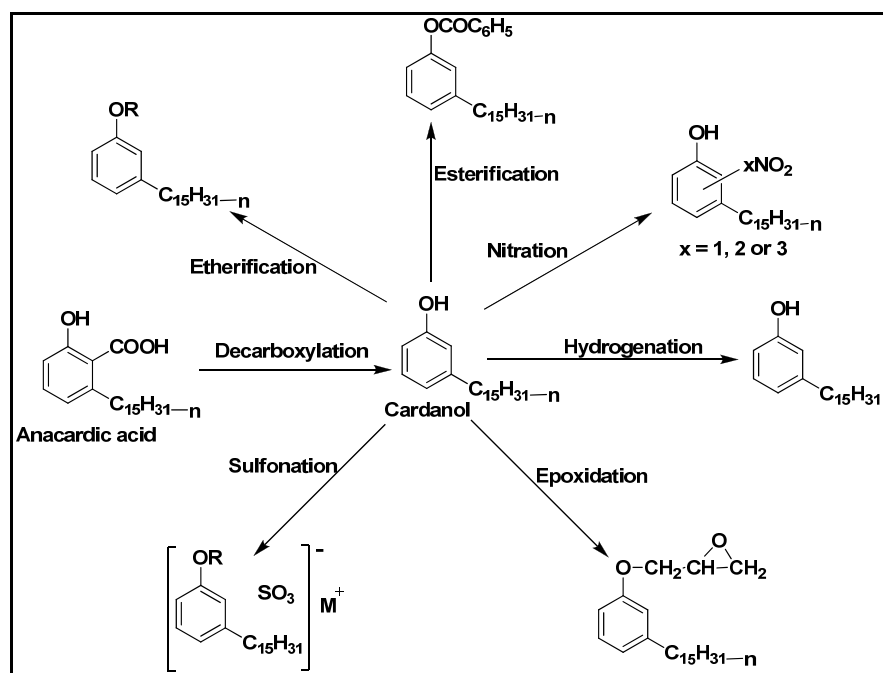
Scheme 1.1 Reactions of Cardanol

1.2.5a Decarboxylation

During the extraction or refining processes, anacardic acid decarboxylates to cardanol upon heating. Distillation of the crude CNSL also leads to decarboxylation as the distillate is found to contain mainly cardanol.[32]

1.2.5b Hydrogenation

Hydrogenation is generally carried out using hydrogen and catalysts such as copper, nickel, palladium, and platinum.[33] Hydrogenated cardanol can be separated by distillation, as is done with crude CNSL.

1.2.5c Sulfonation

CNSL derivatives can be sulphonated to yield alkyl aryl sulphonic acid or their metal salts.[34] Cardanol containing sulfonic acid group was found to act as functionalized dopant for polyaniline.[35]

1.2.5d Nitration

Direct nitration of cardanol or CNSL leads to simultaneous oxidation and polymerization. But nitration of hydrogenated cardanol gives the trinitro-derivative, which is a very useful product.[36]

1.2.5e Halogenation

Halogenation of CNSL can be accomplished with comparative ease. For example, chlorine gas can be passed through CNSL dissolved in kerosene to obtain 15 % (w/w) chlorination.[37] Chlorinated CNSL reacts with active methylenes at a faster rate and is flame-resistant. The halogenation is accomplished by polymerization and thickening.

1.2.5f Etherification

Cardanol can be reacted with dialkyl sulfates in the presence of alkalis to give

corresponding ethers.[38] Similar reactions can be carried out on hydrogenated cardanol.

1.2.5g Esterification

Cardanol can be reacted with acid chlorides in the presence of alkali to give cardanol esters.[39]

1.2.5h Epoxidation

Epoxidation of cardanol can be accomplished by using epichlorohydrin in the presence of caustic soda as a catalyst.[40]

1.2.5i Polymerization

A variety of techniques can be used to polymerize CNSL. The presence of the aliphatic side-chain gives these resins pronounced hydrophobicity, which is a valuable property for many applications. In general, polymers from CNSL and cardanol have been prepared either by condensation with formaldehyde to get phenolic resins with high hardness and excellent heat resistance, or by functionalization to get epoxide resin with good anticorrosive properties, or by oxidative polymerization using enzymatic catalysts.[41] Fe(III)-salen complex can also catalyze an oxidative polymerization of cardanol to give a soluble polyphenol containing the unsaturated alkyl group in the side chain.[42] Recently, Bai et al[43] have reported solvent free polymerization of cardanol using Lewis acid such as $FeCl_3$.

1.2.5j Miscellaneous reactions

Pillai et al[44] investigated the phosphorylation of cardanol and its condensate with phosphoric acid and the prospective applications of the products. Balachandran et al[45] demonstrated that cardanol is a valuable raw material for generating a variety of soft nanomaterials such as nanotubes, nanofibers, gels and surfactants. These nanostructures may then serve as templates for the synthesis of additional nanomaterials.

Urethanes were synthesized from CNSL, as in the case of other hydroxyl compounds, by the reaction with isocyanates.[46] Acetals of CNSL were prepared by the reaction of dimethyl acetal or polymeric acetals such as poly-vinyl acetal or poly-vinyl butyral. 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, less dermatic effect on the skin, and faster reactions compared with phenolic resins. Isocyanates were prepared from hydrogenated cardanol by reaction with SO_2Cl_2 followed by nitration, methylation, reduction and phosgenation.[47] Azo dyes were made by the reaction of phenols with primary aromatic amines after diazotization of hydrogenated cardanol.[48] By reacting CNSL with triethylene-tetramine, phenolic polyamines can be prepared.[49]
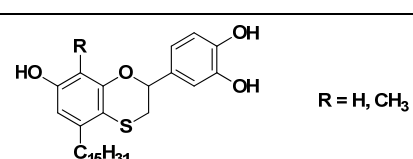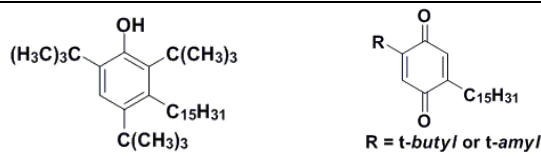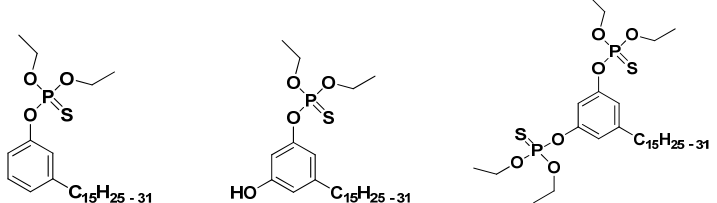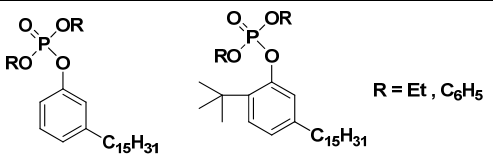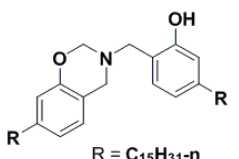
1.2.6 Applications

Polymers derived from CNSL have certain outstanding properties which make them unique for many applications.[50] The most attractive aspect of CNSL is the abundant availability and low cost. 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 a desirable component in brake lining 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.[35] 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. 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.[35] Applications of CNSL-based materials have been reviewed in the literature.[35,50]
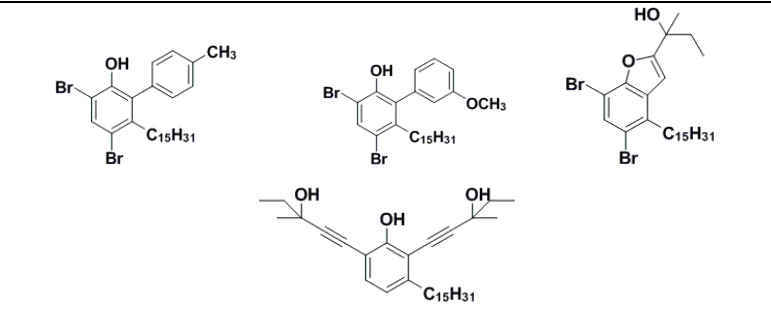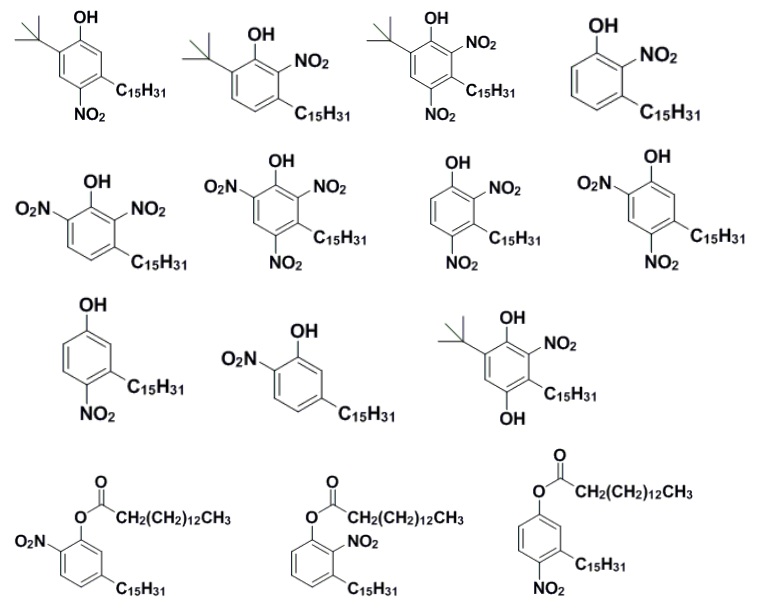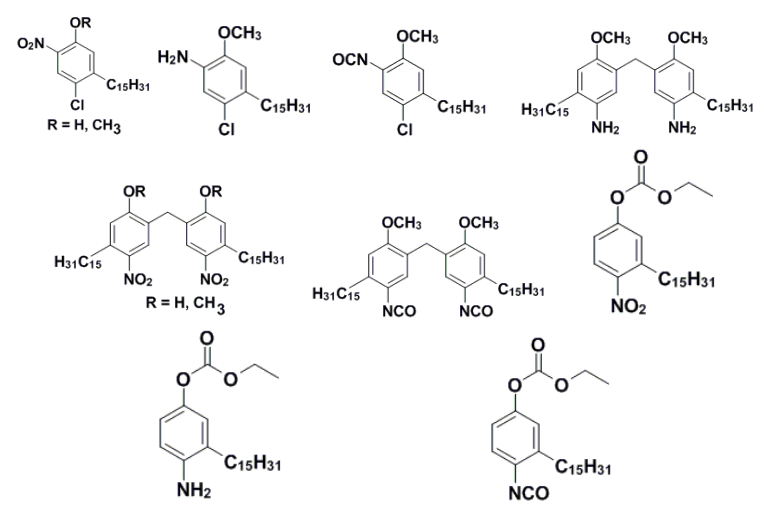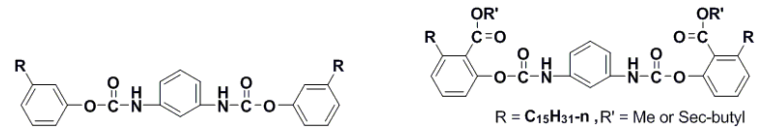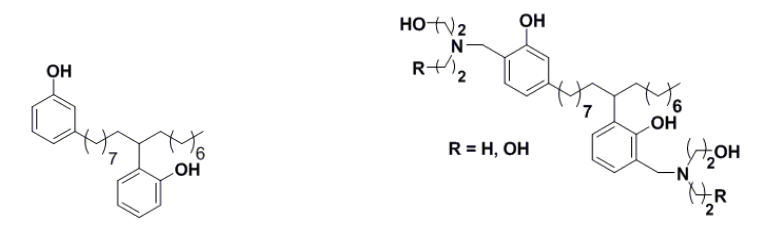
Considerable attention from polymer scientists throughout the world is devoted to utilize potential attributes of CNSL as a substitute for petrochemical derivatives and has found use in many areas. Of late, CNSL has been used in the preparation of many specialty materials such as liquid crystalline polyesters, nanotubes, cross-linkable polyphenols, polyurethanes and a range of other specialty polymers and additives.[51] 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 1.2**

Table 1.2 CNSL-based chemicals

No.	CNSL-based Chemicals	Applications	Ref
1.	R = H, CH$_3$	Antioxidant	52
2.	R = t-*butyl* or t-*amyl*	Antioxidant for gasoline stabilisation	53, 54
3.		Antioxidants for poly(methylmethacrylate)	55
4	R = Et , C$_6$H$_5$	Antioxidants	56
5.	R = C$_{15}$H$_{31}$-n	Polybenzoxazines	57
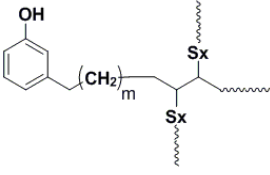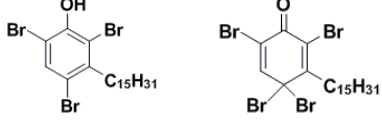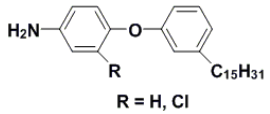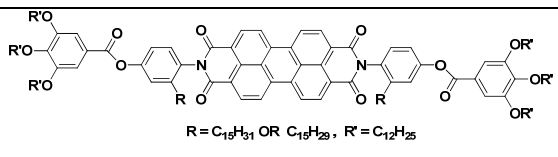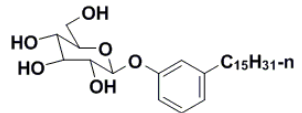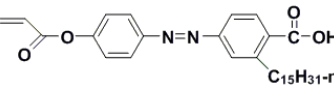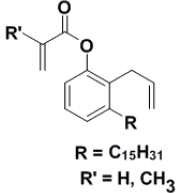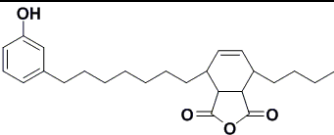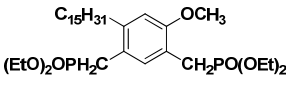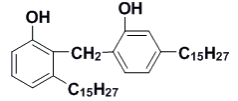
6.	R = C$_{15}$H$_{31}$, C15H$_{29}$, C$_{15}$H$_{27}$, C$_{15}$H$_{25}$	Bisbenzoxazines	58
7.		Surfactant	59, 60
8.	R = C$_{15}$H$_{31}$	Anioninc surfactants	61
9.	m = 1-12 n = 0, 2,4 and 6	Surfactant composition	62
10.		Anionic surfactant for polypyrrole nanospheres	63
11.	R = C$_{15}$H$_{31}$, C$_{15}$H$_{29}$	Urethane methacrylates	64
12.	R = C$_{15}$H$_{31}$, C$_{15}$H$_{29}$	Urethane-methacrylate crosslinkers	65
13.	R = C$_{15}$H$_{31}$-n	Foundry binder, Novolac resins	66
14.		Polyol for polyurethane	67

15.		Thiobisphenols	67
16.		Quaternary ammonium salts as PTC	68
17.		Cardanol-grafted natural rubber	69
18.		Resin to modify the properties of elastomers	70
19.		Antistatic agents for polycarbonates	71
20.		Chromogenic azocrown ethers	72
21.		Biscardanol derivatives	73
22.		Cardanol derivatives	74
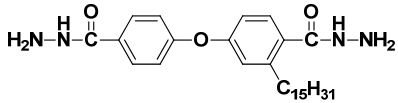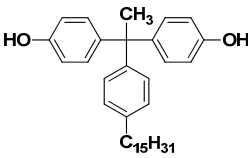
		Cardanol derivatives	74
23.		Cardanol derivatives	75
24.		Cardanol derivatives	47
25.		Blocked isocyanates	77
26.		Mannich bases	78

27.		Conversion of cardols into lasiodiplodin	79
28.		Plasticizer extenders for PVC	80
29.	R' = C₁₅H₂₅₋₃₁ OR (H₂C)₇ C₆H₁₃ R = H, COCH3	Plasticizer for PVC	81
30.		Cardanol-furfural resin	82
31.	R1 = H, t-*butyl*, t-*amyl*, R2 = CH3, Ph	Cardanol based fulleropyrrolidines	83
32.		Resins	84
33.	n = 0, 1, 2.....for dimer, trimer, etc	Cardanol based phenolic resin	85
34.		Cardanol based porphyrins as natural precursors for olefin metathesis	86
35.	R = Et , X = O R = Et , X = S R = Ph , X = O	New biodiesel antioxidant	87

36.		Isocyanates	76
37.		Diisocyanates	88
38.		Polyaniline-clay composite	89
39.		Telechelic urethane acrylate	90
40.		Lipophilic epoxy modifier for viscosifiers in drilling fluids	91
41.		Molecularly imprinted polymers, polycardanyl acrylate	92
42.		Used as a dietary supplement with health-promoting and disease-preventive properties	93
43.		Use in pigment dispersions	94
44.		Hydrosilylation products for grafting self-assembled monolayers onto silicon surfaces	95
45.		Hydrophobically modified polyacrylic acid using 3-pentadecyl cyclohexyl amine	96
46.		Curing agent	97
47.		Curing agent	98

48.		Cardanol polysulfide	99
49.		Brominating agent	100
50.		Petroleum marker dyes	101
51.		Reagent for end-capping of polyimides	102
52.		Cardanol-functionalized fluorescent, room-temperature liquid-crystalline perylene bisimides	103
53.		Monomer for membrane forming amphiphiles	104
54.		Development of soft nanomaterials from bio-based amphiphiles	105
56.		Liquid crystalline polymer with crosslinked network structures	106
57.		UV-curable compositions and adhesive formulations	107
58.		Polyfunctional compounds	108
59.		Monomer for poly(*m*-phenylenevinylene)s	109
60.		Monomer for novolac-type resins	110

61.		Monomer for polyamides, polyimides	111
62.		Monomer for polyamides	112
63.		Dopant (Polyaniline)	113
64.		Monomers for polyether and polyurethanes	114
65.		Monomer for polyesters	115
66.		Monomer for polyurethanes	116
67.		Monomers for polyimides and polyamides	111
68.		Monomer for polyimides	117
69.		Monomer for polycarbonates, polyesters, etc	118
70.		Monomer for polyimides, polyamides, etc.	119
71.		Monomer for polyesters and polyurethanes	120
72.		Monomer for poly(azomethine)s	121
73.		Monomer for polyamides	122

74.		Monomer for poly(amideimide)s, polyhydrazides, poly(oxadiazole)s	123
75.		Monomer for polyesters	124

Considering the special structural features of CNSL and need for finding better opportunities for an appropriate utilization of this material, strategies can be developed to design new cost effective monomers starting from CNSL and high performance polymers therefrom.

The next section will provide brief information about high performance polymers.

1.3   High performance polymers

One of the speciality areas within polymer science is that of high performance polymers. It has been recognized as a separate area within polymer chemistry for more than 50 years. Like many scientific disciplines, it has received most of its momentum from the space program owing to the need for ablative systems, high temperature adhesives and coating and heat- and flame-resistant fibers.

As a loose definition, high performance polymers include all polymeric materials which exhibit thermal stability above 200 ^{o}C and in addition have outstanding mechanical, electrical, optical, surface and rheological properties.[125] High performance polymers such as polyimides, poly(amideimide)s, poly(esterimide)s, polyamides, poly(azomethine)s and polyesters with high thermal stability and good mechanical properties have been identified for a variety of applications, e.g., as engineering plastics for aerospace industries, in optical and electronic devices and also as films or membranes.[126]

The high regularity and high rigidity of the backbone of high performance polymers results in strong interchain interactions, high melting points and low solubility. Therefore, in spite of having excellent combination of properties, most of the high-performance polymers have some serious drawbacks, e.g. insolubility in common organic solvents, intractability and infusibility that make their processing difficult and often limit their utility in various advanced technological applications.

In order to improve processability of high performance polymers, several approaches have been used (**Figure 1.3**) which include: (1) the insertion of flexible spacers between the rigid units; (2) the insertion of bent or 'crankshaft' units along the aromatic backbone; and (3) the introduction of bulky side groups or flexible side chains to the aromatic backbone.
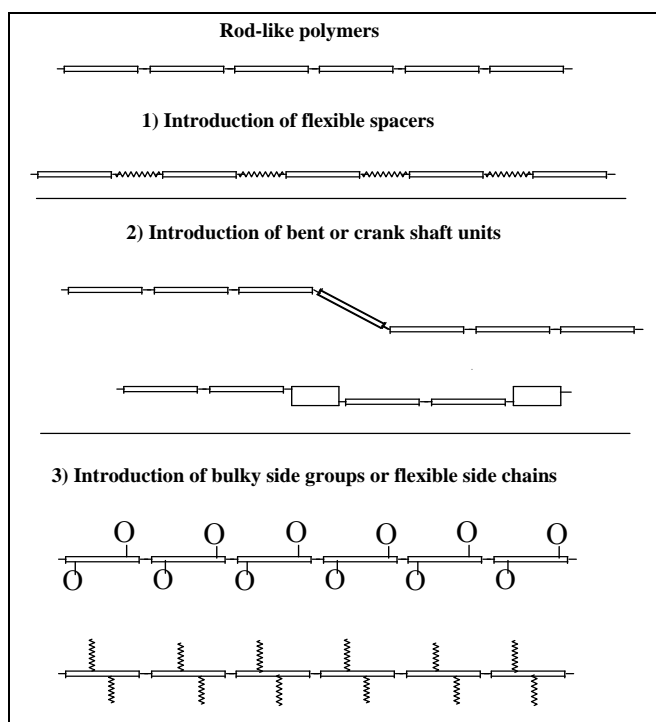
Figure 1.3 Approaches for improving processability of high performance polymers

These structural modifications disrupt molecular symmetry; inhibit close chain packing of the chains and increase free volume consequently leading to improved solubility and processability. In commercial materials one frequently sees the sacrifice of thermal stability to improve the ease of processing. Hence, recent research has been directed not towards higher stability in polymers but towards retention of stability as much as possible while introducing solubility and moldability.

The subsequent sections deal with developments in the chemistry of high performance polymers that have led to improvements in terms of processability. The main focus of these discussions is on polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimides)s and aromatic polyesters.

1.4   Polyimides

The earliest of the high performance polymers, and now one of the most common commercial materials, is polyimide which was initially synthesized by DuPont and marketed under the tradename H-film and later as Kapton.[125] Since then, aromatic polyimides received great attention due to their outstanding thermo-oxidative stability, unique electrical properties, high radiation and solvent resistance, and high mechanical strength.[127,128] Polyimides have found many applications in microelectronics, aircraft and the space industry, and new applications in the field of separation techniques are currently under development.[129] These polymers are further used in the electronics industry for flexible cables, as an insulating film on magnetic wire and for medical tubing. Examples of commercial polyimide films include Apical®, Kapton®, UPILEX®, VTEC PI®, Norton TH®and Kaptrex®. However, their applications have been limited in many

fields because aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass transition or melting temperatures, which preclude melt processability by injection moulding or extrusion. Hence, one of the drawbacks in using aromatic polyimides is their poor processability. Accordingly, great efforts have been made to improve the processing characteristics of intractable polyimides.[129]

1.4.1 Synthesis of polyimides

Polyimides are generally derived from the step or condensation reaction of organic diamines and tetracarboxylic anhydrides.

1.4.1.1 Two-step method *via* poly(amic acid)

This is the most popular method for the synthesis of polyimide. The first step involves reaction of a dianhydride and a diamine under ambient conditions in a dipolar aprotic solvent such as *N,N*-dimethylacetamide (DMAc) or *N*-methylpyrrolidinone (NMP) to yield the corresponding poly(amic acid), which is then cyclized into the final polyimide. The process for most extensively developed Kapton® polyimide utilizes the monomers pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) and is illustrated in **Scheme 1.2**.
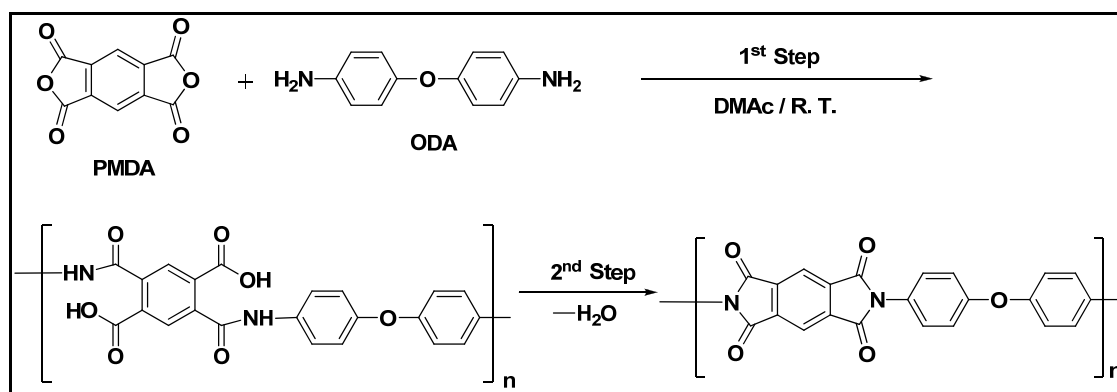
Scheme 1.2 Synthesis of Kapton polyimide by a two-step method

1.4.1.1a First step: Formation of poly(amic acid)s

The reaction mechanism involved in the poly(amic acid) formation is the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride species which results in opening of the anhydride ring to form an amic acid group. The formation of the poly(amic acid) is an equilibration reaction where the forward reaction is thought to start with the formation of a charge transfer complex between the dianhydride and the diamine. The more the electrophilic nature of the dianhydride, the more susceptible it is to nucleophilic attack by the diamine. The reactivity of the dianhydride monomer has been related to its electron affinity, higher values suggest greater reactivity of the dianhydride.[130] Strong electron withdrawing groups activate the anhydride for nucleophilic acyl attack on the anhydride carbonyl. The reactivity of the diamine is related to its basicity. Highly basic amines (e.g. aliphatic amines) may form salts during the initial stages of the reaction, upsetting the stoichiometry and preventing the attainment of high molecular weight.

Solvents also play an important role in the reaction. The common solvents in poly(amic acid) preparation are dipolar aprotic solvents such as DMAc and NMP that can form strong hydrogen bonded complexes with the carboxyl group that shift the equilibrium to the amic acid side. As expected, the reaction rate is faster in more basic solvents.[131] Several other minor important side reactions concurrently proceed with the main reaction. These side reactions may become significant under certain conditions particularly when the main reaction is slow because of low monomer concentration and low monomer reactivity.

1.4.1.1b Second step: Imidization of poly(amic acid)s

(i) Thermal imidization of poly(amic acid)s

This is the most common method used for the conversion of poly(amic acid) to polyimide which involves gradual heating of the poly(amic acid) to 250-350 $^{\circ}$C, depending upon the stability and the glass transition temperature of the polymer.[132] The events occurring during the heating include evolution of solvent and dehydrative cycloimidization. The imidization is accomplished through nucleophilic attack of the amide nitrogen on the acid carbonyl carbon with elimination of water.

This method is suitable for polyimides in the form of films, coatings and powders in order to allow the diffusion of by products and solvent without the formation of voids in the final polyimide products. The problem of film cracking as a result of shrinking can be avoided by carefully controlling the curing profile.

(ii) High temperature solution imidization of poly(amic acid)s

Polyimides resulting from solid state thermal imidization often demonstrate insolubility, infusibility and thus poor processability. To overcome these drawbacks, high temperature solution imidization has been successfully utilized.[133] Cyclodehydration is conducted by heating a poly(amic acid) solution in a high boiling solvent at temperatures of 160-200 °C, in the presence of an azeotropic agent. Compared with bulk thermal imidization, the lower process temperatures and greater mobility in solution ensures the avoidance of degradation and side reactions.

(iii) Chemical imidization of poly(amic acid)

This method involves the use of a chemical dehydrating agent in combination with basic catalyst to promote ring closure reactions in temperature ranges of 20-80 $^{\circ}$C, which is effective for either soluble or insoluble polyimides.[134] Various reagents have been employed including acetic anhydride, propionic anhydride, and *n*-butyric anhydride as dehydrating agents and pyridine, triethylamine and isoquinoline as basic catalysts.

The solubility of polyimides prepared by different imidization methods differs to some extent. In general, polyimides derived from chemical imidization are more soluble than those prepared by thermal imidization. However, the thermal properties of polyimides from thermal imidization, including T_g and decomposition temperatures, are superior to those of polyimides obtained by chemical cyclization. The difference can be ascribed to morphological changes in the

polymers, such as increased ordering from molecular aggregation of the polymer chain segments that occurs during thermal imidization.[135]

1.4.1.2 One-step high temperature solution polymerization

This technique is employed for polyimides that are soluble in organic solvents at polymerization temperatures.[136] The process involves heating a stoichiometric mixture of dianhydride and diamine monomers in a high boiling solvent or a mixture of solvents at 180-220 °C.[137] The imidization proceeds rapidly at these temperatures and water generated due to the reaction is distilled off continuously as an azeotrope alongwith the solvent. The commonly utilized solvents are nitrobenzene, *m*-cresol and dipolar aprotic amide solvents. Hasanain et al[138] have reported salicylic acid as a powerful solvent for one-step synthesis of polyimides. The imidization still proceeds *via* the amic acid route although the concentration of amic acid at any time is very small. The amic acid group rapidly converts to an imide or reverts back to amine and dianhydride. The high temperature solution polymerization is often performed in the presence of catalysts such as quinoline, tertiary amines, alkali metals and zinc salts of carboxylic acids. This process is especially useful for polymerization involving unreactive dianhydrides and diamines. An interesting feature of this method is that there is an absence of "defect sites," of either amic acid or isoimide type, in the resulting polymers. Another advantage of the high temperature solution method is that it allows high molecular weight polyimides to be prepared from monomers with sterically or electronically-hindered groups that would otherwise be hard to successfully polymerize *via* the two-step route. Polyimides whose T_m is ≤ 300 °C or whose T_g is ≤ 250 °C can be prepared by one step melt polycondensation using the extrusion molding method.[139]

1.4.1.3   Other synthetic routes to prepare polyimides

1.4.1.3a Polyimides *via* derivatized poly (amic acid) precursors

The solutions of poly(amic acid)s are susceptible to hydrolytic degradation. This process breaks down the molecular weight of the amic acid and resulting polyimide.[140] To prevent this, efforts have been made to derivatize the amic acid. The preparation of derivatized poly(amic acid)s can be achieved by one of two general pathways: 1) Formation of the poly(amic acid) followed by derivatization of the *ortho*-carboxylic acid groups along the polymer backbone; and 2) Derivatization of the monomer and subsequent activation to allow the monomer to enter a polymer forming reaction to yield the desired polymer. Poly(amic acid ester)s can be isolated by precipitation without degradation and can be stored for an indefinite period at ambient temperatures. Conversion of esters of poly(amic acid) to polyimide readily proceeds thermally but at a slower rate and generally requires a temperature significantly higher than 200 °C. The increased imidization temperature regime offers a wider processing window.

1.4.1.3b Polyimides *via* polyisoimide precursors

In general, polyisoimides are significantly more soluble and possess lower melt

viscosities and lower glass transition temperatures than the corresponding polyimides, mainly because of their lower symmetry and structural irregularity.[141] These features make it possible to prepare rigid rod-like polyimides using soluble and processable polyisoimides. Polyisoimides are formed from the corresponding poly(amic acid), using a dehydrating agent, such as trifluoroacetic anhydride, in conjunction with triethylamine.[142] A polyisoimide can easily be converted to the corresponding polyimide *via* thermal treatment at >250 °C. Alternately, polyisoimides have been reacted with alcohol to produce poly(amic acid ester)s, which could then be thermally converted to polyimides.[143]

1.4.1.3c Polyimides from diester-acids and diamines (Ester-acid route)

Synthesizing polyimides *via* the ester-acid route involves derivatizing the anhydride to ester-acid and subsequently allowing the diamine to react, which yields the desired poly(amic acid) and polyimide. Polyimides are frequently synthesized *via* the ester-acid monomer route because this process is relatively tolerant of water in solvents and reactors.[144] In the initial stage of esterification, the dianhydride is simply refluxed in an excess of alcohol. It should be noted that the rate is greatly enhanced by addition of an amine catalyst, e.g., triethylamine, which acts as an acid acceptor. Once the excess alcohol has been evaporated, the resulting diester diacid is then reacted in solution with a suitable diamine to form a poly(amic acid). A polar, aprotic solvent is needed for the similar reason as for poly(amic acid) route. Polyimide is obtained by thermal or high temperature solution imidization described earlier. Previously, it was thought that the mechanism of amic acid formation from diester-diacid and diamine proceeds by the nucleophilic attack of ester carbonyl by amine resulting in poly(amic acid) with the elimination of alcohol. However, it was later discovered that the anhydride functional group was formed at elevated temperatures *in situ* from the *ortho* ester-acid.[145] The anhydride then reacts with the diamine to yield a poly(amic acid).

1.4.1.3d Polyimides from tetracarboxylic acids and diamines

This synthetic route for producing aliphatic-aromatic polyimides with high molecular weight involves combining aromatic tetracarboxylic acids and aliphatic diamines to form salts, similar to the synthesis of nylons *via* nylon salts. The salts were thermally imidized under high pressure at temperatures above 200 °C to form polyimides (**Scheme 1.3**).
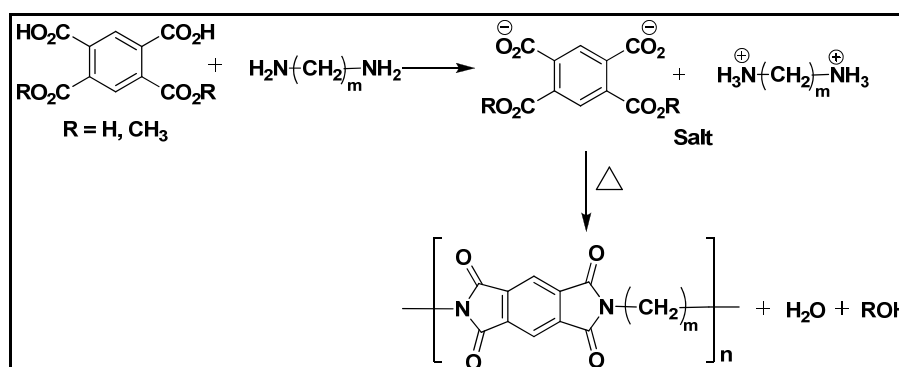
Scheme 1.3 Polyimide synthesis from tetracarboxylic acid-diamine salt

It was observed that the imidization rate is very fast, the formation of poly(amic acid)s and imidization takes place at the same time.[146] In the one-step melt polymerization of polyimides, it is advantageous to use tetracarboxylic acids because high molecular weight poly(amic acid) intermediates of very high melt viscosities are not formed during the initial heating stage. Another advantage of using tetracarboxylic acids is their stability and ease of purification. Many of them can be readily recrystallized from hot water.

1.4.1.3e Polyimides from diisocyanates and dianhydrides

The synthesis of polyimides can be accomplished using diisocyanates in the place of diamines (**Scheme 1.4**).
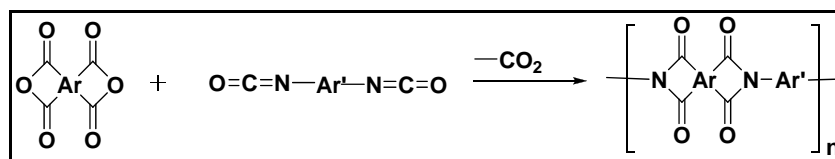
Scheme 1.4 Synthesis of polyimides from diisocyanates and dianhydrides

It has been observed that the reaction of diisocyanate and dianhydride proceeds at relatively moderate temperature in dipolar aprotic solvents.[147] One disadvantage of this method is that there are few diisocyanates to choose from, compared to the numerous diamines available from synthetic or commercial sources.

1.4.1.3f Polyimides from diamines and dithioanhydrides

In addition to dianhydrides, dithioanhydrides can be used to prepare polyimides. Dithioanhydrides can be prepared by reacting the corresponding aromatic tetracarboxylic acids with sodium sulfide.[148] Polyimides were then obtained after removing the hydrogen sulfide by heating, as shown in **Scheme 1.5**
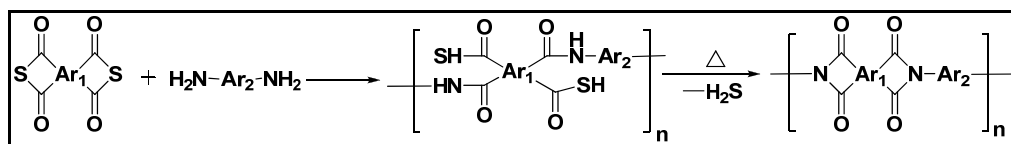
Scheme 1.5 Synthesis of polyimides from dithioanhydrides and diamines

The poly(amic thiocarboxylic acid) cannot be removed during the reaction due to its high reactivity. The inherent viscosities of polyimides derived from dithioanhydrides were comparable to those prepared by the traditional two-step method.[149]

1.4.1.3g Polyimides from diamines and bismaleimides (Michael addition reaction)

The Michael addition of diamines to bismaleimides is another method of preparing polyimides (**Scheme 1.6**).
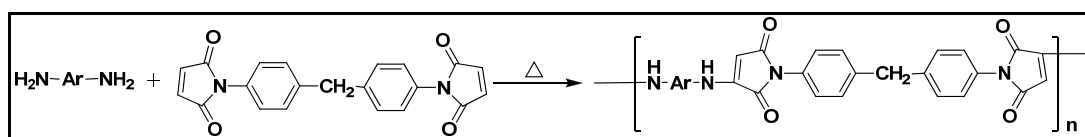
Scheme 1.6 Synthesis of polyimides from diamines and bismaleimides

In contrast to the above methods, the imide ring of polyimides is not formed during the

polymerization but arises from the maleimide structure. Bella et al. reported a polyimide synthesis *via* the Michael addition reaction.[150] This approach is a general strategy for achieving thin films from insoluble or reactive functional polyimides.

1.4.1.3h Polyimides from bisdienes and dienophiles (Diels-Alder reaction)

The Diels-Alder reaction is a thermally driven [4+2] cycloaddition reaction between a dienophile and a conjugated 1,3-diene.(**Scheme 1.7**)
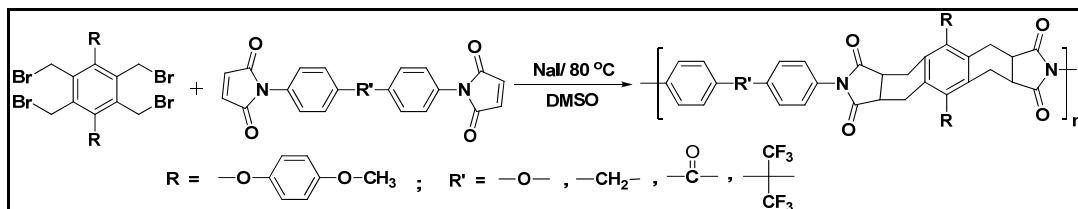
Scheme 1.7 Synthesis of polyimides by Diels-Alder reaction

The Diels-Alder reaction provides a simple, efficient, and clean procedure to generate new bonds by inter- or intra-molecular coupling and it represents one of the most useful synthetic methods in organic chemistry.[151] In this reaction, a dienophile is added to a conjugated diene to give a cyclic product called an adduct.

1.4.1.3i Polyimides from silylated diamines and dianhydrides

The first synthesis of aromatic polyimides using silylated diamines was disclosed by Boldebuck and Klebe[152] in the patent literature in 1967. The *in situ* silylation of aromatic diamines with trimethylchlorosilane (TMSCl) in the presence of a base, such as pyridine, has proved to be a facile and convenient method to obtain high molecular weight polyimides.[153] When sterically hindered amines or amines with strong electron-withdrawing groups are used, silylation can improve the low reactivity of the diamines.[154] The use of silylated amines has several disadvantages, such as the need to synthesize and purify activated monomers, which are difficult to isolate because of their sensitivity to moisture. Silylated amines are also more expensive than diamines.

1.4.1.3j Other approaches for synthesis of polyimides

Palladium- or nickel-catalyzed carbon-carbon coupling reactions for synthesis of polyimides have been reported in the literature.[155]
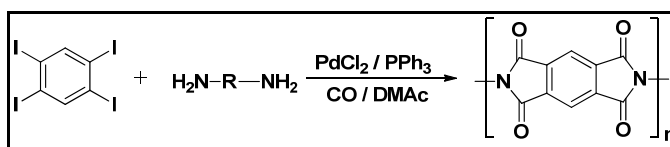
Scheme 1.8 Synthesis of polyimides by Pd-catalyzed carbon-carbon coupling reaction
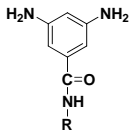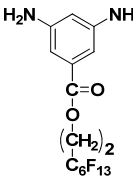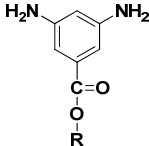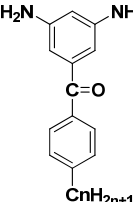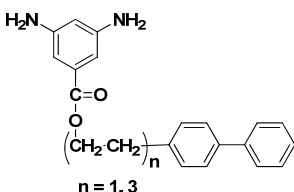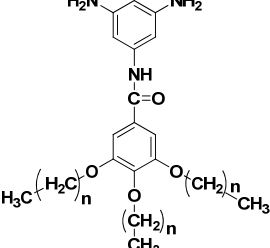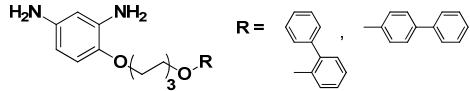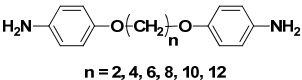
The reaction of di(hydroxyalkyl) compounds and diimides under Mitsunobu conditions (Mitsunobu reaction) gives rise to the direct formation of polyimides in a single step. These reaction conditions offer an alternative and convenient method for the design of NLO-functionalized polyimides.[156] Tsuda et al[157] reported the use of ionic liquids as solvent for
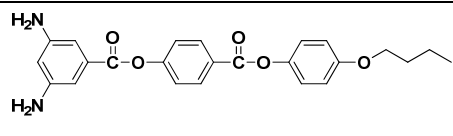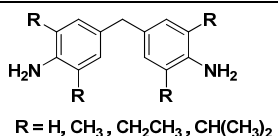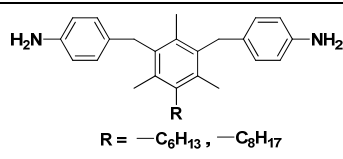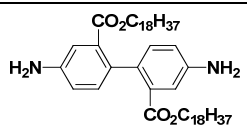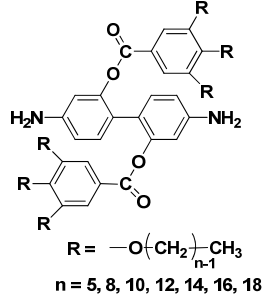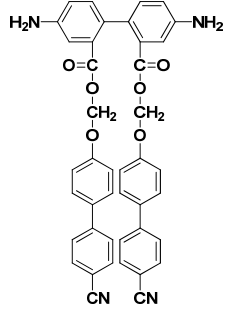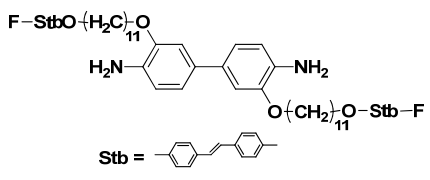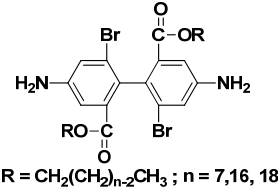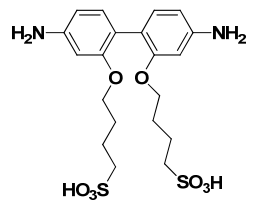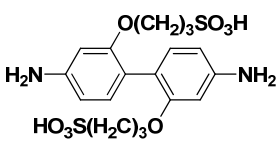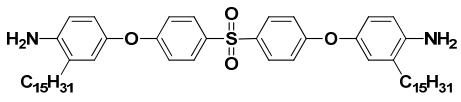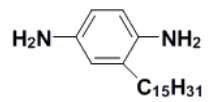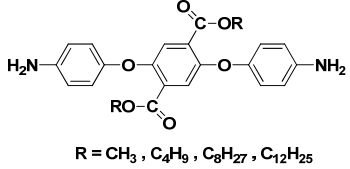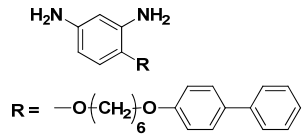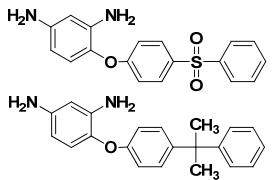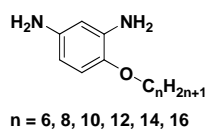
synthesis of polyimides. Chiefari et al[158] demonstrated the use of water as solvent for the synthesis of polyimides. Li et al[159] reported synthesis of polyimides *via* microwave assisted polycondensation of aromatic dianhydrides and diamines.
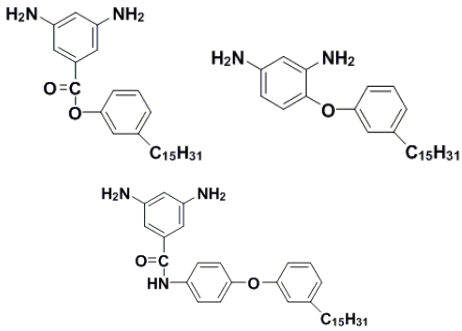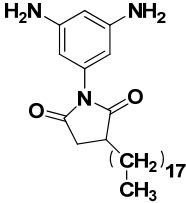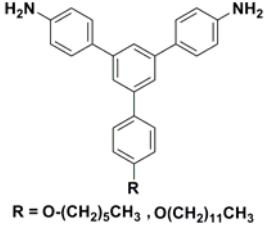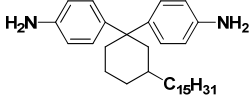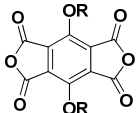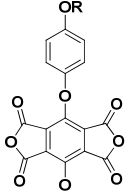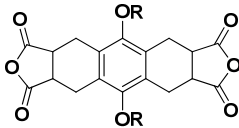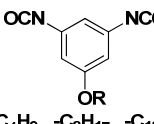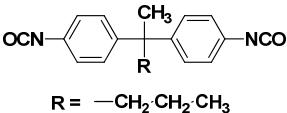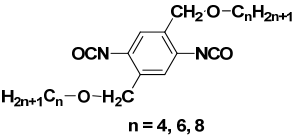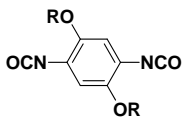
1.4.2 Structure-property relationship in polyimides

The chemistry of polyimides is in itself a vast area with a large variety of monomers available and several methodologies available for synthesis. The subtle variations in the structures of the dianhydride and diamine components have a tremendous effect on the properties of the final polyimide. The introduction of flexible linkages into/along the backbone of polymer will increase the number of degrees of freedom available and tends to lower the T_g. Because of the generality of this effect there is a commonly accepted correlation between flexibility of a polymer and its T_g. Therefore, most of the efforts at reducing the T_g of polyimides have focused on reducing their rigidity by the introduction of flexibilizing linkages, in either the diamine or dianhydride moieties.[129] The representative examples of monomers containing flexible alkyl chains used in the synthesis of polyimides are presented in **Table 1.3**.

Table 1.3 Representative examples of monomers containing flexible alkyl chains used in the synthesis of polyimides

No	Monomer	Ref	No	Monomer	Ref
1.		160	2.		161
3.		162	4.		163
5.		164	6.		165
7.		166	8.		167

No.	Structure	Ref	No.	Structure	Ref
9.		168	10.	R = H, CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$	169
11.	R = —C$_6$H$_{13}$, —C$_8$H$_{17}$	170	12.		171
13.	R = —O(CH$_2$)$_{n-1}$CH$_3$ n = 5, 8, 10, 12, 14, 16, 18	172	14.		173
15.	Stb =	174	16.	R = CH$_2$(CH$_2$)$_{n-2}$CH$_3$; n = 7,16, 18	175
17.		176	18.		177
19.		178	20.		117
21.	R = CH$_3$, C$_4$H$_9$, C$_8$H$_{27}$, C$_{12}$H$_{25}$	179	22.	R = —O(CH$_2$)$_6$O	180
23.		181	24.	n = 6, 8, 10, 12, 14, 16	182

No.	Structure	Ref.	No.	Structure	Ref.
25.	H$_2$N—NH$_2$, O=C, O, C$_{15}$H$_{31}$; H$_2$N—NH$_2$, O, C$_{15}$H$_{31}$; H$_2$N—NH$_2$, O=C, HN, O, C$_{15}$H$_{31}$	111	26.	H$_2$N—NH$_2$, N, O=...=O, (CH$_2$)$_{17}$ CH$_3$	183
27.	H$_2$N—...—NH$_2$, R; R = O-(CH$_2$)$_5$CH$_3$, O(CH$_2$)$_{11}$CH$_3$	184	28.	H$_2$N—...—NH$_2$, C$_{15}$H$_{31}$	112
29.	OR ... OR; R = C$_8$H$_{17}$, C$_{12}$H$_{25}$ = —O—C$_8$H$_{17}$	185	30.	OR ... OR; R = C$_n$H$_{2n+1}$, n = 1, 4, 8, 12	186
31.	OR ... OR; R = C$_4$H$_9$, C$_8$H$_{17}$, C$_{12}$H$_{25}$	187	32.	OCN—NCO, OR; R = -C$_4$H$_9$, -C$_8$H$_{17}$, -C$_{12}$H$_{25}$, -C$_{16}$H$_{33}$	188
33.	OCN—...—NCO, CH$_3$, R; R = —CH$_2$·CH$_2$·CH$_3$	189	34.	CH$_2$·O—C$_n$H$_{2n+1}$, OCN—NCO, H$_{2n+1}$C$_n$—O—H$_2$C; n = 4, 6, 8	190
35.	RO, OCN—NCO, OR; R = C$_n$H$_{2n+1}$; n = 4, 6, 10, 12, 14, 16	191			

1.5 Polyamides

Polyamides are polymers with recurring amide (-CO-NH) groups as an integral part of the main polymer chain and they are the largest and most important group of linear-acyclic nitrogen polymers. The development of polyamide technology established many of the principles and practices for polymerization in general, laying the ground-work for the great array of materials that have followed.[192] Wholly aromatic polyamides are considered to be high-

performance organic materials due to their outstanding thermal and mechanical resistance. Their properties arise from aromatic structure and amide linkages, which result in stiff rod-like macromolecular chains that interact with each other *via* strong and highly directional hydrogen bonds. They are finding increasing demand for use as advantageous replacements for metals or ceramics in currently used goods, or even as new materials in novel technological applications.[193]

However, high transition temperatures of the commercial aromatic polyamides, which lie above their decomposition temperatures, and their poor solubility in common organic solvents give rise to processing difficulties and limit their applications.[194] As a consequence, recent basic and applied research has focused on enhancing their processability and solubility in order to broaden the scope of the technological applications of these materials.

1.5.1   Synthesis of polyamides

1.5.1.1 Low temperature polycondensation of a diamine and a diacid chloride

This method was developed by DuPont and has been used for the preparation of high molecular weight polyamides. The polycondensation of a diamine and a diacid chloride can be carried out in solution or at the interface of two solvents at a temperature less than 100 °C.

1.5.1.1a Solution polycondensation of a diamine and a diacid chloride

Solution polycondensation involves a diamine and a diacid chloride reacting in an amide solvent such as NMP, HMPA, DMAc or tetramethylurea (**Scheme 1.9**)
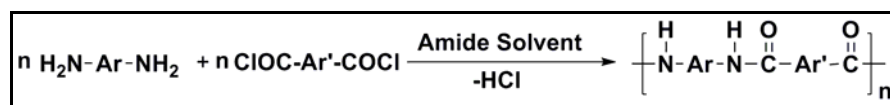
Scheme 1.9 Solution polycondensation of a diamine and a diacid chloride

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$_2$.[195]

1.5.1.1b Interfacial polycondensation of a diamine and a diacid chloride

The polycondensation reaction can also be carried out in a two phase system at room temperature *via* interfacial polymerization. In this method, the two fast reacting reagents are dissolved in a pair of immiscible liquids, one of which is preferably water.[196] The water phase generally contains the diamine and usually an inorganic base, 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. Since the temperatures needed are low, the

side reactions are minimized and also the polymers, which are unstable at high temperatures, can be synthesized.

1.5.1.2 High temperature solution polycondensation of a dicarboxylic acid and a diamine

This method was developed by Yamazaki et al[197] which involves 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 1.10**).
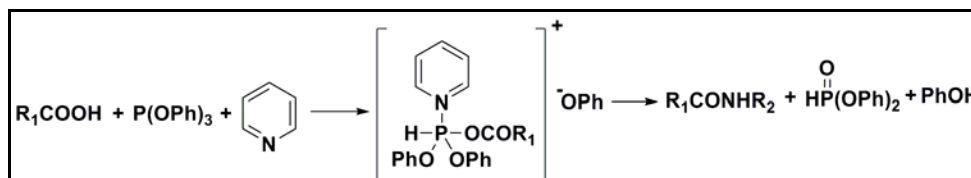
Scheme 1.10 Condensation reaction involving acid and amine to form amide in the presence of triphenylphosphite

$CaCl_2$ 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.

The high-temperature solution polycondensation method was recently modified by the introduction of microwave-assisted polycondensation. The conventional heating system, i.e., temperature controled oil bath, is replaced by microwave radiation system, which reduces the reaction time from 4 h to approximately 2 min.[198] The polymers obtained by both methods have comparable inherent viscosities.

Recent efforts have been directed to the greener promotion of polycondensation under low or high temperature solution methods which include replacements of conventional solvents (DMAc, NMP and pyridine) by ionic liquids.[199] The ionic liquids have high thermal stability, low vapor pressure, are highly polar, and have a high dielectric constant, which makes them suitable to dissolve the aromatic polyamides.

1.5.1.3 Polycondensation of an activated diamine and a diacid

Polycondensation chemistry has been improved in the last two decades through the use of activated monomers. The activation of monomers can be achieved either by activation of the carboxylic acids, mainly through organophosphorous reagents such as phenyl dichlorophosphite (PDCP)[200, 201] or activation of the diamines by their silylation.[202]

1.5.1.4 Polycondensation of diisocyanates and dicarboxylic acids

Another promising route for the preparation of aromatic polyamides has been developed by Simioneseu et al and Onder et al[203] 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.[204] A commercial scale preparation of aromatic polyamides from 1,3-phenylene diisocyanate and isophthalic acid in the presence of a catalyst has been reported.[205] Polyamides have also been prepared by the reaction of aromatic diisocyanates with aromatic hydrocarbons in the presence of Friedel-Crafts catalyst.[206]

1.5.1.5 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[207] (**Scheme 1.11**).
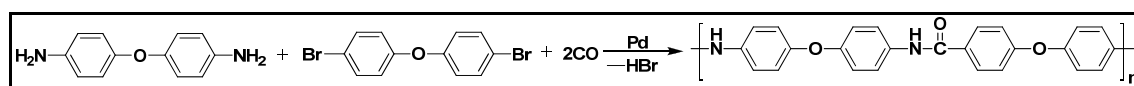
Scheme 1.11 Transition metal-catalyzed carbonylative coupling of aromatic diamine and dihalide
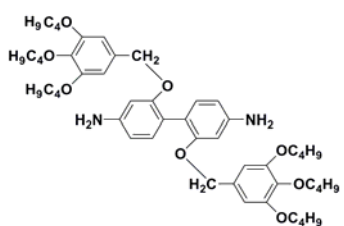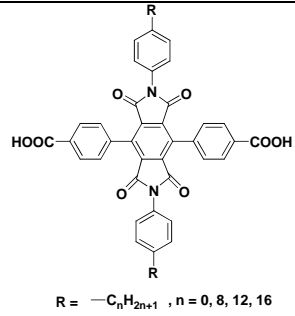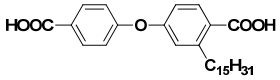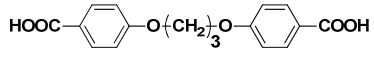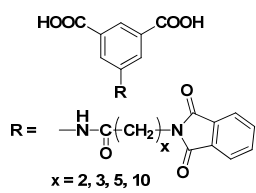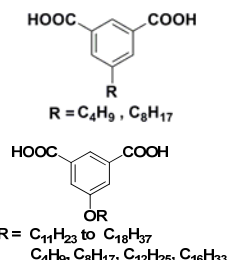
1.5.2   Structure-property relationship in polyamides

The design of new polyamides that show good solubility as well as other specific properties is a process of growing importance for the researchers and end-users worldwide. A number of strategies were adapted to synthesize soluble/processable polyamides without significantly affecting the thermomechanical properties.[208] It has been generally recognized that incorporation of flexible groups or alkyl chains along the polymer backbone, impart better solubility and melt-processing characteristics compared with polymers without these linkages.

The representative examples of monomers containing flexible linkages or pendent alkyl chains for the synthesis of polyamides are given in **Table 1.4.**

Table 1.4 Representative examples of monomers containing pendent flexible alkyl groups used in the synthesis of polyamides

No	Monomer	Ref	No	Monomer	Ref
1.		111	2.		184

3.		209	4.		210
5.		211	6.		212
7.		213	8.		214, 188

1.6   Poly(azomethine)s

Aromatic poly(azomethine)s (PAZs), containing HC=N linkages, prepared for the first time by Adams and co-workers[215] from terephthalaldehyde and benzidine or dianisidine, were known to be insoluble and infusible. The HC=N linkage in PAZs is isoelectronic with C=C group in poly(*p*-phenylene vinylene)s and, therefore, find applications in opto-electronics.[216-218] 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,[219] but also as particularly promising electronic materials with semiconducting properties,[220] and ability to form chelates.[221] Also, many of these polymers can form mesophases by heating or in solution,[222] 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 PAZs.

1.6.1 Synthesis of poly(azomethine)s

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.

PAZs are generally synthesized by solid state or solution polycondensation reaction of a dialdehyde and a diamine. This reaction was first described by Schiff in 1864; hence poly(azomethine)s or imines are often referred to as Schiff bases.[223]

1.6.1.1 Melt polycondensation

This method is rather seldom used because PAZs are usually high melting polymers with melt temperatures close to the decomposition temperature.[224] Also, melt polycondensastion is hard to control and gives side reactions that lead to undesirable by-products.[225] Higher molecular weights are attained by conducting the reaction at elevated temperature in the solid or molten state.

1.6.1.2 Solution polycondensation

PAZs are usually synthesized by solution polycondensation of a dialdehyde and a diamine. In general, synthesis of high molecular weight PAZs is difficult because the polymer product is equilibrated with the by-products and monomers; furthermore, the reverse reaction is favoured at elevated temperature[226] (**Scheme 1.12**).

$$n \ H_2N\text{-}Ar\text{-}NH_2 \ + \ n \ OHC\text{-}Ar'CHO \ \underset{}{\overset{-H_2O}{\rightleftharpoons}} \ \underset{H}{[Ar\text{-}N=\overset{}{C}\text{-}Ar'\text{-}\overset{}{C}=N]}_n$$
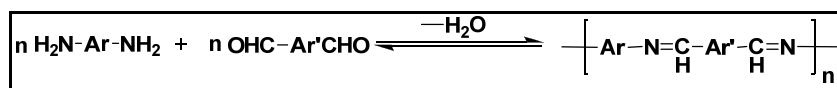
Scheme 1.12 Synthesis of poly(azomethine) from a diamine and dialdehyde

Therefore, it is essential to select a solvent that activates both dialdehyde and diamine monomers and that provides the optimal polymerization conditions. The aldehyde group is highly activated in strongly acidic conditions, whereas the amine group is deactivated in strongly acidic or basic conditions. [227] The reaction between diamines and dialdehydes is rapid at room temperature and can be initiated in water-free solvents such as methanol and ethanol. Appreciable polymerization occurs before the polymer begins to precipitate, and the reaction continues more slowly in the suspension or paste-like state. In most cases, catalyst is not necessary, but removal of water expediates polycondensation.[216] 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.[226] Better results were obtained when polar aprotic solvents, such as THF, DMAc, DMF, NMP, DMSO or HMPA or protic solvents, such as *m*-cresol or *p*-chlorophenol were used because the polymers were more soluble in these polar solvents.[216] To obtain high molecular weight polymers, calcium chloride, lithium chloride or P_2O_5 can be added to the polycondensation system. These salts act as a dehydrating agent and 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. [228]

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 (*Mn*) of the most aromatic PAZs prepared by solution polycondensation are in the range of 500-2000 g/mol. Considerably better results (*Mn* = 5000-25,000) were obtained for their synthesis in *m*-cresol at 200°C, because the polymers remain in solution over the entire course of polycondensation.[216, 218]
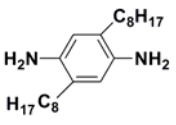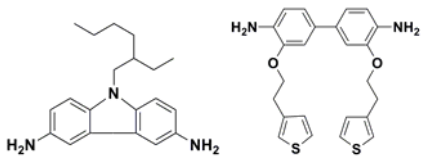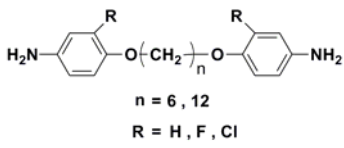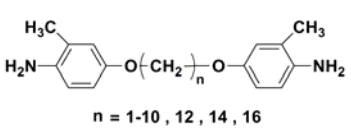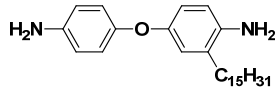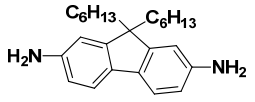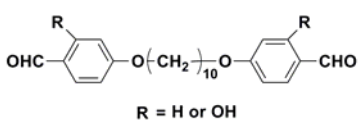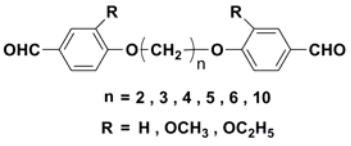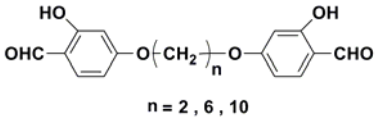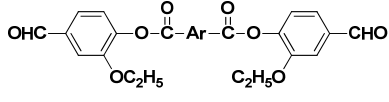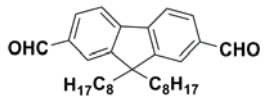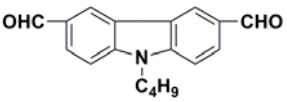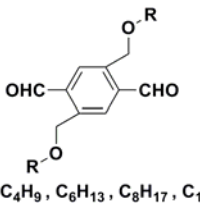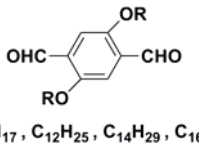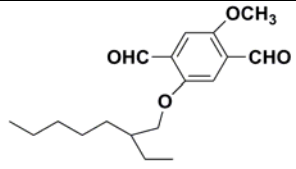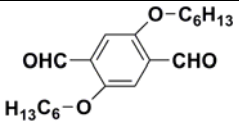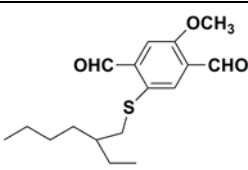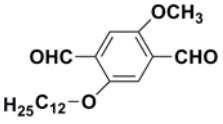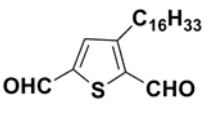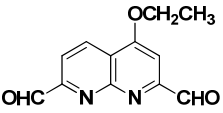
The elementary step in the polycondensation of diamines with dicarbonyl derivatives is the nucleophilic attack of the amine group on the carbonyl bond followed by dehydration of the tetrahedral intermediate. Therefore, the rate of reaction is dependent on the diamine nucleophilicity and the electrophilicity of the carbonyl compound. To obtain PAZs starting from terephthaldehyde and *p*-phenylenediamine chemical vapor deposition polymerization technique was used.[216] This method is very interesting because thin films for new applications can be obtained.

1.6.2 Structure-property relationship in poly(azomethine)s

A major drawback associated with aromatic PAZs is their limited solubility in most of the common organic solvents due to their rigid chain structure, this also being the main reason for their low molecular weight.[229] Since the growing macromolecular chain comes out of solution during the polycondensation at low polymerization degrees; high molecular weight polymers cannot be obtained. Many strategies have been reported to improve the solubility of polyazomethines such as insertion of flexible linkages between main chain aromatic rings[230] or introduction of pendent groups, i.e., aromatic or alkyl substituents onto the polymer chain.[231] The incorporation of bulky substituents such as triphenylamine, tetraphenylethylene or diphenylfluorene have been investigated.[232] The copolymerization of electronrich, solubility-enhancing aromatic or heterocyclic units such as thiophene and carbazole has also been explored.[233]

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 1.5**

Table 1.5 Representative examples of monomers containing pendent alkyl groups used in the synthesis of poly(azomethine)s

No.	Monomer	Ref	No.	Monomer	Ref
1.	C_8H_{17}, H_2N, NH_2, $H_{17}C_8$	234	2.	H_2N ... NH_2; carbazole N, H_2N ... NH_2; thiophene S, S	227
3.	H_2N—Ar—O$+$CH$_2$$)_n$O—Ar—$NH_2$ (R), n = 6, 12, R = H, F, Cl	235	3.	H_3C, CH_3, H_2N—O$+$CH$_2$$)_n$O—$NH_2$, n = 1-10, 12, 14, 16	236
4.	H_2N——O——NH_2, $C_{15}H_{31}$	237	5.	C_6H_{13} C_6H_{13}, H_2N——NH_2	238
6.	OHC——O$+$CH$_2$$)_{10}$O——CHO (R), R = H or OH	239	7.	R, OHC——O$+$CH$_2$$)_n$O——CHO, n = 2, 3, 4, 5, 6, 10, R = H, OCH$_3$, OC$_2$H$_5$	240
8.	HO, OHC——O$+$CH$_2$$)_n$O——CHO, OH, n = 2, 6, 10	241	9.	OHC——O—C(=O)—Ar—C(=O)—O——CHO, OC$_2$H$_5$, C$_2$H$_5$O	242
10.	OHC——CHO, $H_{17}C_8$ C_8H_{17}	243	11.	OHC——CHO, N, C_4H_9	244
12.	O—R, OHC——CHO, R—O, R = C$_4$H$_9$, C$_6$H$_{13}$, C$_8$H$_{17}$, C$_{12}$H$_{25}$	245	13.	OR, OHC——CHO, RO, R = C$_8$H$_{17}$, C$_{12}$H$_{25}$, C$_{14}$H$_{29}$, C$_{16}$H$_{33}$, C$_{18}$H$_{37}$	246
14.	OCH$_3$, OHC——CHO, O—(2-ethylhexyl)	247	15.	O—C$_6$H$_{13}$, OHC——CHO, H$_{13}$C$_6$—O	248
16.	OCH$_3$, OHC——CHO, S—(2-ethylhexyl)	249	17.	OCH$_3$, OHC——CHO, H$_{25}$C$_{12}$—O	250
18.	$C_{16}H_{33}$, OHC—S—CHO	251	19.	OCH$_2$CH$_3$, OHC—N N—CHO	252

1.7   Poly(amideimide)s

Poly(amideimide)s (PAIs) are a class of polymers containing amide and heterocyclic imide units in the polymer backbone (**Figure 1.3**). The presence of amide groups in PAIs improves their solubility, while the aromatic imide units provide thermal resistance and mechanical properties.
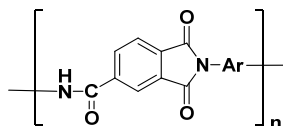
Figure 1.3 General structure of poly(amideimide)

PAIs combine the thermal stability property of polyimides and ease of processability of polyamides and are intermediate in properties of polyimides and polyamides. Aromatic PAIs possess desirable characteristics for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability.[253] PAIs 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.

1.7.1   Synthesis of poly(amideimide)s

Different methods have been reported for the synthesis of PAIs from various aromatic monomers containing anhydride, carboxylic acid, and aromatic diamine by condensation. Following are the most important routes:

1.7.1.1 Imide forming reaction using amide containing monomers

PAIs can be synthesized by a polycondensation reaction involving the formation of imide rings.[254,255] This method usually yields unstable poly(amic acid)s which have to be thermally or chemically cured to provide fully cyclized PAIs (**Scheme 1.13**).

Scheme 1.13 Imide forming reaction using amide containing monomer

1.7.1.2 Amide forming reaction using imide containing monomers

PAIs can be synthesized by amide-forming reaction from imide containing monomers such as dicarboxylic acids or diamines (**Scheme 1.14**).
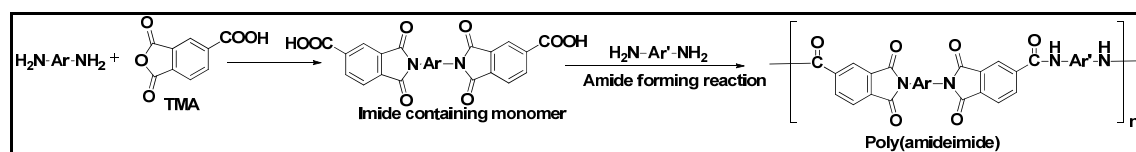
Scheme 1.14 Amide forming reaction using imide containing monomers

This route generally involves the use of trimellitic anhydride (TMA) as a major component, where TMA is first reacted with a specific diamine or amino acid to synthesize a

diimide-dicarboxylic acid which is then reacted with various aromatic diamines to synthesize PAIs.[256]

1.7.1.3 Amide-imide forming reaction,

This route goes through amide-imide forming reaction,[257] by which trimellitic anhydride (TMA) reacts with diisocyanate to produce poly(amide-imide)[258] or 4-chloroformylphthalic anhydride (CPA) reacts with diamine to produce poly(amide-imide) by two-step procedure involving the formation of poly(amide amic acid) and subsequent cyclodehydration[259] (**Scheme 1.15**).
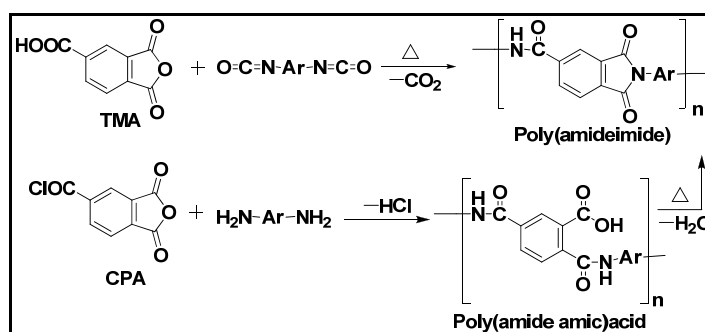
Scheme 1.15 Amide-imide forming reaction

1.7.1.4 Acid hydrazide route

Apart from above mentioned routes, PAIs can also be prepared by the reaction of a diacylhydrazide and a dianhydride by two stage process.[260,261] (**Scheme 1.15**)
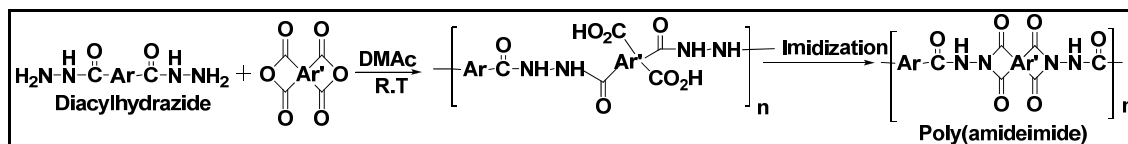
Scheme 1.16 Poly(amideimide) synthesis by diacylhydrazide route
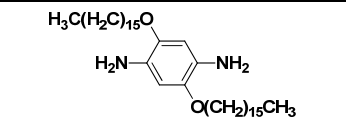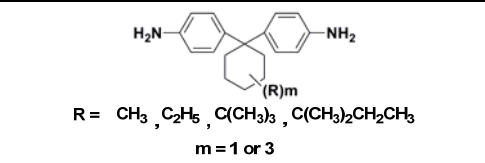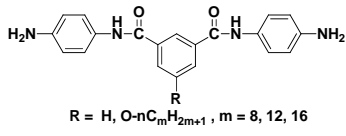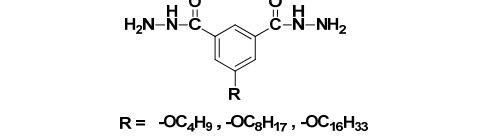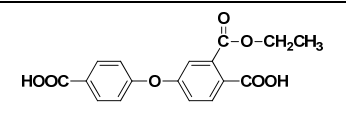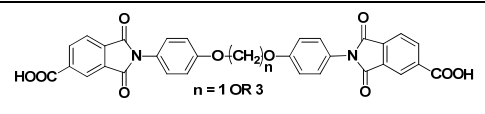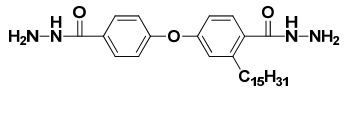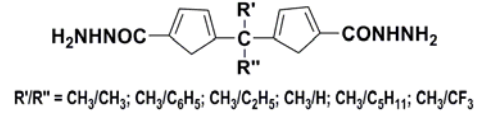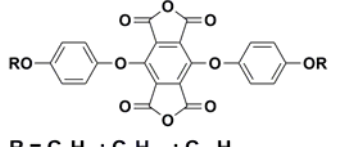
The first stage is the ring opening polyaddition reaction of a dianhydride and a diacylhydrazide to form a poly(hydrazide acid), while second step consists of the subsequent cyclodehydration of poly(hydrazide acid) to form PAI.

1.7.2 Structure-property relationship in poly(amideimide)s

Being the class of copolyimides, PAIs have deserved particular attention. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and moldability. However, these are still difficult to process because of their high softening temperatures and poor solubility in common organic solvents.[263] In order to improve their solubility and processability, several approaches have been proposed based on the incorporation of different segments such as flexible linkages (-O-, -SO_2-, -$(CH_2)_n$-, -$C(CF_3)_2$), [263] bulky pendent groups (such as t-butyl, adamantyl, cardo, and naphtyl),[264] use of asymmetric monomers, etc. Among these approaches, introduction of alkyl substituents along the polymer backbone has been of particular interest because it increases the solubility while maintaining thermal stability, which makes PAIs easier to process.[254, 261]

Representative monomers containing flexibilizing groups which have been used for synthesis of PAIs are collected in **Table 1.6**

Table 1.6 Representative examples of monomers containing flexible alkyl groups for synthesis of organo-soluble poly(amideimide)s

No	Monomer	Ref	No.	Monomer	Ref
1.		265	2.		266
3.		254	4.		261
5.		267	6.		268
7.		269	8.		270
9.		186			

1.8 Poly(esterimide)s

Poly(esterimide)s (PEIs) are copolyimides containing ester functionality at regular intervals in the polyimide chain due to which they have advantages of both polyester and polyimide and thus possesses thermal stability balanced with processability.[271] Relatively lower cost and better outdoor stability of a poly(esterimide) are additional advantages.[272] Over the past three decades, PEIs have attracted increasing interest because a relatively slight change of the chemical structure allows a broad variation of their physical properties, and thus, of their potential applications.[273] Their main applications are in coatings for enameled wires, high-strength fibers, hot melt adhesives, heat resistant films, and printed circuit boards.[274]

1.8.1 Synthesis of poly(esterimide)s

Aromatic poly(esterimide)s can be synthesized from three kinds of condensing monomers: a) trimellitic anhydride (TMA), aromatic diamine, and bisphenol; b) aromatic aminophenol, dianhydride, and aromatic diacid; and c) aromatic amino acids, dianhydride, and bisphenol.[275] The five general methods used in the synthesis of poly(esterimides)s are i)
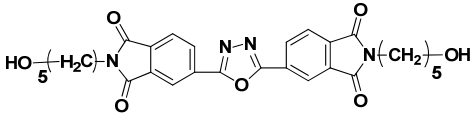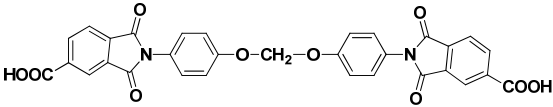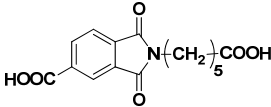
polycondensation of an ester-group-containing dianhydride with a diamine,[276] ii) polycondensation of an ester-group-containing diamine with a dianhydride,[277] iii) reaction between a dicarboxylic acid containing an imide ring with a bisphenol,[278] iv) reaction between a bisphenol containing an imide ring with a dicarboxylic acid, and v) self-reaction of an imide-containing phenol-acid monomer.[279] The first two methods proceed through the solution polycondensation of polyimide, and the other three methods proceed through melt-transesterification of an imide-group-containing monomer or the solution ester polycondensation of its derivative. There is usually difficulty in stirring in the process of melt-transesterification, but solution polycondensation goes smoothly because it is easy to stir. However, there are few common solvents for dissolving imide and ester groups. The unsatisfactory results obtained from solution polycondensation are caused by the poor solubility of these polymers, resulting in early precipitation within the reaction medium and retarding further polymerization.
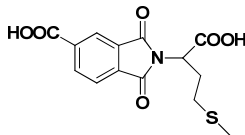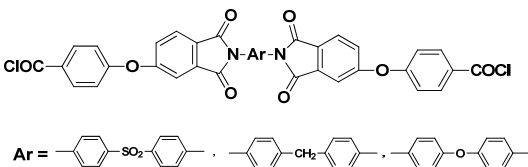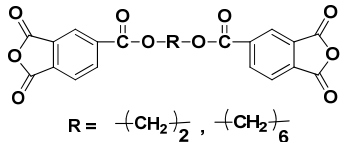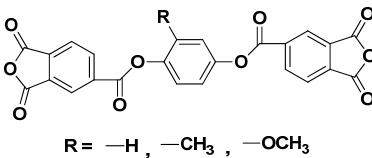
Direct polycondensation using condensing agents for the *in situ* activation of carboxylic acids is a useful procedure for the synthesis of PEIs. [280, 281] The direct polycondensation route avoids using moisture-sensitive acid chlorides and provides significant advantages in manufacturing operations compared with conventional methods.

1.8.2   Structure-property relationship in poly(esterimide)s

Aromatic PEIs are generally infusible and insoluble in common organic solvents and pose processing difficulties, limiting their widespread utility.[282] Of the various alternatives to design processable PEIs, some general approaches that have been commonly implemented are incorporation of bulky substituents,[283] introduction of flexible linkages[284] or aliphatic spacers,[285] etc. Among these approaches, introduction of alkyl substituents into the polymer backbone has been of particular interest because it increases the solubility and lowers T_g, which makes PEIs easier to process. **Table 1.7** gives a list of monomers containing flexibilizing groups used in the synthesis of PEIs.

Table 1.7 Representative examples of monomers containing flexibilizing groups used in the synthesis of poly(esterimide)s

No.	Monomers	Ref.
1.		286
2.		287
3.		288

4.		289
5.		290
6.		285
7.		291

1.9   Aromatic Polyesters

Aromatic polyesters or polyarylates are an important class of high performance materials consisting of recurring ester groups as an integral part of the main polymer chain. The reaction of aromatic dicarboxylic acids and diphenols was first noted by Conix[292] 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.[293]

Polyesters have found applications in a wide variety of areas such as automobile, aviation and electronic industries by virtue of their attractive electrical and mechanical properties.[294] 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.

1.9.1   Synthesis of polyesters

Aromatic polyesters are prepared by two routes:

1. Acid chloride route

2. Transesterification route

1.9.1.1 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 polycondensation with diphenols. The

reaction can be performed by three different processes.

1.9.1.1a Interfacial polycondensation

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. 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.[295] 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. The most commonly used PTC's are benzyltriethyl-ammonium chloride, tetraethylammonium chloride, tetramethylammonium chloride, benzyltriphenyl phosphonium chloride, 15-crown-5, and 18-crown-6.[295]

1.9.1.1b Low temperature solution polycondensation

Low temperature solution polycondensations are generally run 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 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.[296] **Scheme 1.17** depicts the synthesis of polyester from bisphenol-A and terephthalic acid chloride or isophthalic acid chloride.
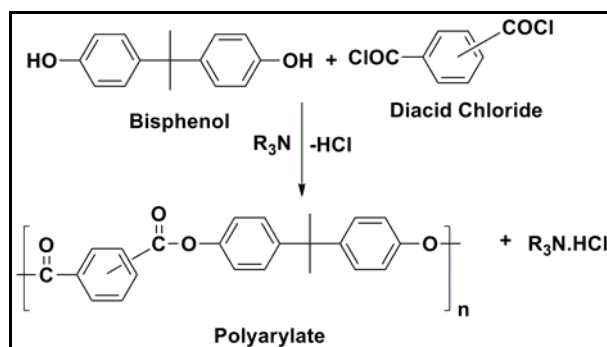
Scheme 1.17 Solution polycondensation of bisphenol and diacid chloride

High molecular weight polyarylates are successfully synthesized in pyridine alone or in combination with a tertiary amine in an inert organic solvent.[297]

1.9.1.1c 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 $^{\circ}$C) in an inert high boiling solvent such as nitrobenzene or o-dichlorobenzene. The o-dichlorobenzene and pyridine system is the most effective one to produce the polymer with high molecular weight.[298] Polyarylates are also prepared in good yields at 215-220 $^{\circ}$C in dichloro- ethylbenzene.[299] 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, chlorinated biphenyls or diphenylethers, chlorinated naphthalenes, as well as non-chlorinated aromatics such as terphenyl, benzophenones, etc.

1.9.1.2 Transesterification route

Transesterification reactions are carried out by three different routes:

1.9.1.2a Phenyl ester route

The reaction between a diarylester of an aromatic dicarboxylic acid and an aromatic diphenol results in high molecular weight polyester (**Scheme 1.18**). This method was successfully employed for the first time by Blaschke and Ludwing[300] for the synthesis of polyarylates. The diphenylesters are less reactive as compared to the corresponding acid chlorides, hence, higher reaction temperatures and longer reaction times are necessary to obtain high molecular weight polyarylates.
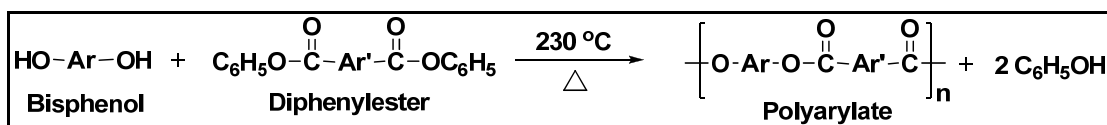
Scheme 1.18 Polyester synthesis *via* diphenylester route

1.9.1.2b Phenol acetate route

In this process, polyarylates are synthesized by the reaction of stoichiometric amounts of an aromatic dicarboxylic acid and the diacetate derivative of an aromatic diphenol at high temperature under inert atmosphere (**Scheme 1.19**).
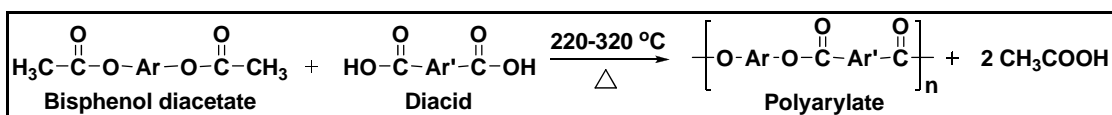
Scheme 1.19 Polyester synthesis *via* phenol acetate route

Generally, the polycondensation is carried out in the melt or solid state at a temperature ranging from 200-350°C under nitrogen atmosphere with or without catalyst.[301]

1.9.1.2c Phenyl ester and phenol acetate route

One variation of the diacetate route involves the reaction of bisphenol-A diacetate with dimethyl ester of aromatic dicarboxylic acids i.e. dimethyl tere/isophthalates. In this sequence, condensation would occur with the liberation of methylacetate; however, the reaction proceeds

only to very low molecular weights (catalyzed or uncatalyzed).[302]

1.9.1.3 Miscellaneous routes for polyester synthesis

Various routes other than those mentioned above have been used for polyester synthesis. For example, polyarylates have been synthesized by direct esterification route[303] which involves direct polycondensation of a dicarboxylic acid and a diphenol in the presence of a condensing agent such as diphenylchlorophosphate (DPCP) which activates dicarboxylic acid (**Scheme 1.20**). The activated diacid intermediate formed condenses with bisphenol to form polyarylates.
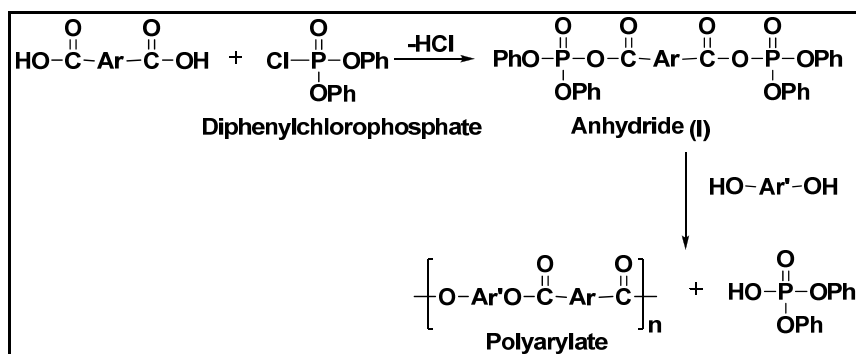
Scheme 1.20 Polyester synthesis *via* activated polycondensation

The reaction was assumed to proceed *via* the mixed anhydride (**I**) of the carboxylic acid and diphenyl phosphate followed by alcoholysis with the bisphenol. The direct polyesterification method is useful for the laboratory scale preparation of polyarylates. The effective condensing agents investigated so far for the preparation of polyarylates are triphenylphosphine chloride, aryl sulfonyl chloride, phosphorous oxychloride with metal salts, thionyl chloride and *p*-toluenesulfonyl chloride with dimethylformamide.[304]

Other reported routes for synthesis of polyester were phenol silyl ether route and palladium-catalyzed carbonylation of aromatic dihalides with bisphenols.[305]
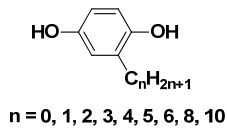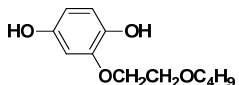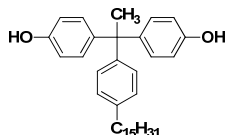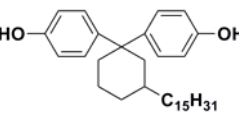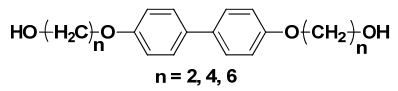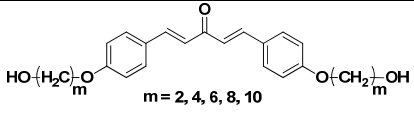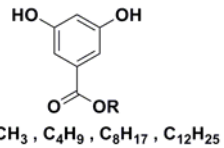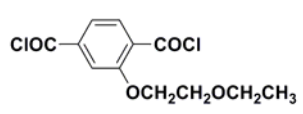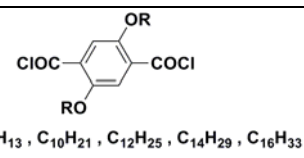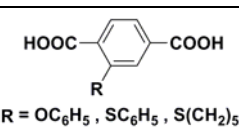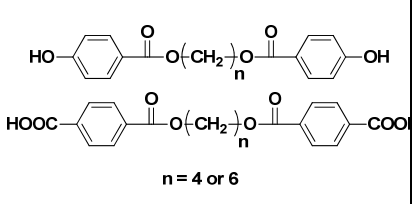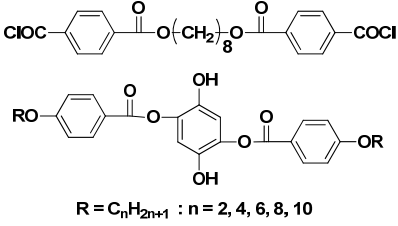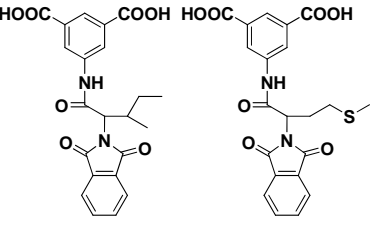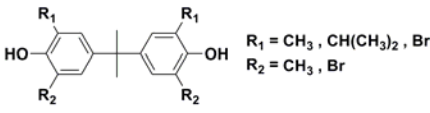
1.9.2 Structure-property relationship in polyesters
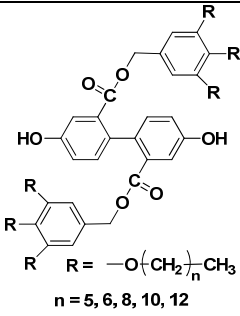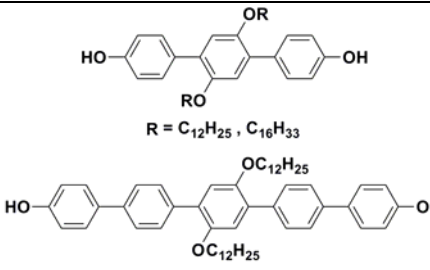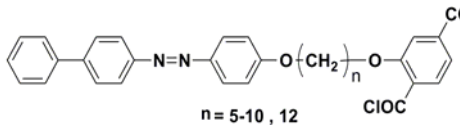
Numerous efforts have been made to overcome the issues related to solubility and processability of aromatic polyesters and clarify the structure-property relationships in aromatic polyesters.[306] Different types of aromatic polyesters have been synthesized over the past decades from various kinds of aromatic dicarboxylic acid chlorides and bisphenols. 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.[307] Also the inclusion of $-CF_3$ group into the polyester backbone improves the solubility and thermal stability of the resulting polymers.[295] Introduction of cardo "loop" groups along the polymer backbone has been shown to impart greater solubility as well as better mechanical and thermal properties.[308] 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 pendent functional groups

also lead to polyesters with improved solubility. [309]

Thermally stable polyarylate derived from a mixture of isophthalic acid and terephthalic acid with bisphenol A has been commercialized.[310] 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[311] to control the final properties of the polymers. Introduction of bulky pendent substituents or pendent flexible alkyl chains along the polymer backbone is one of the approaches to obtain processable/ soluble polyesters. Representative examples of monomers containing flexible alkyl chains used in the synthesis of aromatic polyesters are presented in **Table 1.8.**

Table 1.8 Representative examples of monomers containing flexible alkyl chains used in the synthesis of polyesters

No	Monomer	Ref	No	Monomer	Ref
1.	HO—⟨⟩—OH, C_nH_{2n+1}, n = 0, 1, 2, 3, 4, 5, 6, 8, 10	312	2.	HO—⟨⟩—OH, $OCH_2CH_2OC_4H_9$	313
3.	HO—⟨⟩—C(CH_3)—⟨⟩—OH, ⟨⟩—$C_{15}H_{31}$	314	4.	HO—⟨⟩—⟨cyclohexane⟩—⟨⟩—OH, $C_{15}H_{31}$	315
5.	HO—$(H_2C)_n$—O—⟨⟩—⟨⟩—O—$(CH_2)_n$—OH, n = 2, 4, 6	316	6.	HO—$(H_2C)_m$—O—⟨⟩—CH=CH—CO—CH=CH—⟨⟩—O—$(CH_2)_m$—OH, m = 2, 4, 6, 8, 10	317
7.	HO—⟨⟩—OH, CO—OR, R = CH_3, C_4H_9, C_8H_{17}, $C_{12}H_{25}$	318	8.	ClOC—⟨⟩—COCl, $OCH_2CH_2OCH_2CH_3$	319
9.	ClOC—⟨⟩—COCl, OR / RO, R = C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$	320	10.	HOOC—⟨⟩—COOH, R, R = OC_6H_5, SC_6H_5, $S(CH_2)_5CH_3$	321
11.	HO—⟨⟩—CO—O—$(CH_2)_n$—O—CO—⟨⟩—OH, HOOC—⟨⟩—CO—O—$(CH_2)_n$—O—CO—⟨⟩—COOH, n = 4 or 6	322	12.	ClOC—⟨⟩—CO—O—$(CH_2)_8$—O—CO—⟨⟩—COCl, RO—⟨⟩—CO—O—⟨⟩—O—CO—⟨⟩—OR, OH / OH, R = C_nH_{2n+1} : n = 2, 4, 6, 8, 10	323
13.	HOOC—⟨⟩—COOH HOOC—⟨⟩—COOH, NH / NH, phthalimide structures	324	14.	R_1 / HO—⟨⟩—C—⟨⟩—OH / R_2, R_1 = CH_3, $CH(CH_3)_2$, Br; R_2 = CH_3, Br	325

15.		326	16.		327
17.					328

1.10　Concluding Remarks

➢ The chemistry of renewable resources applied to the production of new products, represents a very important subject and has captured the attention of researchers of the academic and industrial world. In particular, in the past few years, the synthesis of polymers starting from renewable resources is the object of significant research efforts due to the increasing prices of petro-chemical products associated with growing environmental concerns.

➢ 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.

➢ Due to increasing demands for high performance polymers as replacements for ceramic or metal components in the microelectronic, aerospace and automotive industries, these polymers have received much interest over the past decades. Although their excellent thermal stability is complimented by excellent chemical resistance, mechanical and electrical performance, their insolubility in common organic solvents, high glass transition and softening temperatures limit their widespread applications. Among the several approaches to modify the properties of these polymers so as to make them processable, one of the promising strategy is the introduction of alkyl substituents *via* monomer molecule, which consequently becomes a part of repeat unit of the polymer chain. This modification increases interchain distance, disrupts the geometrical regularity of the chains thus reducing the interchain interactions and thereby enhancing the solubility/ processability.

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Chapter 2

Scope and Objectives

Currently, a wide range of industrial materials such as solvents, fuels, synthetic fibers, etc. are being manufactured from petroleum resources. However, rapid depletion of fossil and petroleum resources is encouraging chemists to orient their research towards designing safer chemicals, products, and processes from renewable feedstocks with an increased awareness of environmental and industrial impact.[1] An agricultural and biological feedstocks can be excellent alternative, renewable raw materials.[2] It has been demonstrated that a host of agricultural products can be transformed into consumer products. However, the search for biological sources of alternative feedstocks need not be limited to agricultural products: agricultural waste may also provide important raw materials for the production of consumer compounds. The use of an otherwise unused waste product that would need to be disposed off is very attractive for obvious environmental and economic reasons.[3] In this context, the utilization of 'Cashew Nut Shell Liquid'(CNSL)- an agricultural waste product- seems very attractive.

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.[4,5] Because of the large demand and high commercial value of the edible kernel, world-wide cashew nut production has shown an increasing trend over the past ten years. As a consequence, CNSL represents a renewable, abundantly available, and relatively low-cost organic natural material.

Cardanol, obtained by vacuum distillation of CNSL consists of one *meta*-alkyl phenol and three *meta*-alkenyl phenols with alkenyl chains differing in their degree of unsaturation.[4] The dual phenolic/ alkenyl nature of cardanol makes it an ideal natural raw material for the synthesis of water-resistant resins and polymers. Cardanol derivatives represent a simple entry point for the preparation of additives for lubricants, diesel engine fuels, pour-point depressants, flame retardants, resins, inks, hydrorepellents, and antioxidants.[6] Selective oxidation of cardanol derivatives by methylrhenium trioxide has also been reported.[7] Furthermore, cardanol derivatives of phthalocyanines,[8] porphyrins[9] and fullerenes[10] indicated that the introduction of a cardanol moiety in these compounds was important in order to improve their solubility in organic solvents. Cardanol-based derivatives have also enabled a new class of dyes to be developed that have real prospects not only for photocatalytic processes, but also for other technological applications.[11] More et al[12] and Jinu et al[13] have utilized CNSL as a starting material to obtain a range of difunctional monomers *via* simple organic transformations. 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 based on CNSL could be an attractive proposition.

Aromatic polyimides, polyamides, poly(amideimide)s, poly(azomethine)s, etc. are classes of high performance polymers which exhibit excellent thermal, mechanical and electrical

properties over a wide range of temperature.[14] However, these polymers are processable only under extreme conditions which limit their application areas. Therefore, chemical / structural modification of these high-performance polymers for increasing the solubility and lowering the transition temperatures while maintaining thermal stability is of particular interest. Many studies have been conducted to improve the processability of these polymers by making use of structurally modified monomers.[15] The majority of these studies involved three main structural modifications to tailor the properties: i) introduction of flexible side chains/ segments or groups into/ along the polymer backbone, which reduces the chain stiffness, ii) use of 1,3-disubstituted instead of 1,4-disubstituted monomers or use of asymmetric monomers which lower the regularity and molecular ordering, and iii) introduction of bulky side substituent which help for the separation of polymer chains and hinder the molecular packing and crystallization.

Among the various structural modification methods mentioned above, the appendance of flexible side chains along the polymer backbone is a particularly interesting approach,[16] since 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 pendent flexible groups greatly reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. In general, such pendent groups not only bring about improved solubility but also help lower the melting and glass transition temperatures *via* "internal plasticization" effect.[12,17,18]

The aim of the present work was to make use of one or more of the structural modifications mentioned above, to have a cumulative effect on the properties of the resulting polymers.

Thus, our synthetic research effort was directed towards designing monomers with features that disturb structural regularity and chain packing hence imparting improved processability to the polymers. The goal of the present research was to utilize CNSL as a starting material to design and synthesize various difunctional monomers such as aromatic diamines, diacid, diphenol, and diisocyanate. Important considerations in designing monomers were: i) *meta*-linkage introduces "kinks" to the main chain which decrease the rigidity of the polymer backbone and inhibit packing, thus reducing the interchain interactions leading to enhanced solubility,[19] ii) the presence of pendent pentadecyl chain along the polymer backbone reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect and consecutively aid in improved processability,[12] iii) the presence of pendent pentadecyl chain on aromatic ring offers asymmetry to the polymer backbone leading to constitutional isomerism, which could impart interesting properties to the derived polymers.[20]

The second objective of this work was to investigate the effect of incorporation of pendent pentadecyl chains on the polymer properties, such as solubility and thermal stability. For

this study, polymers such as polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and polyesters 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.,* aromatic diamines, diacid, diol and diisocyanate containing pendent flexible pentadecyl chain starting from CNSL.

2. Synthesis of aromatic polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and polyesters containing pendent pentadecyl chains.

3. To study the effect of incorporation of pendent pentadecyl chains on polymer properties such as solubility and thermal stability.

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Chapter 3

Synthesis and Characterization of Condensation Monomers

3.1   Introduction

Step growth polymers have been known since the discovery of synthetic polymers as useful polymeric materials with wide application areas. Now a days, they have a huge industrial impact and it would be difficult to imagine life without them. The condensation monomers should carry appropriate functional groups, which react with each other to form high molecular weight linear polymers. Thus, diamines, diacids, diols, diisocyanates, dialdehydes, etc. are the main classes of condensation monomers.[1]

There have been always a constant search for new cost effective monomers that can be used in the synthesis of polymers for specialty applications. The cost of raw materials, market size, energy needs and health /environmental concerns have been important factors especially for introduction of new monomers. In this respect, synthesis of monomers and polymers from renewable resources has attracted considerable attention of research workers throughout the world. Several examples of monomers and polymers based on renewable resources are available,[2] including materials based on monosaccharides, fatty acids, starch, cellulose, lactic acid, natural amino acids, etc.

In the present work, a variety of difuncitional monomers *viz.,* aromatic diamines, diacid, diphenol, diisocyanate and dinitrile were designed and synthesized strating from 3-pentadecyl phenol which in turn is obtainable from CNSL- a renewable resource material (**Figure 3.1**).
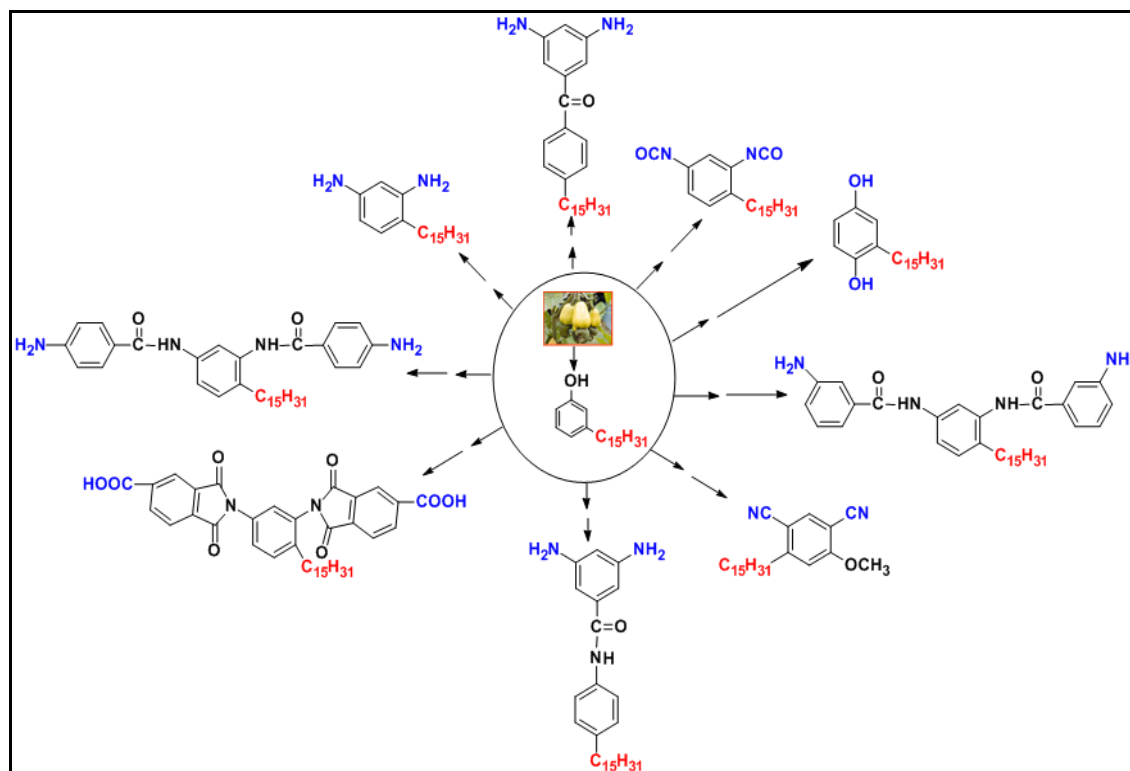
Figure 3.1 Difunctional monomers synthesized from CNSL

3.2   Experimental

3.2.1   Materials

3-Pentadecyl phenol, 1,3-phenylene diamine, trifluroacetic anhydride, (Aldrich Chemicals), sulfanilic acid (Fluka), acetic anhydride, ethanol, acetic acid (Merck, India) and methanesulfonyl chloride (Loba Chemie) were used as received. *m*-Phenylene diamine (*m*-PDA) (Sigma-Aldrich) was purified before use by sublimation under reduced pressure. Nitrobenzene, pyridine and triethyl amine (Loba Chemie) were distilled prior to use. 4-Nitrobenzoyl chloride and 3-nitrobenzoyl chloride were synthesized in the laboratory.[3]

Bromine, magnesium metal, copper cyanide, palladium-10 wt % on activated carbon (Pd-C, 10 wt %), calcium hydride (Aldrich Chemicals), ammonia solution, copper sulfate, zinc powder, hydrochloric acid, sulfuric acid, ammonium acetate, aluminium chloride, 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, and potassium dichromate (Loba Chemie) were used as received. Hydrazine hydrate (99 %) (S.D. Fine, India) was used as received. Fuming nitric acid was prepared as per the reported procedure.[4] Zeolite H-β (Si:Al = 28.5 Surface Area 540 m^2/g, particle size 0.5–1.0 lm, bulk density 0.55 g/cc) was synthesized in our laboratory.[5]

The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[6]

3.2.2   Measurements

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

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

NMR spectra were recorded on Bruker 200, 400 or 500 MHz spectrophotometer at resonance frequencies of 200, 400 or 500 MHz for ^{1}H and 50, 100 or 125 MHz for ^{13}C measurements using CDCl$_3$, DMSO-d$_6$, pyridine-d$_5$ or acetone-d$_6$ as a solvent. The peak assignments in ^{13}C-NMR spectra were confirmed by the corresponding DEPT spectra.

Elemental analyses were performed on Thermo Finnigan FLASH EA 1112 Series Elemental Analyzer.

3.3   Preparations

3.3.1   Synthesis of 4-pentadecylbenzene-1,3-diamine

3.3.1.1 Synthesis of 1-methylsulfonyloxy-3-pentadecylbenzene

Into a 500 mL two-necked round bottom flask equipped with an addition funnel, a magnetic stirring bar and a reflux condenser were placed 3-pentadecylphenol (30.0 g, 0.098 mol), triethylamine (15.10 ml, 0.011 mol) and dichloromethane (300 mL) and the reaction mixture was

cooled to 0 °C. To the reaction mixture was added methanesulfonyl chloride (9.33 mL, 0.12 mol) drop-wise over a period of 15 min. After completion of addition, reaction mixture was allowed to attain room temperature and stirred for 48 h. The reaction mixture was successively washed with water (2 x 100 mL), brine (2 x 100 mL) and water (2 x 100 mL). The organic layer was separated, dried over anhydrous sodium sulfate and filtered. Removal of solvent on a rotary evaporator afforded crude 1-methylsulfonyloxy-3-pentadecylbenzene which was purified by recrystallization from methanol.

Yield: 33.1 g (88 %).

M.P.: 58 °C (Lit. M.P.: 58 °C)[8]

IR (CHCl$_3$, cm^{-1}): 1371 (-SO$_2$ asymmetric stretch), 1127 (-SO$_2$ symmetric stretch).

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 7.07 - 7.34 (m, 4H, Ar-H), 3.12 (s, 3H, S-CH$_3$), 2.61 (t, 2H, Ar-CH$_2$), 1.24 - 1.38 (m, 26H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$): δ (ppm) 149.33, 145.59, 129.67, 127.49, 121.85, 119.02, 37.25, 35.68, 31.94, 29.68, 29.59, 29.38, 29.25, 22.71, 14.14.

Elemental analysis: Calcd. for C$_{22}$H$_{38}$O$_3$S: C, 69.06; H,10.01; S, 8.38. Found: C, 69.12; H, 9.65; S, 8.05.

3.3.1.2 Synthesis of pentadecylbenzene

After two vacuum / N$_2$ cycles to remove air from a 1 L two-necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser, 1-methylsulfonyloxy-3-pentadecylbenzene (50 g, 0.13 mol), 10 % Pd-C (5.0 g), magnesium metal (3.9 g, 0.16 mol), ammonium acetate (147.0 g, 1.9 mol) and methanol (500 mL) were taken and the reaction mixture was stirred under nitrogen atmosphere at room temperature. After 48 h, the reaction mixture was filtered and the filtrate was extracted with dichloromethane (2 x 250 mL). The dichloromethane solution was successively washed with water (2 x 100 mL), brine (2 x 100 mL) and water (2 x 100 mL). The organic layer was separated, dried over anhydrous sodium sulfate and filtered. Removal of solvent on rotary evaporator afforded a crude product which was chromatographed on silica gel (60-120 mesh) column with pet ether as an eluent to obtain pure pentadecylbenzene as a viscous liquid.

Yield: 25.2 g (67 %).

IR (liquid smear, cm^{-1}): 1600 (aromatic C=C stretch).

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 7.15-7.26 (m, 5H, Ar-H), 2.59 (t, 2H, Ar-CH$_2$), 1.24 -1.38 (m, 26H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$): δ (ppm) 142.97, 128.41, 128.22, 125.55, 36.04, 31.97, 31.56, 29.73, 29.41, 22.73, 14.14.

Elemental analysis: Calcd. for C$_{21}$H$_{36}$: C, 87.42; H, 12.58. Found: C, 87.29; H, 12.68.

3.3.1.3 Synthesis of 2,4-dinitro-1-pentadecylbenzene

Into a 100 ml two-necked round bottom flask equipped with a dropping funnel and a magnetic stirring bar were placed fuming nitric acid (1.5 mL, 35 mmol) and zeolite H-β (1.0 g). The reaction mixture was cooled to 0 °C and acetic anhydride (4.5 mL, 48 mmol) was added drop-wise over a period of 10 min and stirred. Pentadecylbenzene (10.0 g, 35 mmol) was added drop-wise to the reaction mixture over a period of 45 min and stirred for additional 30 min. Next, zeolite H-β catalyst (1.0 g), fuming nitric acid (1.5 mL, 35 mmol) and trifluoroacetic anhydride (6.8 mL, 48 mmol) were added and the reaction mixture was stirred for 2 h. The reaction mixture was filtered to remove zeolite H-β catalyst and the catalyst was washed with acetone (50 mL) and filtered. The solvent was removed on a rotary evaporator to obtain crude 2,4-dinitro-1-pentadecylbenzene which was chromatographed on silica gel (60-120 mesh) column with pet ether as an eluent to obtain pure 2,4-dinitro-1-pentadecylbenzene.

Yield: 10.5 g (80 %).

M.P.: 51 °C.

IR (CHCl$_3$, cm^{-1}): 1592 (aromatic C=C stretch), 1530 (-NO$_2$ asymmetric stretch), 1345 (-NO$_2$ symmetric stretch).

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 8.72 (d, 1H, Ar-H), 8.33 (dd, 1H, Ar-H), 7.54 (d, 1H, Ar-H), 2.97 (t, 2H, Ar-CH$_2$), 1.25 - 1.38 (m, 26H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$): δ (ppm) 149.22, 146.17, 144.86, 133.07, 126.75, 120.20, 33.11, 31.92, 30.52, 29.67, 29.65, 29.44, 29.35, 22.68, 14.10.

Elemental analysis: Calcd. for C$_{21}$H$_{34}$N$_2$O$_4$: C, 66.64; H, 9.05; N, 7.40. Found: C, 66.24; H, 9.26; N, 7.21.

3.3.1.4 Synthesis of 4-pentadecylbenzene-1,3-diamine (PBDA)

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed 2,4-dinitro-1-pentadecylbenzene (10.0 g, 0.026 mol),   Pd-C (10 wt %) (0.3 g, 3 wt % based on dinitro compound) and absolute ethanol (50 mL). The reaction mixture was heated to 70 °C and hydrazine hydrate (39.7 mL, 0.79 mol) was added drop-wise over a period of 15 min and refluxed for 6 h. The reaction mixture was filtered while hot and the solvent was distilled on a rotary evaporator to obtain the crude diamine. The diamine was chromatographed over neutral alumina with dichloromethane as an eluent to obtain pure 4-pentadecylbenzene-1,3-diamine.

Yield: 6.0 g (71 %).

M.P.: 75 °C.

IR (CHCl$_3$, cm^{-1}): 3405, 3319 and 3209 (-N-H stretch), 1600 (aromatic C=C stretch).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 6.81 (d, 1H, Ar-H), 6.12 (dd, 1H, Ar-H), 6.06 (d, 1H, Ar-H), 3.29 (s, 4H, -NH$_2$), 2.38 (t, 2H, Ar-CH$_2$), 1.25–1.38 (m, 26H, -CH$_2$), 0.88 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 145.36, 144.84, 130.27, 117.79, 106.15, 102.62, 31.94, 30.62, 29.71, 29.38, 29.30, 22.71, 14.13.

Elemental analysis: Calcd. for C$_{21}$H$_{38}$N$_2$: C, 79.18; H, 12.02; N, 8.79. Found: C, 79.27, H, 11.90; N, 8.65.

3.3.2 Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) (PDP-4AB) (I)

3.3.2.1 Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-nitrobenzamide) (PDP-4NB)

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed PBDA (5.0 g, 16 mmol), DMAc (25 mL) and triethylamine (4.4 mL, 31 mmol). 4-Nitrobenzoyl chloride (5.84 g, 31 mmol) dissolved in DMAc (25 mL), was added drop-wise into the reaction mixture over a period of 30 min. After completion of addition, the reaction mixture was stirred overnight at room temperature. The product was precipitated by the addition of methanol (150 mL) and then filtered. The crude product was purified by recrystallization from a mixture of DMAc and ethanol (1:2, v/v) to obtain pure PDP-4NB.

Yield: 8.53 g (88 %).

M.P.: 174 ^{o}C.

IR (KBr, cm^{-1}): 3280 (-N-H stretch), 1678 (C=O), 1524 (-NO$_2$ asymmetric stretch), 1346 (-NO$_2$ symmetric stretch).

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.62 (s, 1H, -NH-CO), 10.34 (s, 1H, -NH-CO), 8.37 (d, 4H, Ar-H), 8.20 (d, 4H, Ar-H), 7.79 (s, 1H, Ar-H), 7.63 (d, 1H, Ar-H), 7.30 (d, 1H, Ar-H), 1.18 – 1.47 (m, 26H, -CH$_2$), 0.83 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 164.33, 163.97, 149.54, 149.48, 140.92, 140.53, 137.27, 135.76, 134.83, 129.74, 129.45, 129.38, 123.77, 123.7, 119.92, 119.16, 31.64, 30.94, 29.41, 29.07, 29.03, 28.64, 22.40, 13.95

Elemental analysis: Calcd. for C$_{35}$H$_{44}$N$_4$O$_6$: C, 79.18; H, 12.02; N, 8.79. Found: C, 79.27, H, 11.86; N, 8.65.

3.3.2.2 Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide)
    (PDP-4AB) (I)

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed PDP-4NB (4.0 g, 6.5 mmol), Pd–C (10 wt.%) (0.12 g, 3 wt % based on dinitro compound) and absolute ethanol (50 mL). The reaction mixture was heated to 70 ^{o}C and hydrazine hydrate (9.8 mL, 0.195 mol) was added drop-wise over a period of 15 min and the reaction mixture was refluxed for 6 h. The reaction mixture was filtered while hot and the solvent was removed on a rotary evaporator to obtain the crude diamine which was purified by recrystallization from methanol.

Yield: 2.8 g (78 %).

M.P.: 137 $^\circ$C.

IR (KBr, cm^{-1}): 3429, 3346, 3232 (-N-H stretch), 1635 (C=O).

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 9.17 (s, 1H, -NH-CO), 8.47 (s, 1H, -NH-CO), 7.95 (d, 1H, Ar-H), 7.78 (d, 2H, Ar-H), 7.74 (d, 2H, Ar-H), 7.16 (d, 1H, Ar-H), 6.68 (d, 2H, Ar-H), 6.65 (d, 2H, Ar-H), 4.65 (d, 4H, -NH$_2$), 2.60 (t, 2H, Ar-CH$_2$), 1.25–1.50 (m, 28H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 165.16, 165.13, 150.14, 150.05, 136.77, 135.24, 130.93, 128.64, 128.38, 122.59, 122.35, 117.33, 117.19, 113.05, 112.89, 31.10, 30.35, 29.25, 28.87, 28.78, 28.74, 28.54, 21.87, 13.43.

Elemental analysis: Calcd. for C$_{35}$H$_{48}$N$_4$O$_2$: C, 75.50; H, 8.69; N,10.06. Found: C, 75.25, H, 8.82; N, 9.94.

3.3.2.3 Synthesis of *N,N'*-(1,3-phenylene) bis(4-nitrobenzamide)

N,N'-(1,3-Phenylene) bis(4-nitrobenzamide) was synthesized by condensing *m*-phenylene diamine with 4-nitrobenzoyl chloride, as per the reported procedure.[7]

IR (KBr, cm^{-1}): 3280 (-N-H stretch), 1670 (C=O), 1520, 1340 (-NO$_2$)

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.66 (s, 2H, -NH-CO), 8.39 (d, 4H, Ar-H), 8.37 (s, 1H, Ar-H), 8.20 (d, 4H, -CH$_2$), 7.37 (t, 1H, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 113.06, 116.67, 123.68, 129.0, 129.45, 139.21, 140.77, 149.33, 164.13.

Elemental analysis: Calcd. for C$_{20}$H$_{14}$N$_4$O$_6$: C, 59.12; H, 3.47; N,13.79. Found: C, 58.98; H, 3.10; N, 13.60.

3.3.2.4 Synthesis of *N,N'*-(1,3-phenylene) bis(4-aminobenzamide) (Ref I)

N,N'-(1,3-Phenylene) bis(4-aminobenzamide) (Ref I) was synthesized from *N,N'*-(1,3-phenylene) bis(4-nitrobenzamide) using the same procedure as described above for the synthesis of **I**.

Yield: 2.73 g (80 %).

M.P.: 226 $^\circ$C

IR (KBr, cm^{-1}): 3420, 3330, 3215 (-NH stretch), 1660 (-C=O)

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 9.77 (s, 2H, -NH-CO), 8.22 (s, 1H, Ar-H), 7.74 (d, 4H, Ar-H), 7.40 (d, 2H, Ar-H), 7.22 (t, 1H, Ar-H), 6.60 (d, 4H, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 165.59, 152.33, 140.05, 129.67, 128.52, 121.50, 115.68, 113.11, 112.66.

Elemental analysis: Calcd. for C$_{20}$H$_{18}$N$_4$O$_2$: C, 69.35; H, 5.24; N,16.17. Found: C, 69.10; H, 5.25; N, 16.23.

3.3.3 Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-aminobenzamide) (PDP-3AB) (II)

3.3.3.1 Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-nitrobenzamide) (PDP-3NB)

Into a 100 mL three-necked round bottom flask containing a magnetic stirring bar, were taken PBDA (5.0 g, 16 mmol) and DMAc (25 mL) and the mixture was stirred vigorously. The reaction mixture was cooled to 0 ^{o}C and 3-nitrobenzoyl chloride (5.84 g, 31 mmol) was added in portions. After completion of addition, pyridine (2.5 mL, 31 mmol) was added. The temperature was raised slowly to 100 ^{o}C and maintained at that temperature for 2 h. The reaction mixture was then allowed to cool to room temperature. The product was precipitated by addition of cold water and then filtered. The crude product was purified by recrystallization from a mixture of DMAc and ethanol (1:2, v/v) to obtain pure PDP-3NB.

Yield: 6.78 g (70 %).

M.P.: 181 ^{o}C.

IR (KBr, cm^{-1}): 3290 (-N-H stretch), 1662 (C=O), 1529 (-NO$_2$ asymmetric stretch), 1350 (-NO$_2$ symmetric stretch).

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.63 (s, 1H, -NH-CO), 10.37 (s, 1H, -NH-CO), 8.82 (s, 2H, Ar-H), 8.44 (dd, 4H, Ar-H), 7.85 (dd, 2H, Ar-H), 7.82 (d, 1H, Ar-H), 7.67 (d, 1H, Ar-H), 7.30 (d, 1H, Ar-H), 2.60 (t, 2H, Ar-CH$_2$), 1.11–1.51 (m, 28H, -CH$_2$), 0.85 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 162.48, 161.83, 146.48, 135.46, 135.10, 134.78, 133.95, 133.36, 132.74, 132.57, 128.25, 128.21, 124.43, 121.34, 121.24, 118.57, 117.92, 30.20, 27.96, 27.93, 27.63, 20.99, 12.64

Elemental analysis: Calcd. for C$_{35}$H$_{44}$N$_4$O$_6$: C, 68.16; H, 7.19; N, 9.08. Found: C, 68.10; H, 6.95; N, 8.93.

3.3.3.2 Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-aminobenzamide) (PDP-3AB)

PDP-3AB was prepared from PDP-3NB using the procedure as described above for the synthesis of **I**.

Yield: 2.82 g (78 %).

M.P.: 135 ^{o}C.

IR (KBr, cm^{-1}): 3415, 3310, 3219 (-N-H stretch), 1673 (C=O).

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.07 (s, 1H, -NH-CO), 9.70 (s, 1H, -NH-CO), 7.73 (d. 1H, Ar-H), 7.59 (d, 2H, Ar-H), 7.09-7.18 (m, 7H, Ar-H), 6.74 (d, 2H, Ar-H), 5.32 (d, 4H, -NH$_2$), 1.19–1.49 (m, 28H, -CH$_2$), 0.85 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 166.63, 166.45, 149.00, 137.61, 136.29, 136.17, 135.74, 133.94, 128.96, 119.75, 118.41, 116.98, 116.90, 114.94, 114.74, 113.34, 113.21, 31.58, 30.91, 29.87, 29.34, 29.16, 29.00, 22.38, 14.20.

Elemental analysis: Calcd. for $C_{35}H_{48}N_4O_2$: C, 75.50; H, 8.69; N, 10.06. Found: C, 75.25; H, 8.45; N, 9.86.

3.3.3.3 Synthesis of *N,N'*-(1,3-phenylene) bis(3-nitrobenzamide)

N,N'-(1,3-Phenylene) bis(3-nitrobenzamide) was synthesized by condensing *m*-phenylene diamine with 3-nitrobenzoyl chloride using the procedure reported in the literature.[7]

Yield: 13.15 g (70 %).

M.P.: 267 ^{o}C (Lit. M.P. 266-267 ^{o}C)[7]

IR (KBr, cm^{-1}): 1670 (-C=O), 1515 and 1340 (-NO$_2$).

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 10.68 (s, 2H, -NH-CO), 8.81 (s, 2H, Ar-H), 8.44 (d, 4H, Ar-H), 8.38 (s, 1H, Ar-H), 7.85 (t, 2H, Ar-H), 7.55 (d, 2H, Ar-H), 7.39 (d, 1H, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 165.59, 152.33, 140.05, 129.67, 128.52, 121.50, 115.68, 113.11, 112.66.

Elemental analysis: Calcd. for $C_{20}H_{14}N_4O_6$: C, 59.12; H, 3.47; N, 13.79. Found: C, 58.95; H, 3.45; N, 13.80.

3.3.3.4 Synthesis of *N,N'*-(1,3-phenylene) bis(3-aminobenzamide) (Ref II)

Ref **II** was synthesized from *N,N'*-(1,3-phenylene) bis(3-nitrobenzamide) following the procedure as described for synthesis of **I**.

Yield: 2.72 g (80 %).

M.P.: 214 ^{o}C (Lit. M.P. 214 ^{o}C)[7]

IR (KBr, cm^{-1}): 3420, 3330, 3150 (-N-H stretch), 1665 (-C=O)

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 8.84 (s, 2H, -NH-CO), 8.37 (d, 1H, Ar-H), 7.59 (m, 2H, Ar-H), 7.12- 7.31 (m, 8H, Ar-H), 6.86 (dd, 2H, Ar-H), 5.03 (s, 1H, -NH$_2$).

Elemental analysis: Calcd. for $C_{20}H_{18}N_4O_2$: C, 69.35; H, 5.24; N, 16.17. Found: C, 69.27; H, 5.15; N, 16.18.

3.3.4   Synthesis of 2,4-diisocyanato-1-pentadecylbenzene

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a reflux condenser, a dropping funnel and a nitrogen inlet was placed 4-pentadecylbenzene-1,3-diamine (1.0 g, 3.15 mmol) and dry toluene (50 mL). The flask was flushed with nitrogen gas and the solution was stirred at 0 ^{o}C. In another 100 mL flask, bis(trichloromethyl)carbonate or triphosgene (5.60 g, 18.86 mmol) was weighed and dissolved in dry toluene (50 mL). The solution of triphosgene was transferred to the dropping funnel under nitrogen atmosphere and slowly added to the solution containing PBDA with constant stirring for 15 minutes at 0 ^{o}C. After completion of addition, the reaction mixture was stirred at room temperature for 2 h and then refluxed for 6 h. Finally, excess of phosgene was removed by flushing the stream of nitrogen through the solution at 80 ^{o}C and remaining toluene was distilled off under vacuum to yield

crude product which was purified by recrystallization from dry *n*-hexane to obtain pure 2,4-diisocyanato-1-pentadecylbenzene.

Yield: 0.93 g (80 %).

M.P.: 48 $^{\circ}$C

IR (CHCl$_3$, cm^{-1}): 2262 (-NCO).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.10 (d, 1H, Ar-H), 6.86 (dd, 1H, Ar-H), 6.81 (d, 1H, Ar-H), 2.58 (t, 2H, Ar-CH$_2$), 1.25-1.56 (m, 28H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 135.08, 132.74, 131.94, 130.75, 124.91, 124.65, 122.29, 121.44, 31.92, 31.76, 29.98, 29.66, 29.54, 29.41, 29.36, 29.26, 22.69, 14.10.

Elemental analysis: Calcd. for C$_{23}$H$_{34}$N$_2$O$_2$: C, 74.55; H, 9.25; N, 7.56. Found: C, 74.10; H, 8.87; N, 7.38.

3.3.5   Synthesis of 3,5-diamino-4'-pentadecylbenzophenone

3.3.5.1 Synthesis of 3,5-dinitro-4'-pentadecylbenzophenone

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a reflux condenser and a dropping funnel were placed 3,5-dinitrobenzoylchloride (1.19 g, 5.2 mmol), pentadecylbenzene (1.5 g, 5.2 mmol) and dry nitrobenzene (50 mL). The resulting solution was cooled to 10 $^{\circ}$C in an ice bath after which anhydrous AlCl$_3$ (0.76 g, 5.72 mmol) was added slowly in small portions so that reaction temperature did not rise above 15 $^{\circ}$C. After completion of addition, the ice bath was removed and the reaction mixture was stirred at 80 $^{\circ}$C for 3 h. The reaction mixture was poured into a mixture of conc. HCl (2 mL) and ice-water (100 mL). The organic layer was washed with water (2 x 50 mL) followed by brine solution (2 x 50 mL) and water (2 x 50 mL). The organic layer was separated and dried over sodium sulfate and filtered. The evaporation of solvent afforded crude product which was recrystallized from ethanol to yield pure 3,5-dinitro-4'-pentadecylbenzophenone.

Yield: 1.43 g (91 %).

M.P.: 67 $^{\circ}$C

IR (CHCl$_3$, cm^{-1}): 1667 (-C=O), 1546 (-NO$_2$ asymmetric stretch), 1346 (-NO$_2$ symmetric stretch).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 9.23 (s, 1H, Ar-H), 8.91 (s, 2H, Ar-H), 7.72 (d, 2H, Ar-H), 7.37 (d, 2H, Ar-H), 2.72 (t, 2H, Ar-CH$_2$), 1.24-1.67 (m, 26H, -CH$_2$), 0.86 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 191.19, 150.41, 148.40, 141.04, 132.51, 130.21, 129.21, 129.10, 121.22, 36.09, 31.86, 30.98, 29.60, 29.50, 29.40, 29.30, 22.62, 14.03.

Elemental analysis: Calcd. for C$_{28}$H$_{38}$N$_2$O$_5$: C, 69.68; H, 7.94; N, 5.80. Found: C, 69.55; H, 7.86; N, 5.65.

3.3.5.2 Synthesis of 3,5-diamino-4'-pentadecylbenzophenone

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed 3,5-dinitro-4'-pentadecylbenzophenone (2.0

g, 4.14 mmol), Pd-C (10 wt %) (0.06 g, 3 wt % based on dinitro compound) and absolute ethanol (50 mL). The reaction mixture was heated to 70 ^{o}C and hydrazine hydrate (6.5 mL, 0.12 mol) was added drop-wise over a period of 15 min and refluxed for 6 h. The reaction mixture was filtered while hot and the solvent was distilled on a rotary evaporator to obtain the crude product which was purified by recrystallization from methanol.

Yield: 1.54 g (88 %).

M.P.: 113 ^{o}C

IR (CHCl$_3$, cm^{-1}): 1733 (-C=O), 3450, 3355 and 3220 (-N-H stretch).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.43 (d, 2H, Ar-H), 7.08 (d, 2H, Ar-H), 6.06 (s, 1H, Ar-H), 5.97 (s, 2H, Ar-H), 3.65 (s, 4H, -NH$_2$), 2.58 (t, 2H, Ar-CH$_2$), 1.24-1.59 (m, 26H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 190.20, 148.28, 141.95, 135.27, 134.20, 127.33, 125.63, 104.13, 100.77, 31.18, 28.94, 28.61, 21.96, 13.49.

Elemental analysis: Calcd. for C$_{28}$H$_{42}$N$_2$O: C, 79.57; H, 10.02; N, 6.63. Found: C, 79.50; H, 9.86; N, 6.60.

3.3.6   Synthesis of 3,5-diamino-*N*-(4-pentadecylphenyl)benzamide

3.3.6.1   Synthesis of 1-nitro-4-pentadecylbenzene

Into a 100 ml two-necked round bottom flask equipped with a dropping funnel and a magnetic stirring bar were placed fuming nitric acid (1.5 mL, 35 mmol) and zeolite H-β (1.0 g). The reaction mixture was cooled to 0 ^{o}C and acetic anhydride (4.5 mL, 48 mmol) was added drop-wise over a period of 10 min. and the reaction mixture was stirred. Pentadecylbenzene (10.0 g, 35 mmol) was added drop-wise to the reaction mixture over a period of 45 min and the reaction mixture was stirred for additional 30 min. The reaction mixture was filtered to remove zeolite H-β catalyst and the catalyst was washed with acetone (50 mL) and filtered. The solvent was removed on a rotary evaporator to obtain the crude product which was chromatographed on silica gel (230-400 mesh) column with pet ether as an eluent to obtain pure 1-nitro-4-pentadecylbenzene.

Yield: 7.8 g (68 %).

M.P.: 51 ^{o}C.

IR (CHCl$_3$, cm^{-1}): 1520 (-NO$_2$ asymmetric stretch), 1342 (-NO$_2$ symmetric stretch).

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 8.13 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 2.69 (t, 2H, Ar-CH$_2$), 1.24-1.63 (m, 26H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 150.81, 146.20, 129.11, 123.52, 35.85, 31.90, 30.97, 29.64, 29.34, 29.16, 22.67, 14.08.

Elemental analysis: Calcd. for $C_{21}H_{35}NO_2$: C, 75.63; H, 10.58; N, 4.20. Found: C, 74.98; H, 10.36; N, 3.80.

3.3.6.2 Synthesis of 4-pentadecylaniline

Into a 250 ml three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed 1-nitro-4-pentadecylbenzene (5 g, 15 mmol), Pd-C (10 wt %) (0.15 g, 3 wt % based on nitro compound) and absolute ethanol (50 mL). The reaction mixture was heated to 70 ^{o}C and hydrazine hydrate (22.5 mL, 0.45 mol) was added drop-wise over a period of 15 min and refluxed for 6 h. The reaction mixture was filtered while hot and the solvent was distilled on a rotary evaporator to obtain the crude product which was recrystallized from methanol to yield pure 4-pentadecylaniline.

Yield: 3.86 g (85 %).

M.P.: 47 ^{o}C.

IR (CHCl$_3$, cm^{-1}): 3400, 3320 and 3220 (-N-H stretch)

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 6.96 (d, 2H, Ar-H), 6.62 (d, 2H, Ar-H), 3.52 (s, 2H, -NH$_2$), 2.48 (t, 2H, Ar-CH$_2$), 1.25-1.55 (m, 26H, -CH$_2$), 0.88 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 143.96, 133.09, 129.09, 115.17, 35.07, 31.91, 29.67, 29.53, 29.34, 22.67, 14.08.

Elemental analysis: Calcd. for $C_{21}H_{37}N$: C, 83.10; H, 12.29; N, 4.61. Found: C, 82.65; H, 11.98; N, 4.25.

3.3.6.3 Synthesis of 3,5-dinitro-*N*-(4-pentadecylphenyl)benzamide

Into a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed 4-pentadecyl aniline (2.0 g, 66 mmol), DMAc (16 mL) and triethylamine (0.67 mL, 66 mmol). 3,5- Dinitrobenzoyl chloride (1.52 g, 66 mmol) dissolved in DMAc (7 mL), was added drop-wise into the reaction mixture over a period of 30 min. After completion of addition, the reaction mixture was stirred overnight at room temperature. The product was precipitated by the addition of methanol (150 mL) and then filtered. The crude product was purified by recrystallization from a mixture of DMAc and ethanol (1:2, v/v) to obtain pure 3,5-dinitro-*N*-(4-pentadecylphenyl)benzamide.

Yield: 2.89 g (88 %).

M.P.: 139 ^{o}C.

IR (KBr, cm^{-1}): 1655 (-C=O), 1525 (-NO$_2$ asymmetric stretch), 1340 (-NO$_2$ symmetric stretch).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ (ppm) 10.16 (s, 1H, -NH), 9.18 (s, 2H, Ar-H), 9.08 (d, 1H, Ar-H), 7.72 (d, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 2.60 (t, 2H, Ar-CH$_2$), 1.27-1.61 (m, 26H, -CH$_2$), 0.86 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, Acetone-d$_6$): δ (ppm) 161.92, 149.56, 140.12, 139.30, 137.07, 129.51, 128.53, 121.74, 121.33, 121.24, 35.91, 32.60, 32.31, 23.29, 14.32.

Elemental analysis: Calcd. for $C_{28}H_{39}N_3O_5$: C, 67.58; H, 7.90; N, 8.44. Found: C, 66.99; H, 7.46; N, 7.98.

3.3.6.4 Synthesis of 3,5-diamino-*N*-(4-pentadecylphenyl)benzamide

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a dropping funnel and a reflux condenser were placed 3,5-dinitro-*N*-(4-pentadecylphenyl)benzamide (2.0 g, 4.0 mmol), Pd-C (10 wt. %) (0.06 g, 3 wt % based on dinitro compound) and absolute ethanol (50 mL). The reaction mixture was heated to 70 ^{o}C and hydrazine hydrate (6.1 mL, 0.12 mol) was added drop-wise over a period of 15 min and the reaction mixture was refluxed for 6 h. The reaction mixture was filtered while hot and the solvent was removed on a rotary evaporator to obtain a crude diamine which was purified by recrystallization from methanol.

Yield: 1.5 g (85 %).

M.P.: 164 ^{o}C.

IR (KBr, cm^{-1}): 1650 (-C=O), 3200, 3335, 3425 (-N-H stretch)

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) 9.48 (s, 1H, -NH), 7.63 (d, 2H, Ar-H), 7.10 (d, 1H, Ar-H), 6.52 (d, 2H, Ar-H), 6.14 (s, 1H, Ar-H), 4.26(s, 4H, -NH$_2$), 1.25-1.57 (m, 26H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ (ppm) 167.29, 149.30, 137.57, 137.20, 137.12, 128.32, 120.14, 102.50, 102.39, 34.89, 31.58, 29.35, 29.03, 22.38, 14.15.

Elemental analysis: Calcd. for $C_{28}H_{43}N_3O$: C, 76.84; H, 9.90; N, 9.60. Found: C, 76.67; H, 9.66; N, 9.45.

3.3.7 Synthesis of 2,2'(4-pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid)

Into a 250 mL three-necked round bottom flask equipped with a reflux condenser and a magnetic stirring bar, were added 4-pentadecylbenzene-1,3-diamine (3 g, 9.43 mmol), trimellitic anhydride (3.63 g, 18.9 mmol) and acetic acid (70 mL). The reaction mixture was stirred for 1 h and then refluxed at 120 ^{o}C for 12 h. The reaction mixture was cooled to room temperature and poured into methanol (500 mL). The pale yellow precipitate was filtered, washed with methanol, recrystallized from a mixture of DMF and water (7:1, v/v) and dried in a vacuum oven at 70 ^{o}C overnight.

Yield: 3.84 g (98 %).

M.P.: 234 ^{o}C

IR (KBr, cm^{-1}): 3500 (-O-H of COOH), 1800 and 1715 (-C=O stretching of imide), 1390 (imide-II), 750 (imide-IV), 1109 (imide-III).

^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 8.43 (dd, 2H, Ar-H), 8.32 (d, 2H, Ar-H), 8.10 (d, 2H, Ar-H), 7.59 (s, 2H, Ar-H), 7.53 (s, 1H, Ar-H), 1.21-1.47 (m, 26H, -CH_2), 0.84 (t, 3H, -CH_3).

^{13}C-NMR (100 MHz, DMSO-d_6): δ (ppm) 166.76, 166.72, 166.34, 166.31, 166.03, 165.96, 141.42, 136.95, 136.82, 135.86, 135.07, 135.0, 132.26, 132.14, 130.87, 130.43, 128.42, 128.11, 124.23, 124.18, 123.91, 31.66, 30.01, 29.40, 29.11, 28.95, 22.45, 14.19.

Elemental analysis: Calcd. for $C_{39}H_{42}N_2O_8$: C, 70.25; H, 6.35; N, 4.20. Found: C, 69.90; H, 6.20; N, 4.11.

3.3.8 Synthesis of 2-pentadecylbenzene-1,4-diol

3.3.8.1 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 stirring bar were placed 3-pentadecyl phenol (10.0 g, 32.8 mmol), potassium hydroxide (9.2 g, 164.2 mmol), and ethyl alcohol (50 mL). The reaction mixture was stirred and to the reaction mixture was added diazonium chloride prepared from sulphanilic acid dihydrate (6.90 g, 32.8 mmol) at −5 °C. The resulting red dye solution was stirred for 2 h and then heated at 75 °C on a water bath. At that temperature, a saturated solution of sodium dithionite (17.5 g, 98.5 mmol) 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 (6.0 g, 98.5 mmol) dissolved in water (10 mL) and was refluxed for 1 h (color changed to pale tan). The reaction mixture was poured into water (1 L), the product was filtered and dried under reduced pressure at 50 °C for 2 h. The crude product was purified by recrystallisation using toluene.

Yield: 8.2 g (79 %).

M.P.: 104 °C (Lit. M.P.: 104 °C).[8]

IR (KBr, cm^{-1}): 3400, 3350 and 3220 (-N-H stretch)

^{1}H-NMR (200 MHz, DMSO-d_6): δ (ppm) 8.26 (s, 1H, -OH), 6.30- 6.45 (m, 3H, Ar-H), 4.14 (s, 2H, -NH_2), 2.32 (t, 2H, Ar-CH_2), 1.23- 1.45 (m, 26 H, -CH_2), 0.85 (t, 3H, -CH_3).

^{13}C-NMR (50 MHz, DMSO-d_6): δ (ppm) 150.14, 135.40, 128.97, 117.43, 116.07, 113.24, 31.61, 30.87, 29.41, 28.86, 22.39, 14.15.

Elemental analysis: Calcd. for $C_{21}H_{37}NO$: C, 78.94; H, 11.67; N, 4.38. Found: C, 78.77; H, 11.35; N, 4.15.

3.3.8.2 Synthesis of 2-pentadecylcyclohexa-2,5-diene-1,4-dione

Into a 250 ml three-necked round bottom flask equipped with a reflux condenser and a magnetic stirring bar, were added 4-amino-3-pentadecyl phenol (5.752 g, 18 mmol), conc. sulfuric acid (5 mL, 0.093 mol) and distilled water (100 mL). Potassium dichromate (3.5 g, 11.9 mmol) dissolved in distilled water (55 mL) was added to the reaction mixture with constant

stirring and the reaction mixture was heated at 60 ^{o}C for 4 h. Then reaction mixture was filtered, washed with distilled water till it became acid free to obtain crude product which was recrystallized from acetone to get pure 2-pentadecylcyclohexa-2,5-diene-1,4-dione.

Yield: 4.3 g (75 %).

M.P.: 78 ^{o}C (Lit. M.P.: 77-78 ^{o}C).[9]

IR (CHCl$_3$, cm^{-1}): 1656 (-C=O)

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 6.71 (d, 2H, Ar-H), 6.54 (d, 1H, Ar-H), 2.40 (t, 2H, Ar-CH$_2$), 1.24- 1.48 (m, 26H, -CH$_2$), 0.86 (t, 3H, -CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$): δ (ppm) 187.85, 187.52, 149.70, 136.77, 136.20, 132.32, 31.89, 29.63, 29.29, 28.99, 27.74, 22.66, 14.10.

Elemental analysis: Calcd. for C$_{21}$H$_{34}$O$_2$: C, 79.19; H, 10.76. Found: C, 78.86; H, 9.98.

3.3.8.3 Synthesis of 2-pentadecylbenzene-1,4-diol

Into a 250 mL three-necked flask equipped with a reflux condenser, a magnetic stirring bar and a dropping funnel were placed 2-pentadecylcyclohexa-2,5-diene-1,4-dione (2.5 g, 7.85 mmol), zinc powder (1.60 g, 24.5 mmol) and water (25 mL). The reaction mixture was refluxed to 100 ^{o}C and HCl (20 mL) was added drop-wise over a period of 30 min and refluxed for 2 h. The reaction mixture was filtered while hot and the filtrate was poured into a large amount of water. The obtained solid was filtered and recrystallized from ethanol to yield pure 2-pentadecylbenzene-1,4-diol.

Yield: 2.46 g (98 %).

M.P.: 106-107 ^{o}C

IR (CHCl$_3$, cm^{-1}): 3265 (-O-H)

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 8.49 (s, 1H, -OH), 8.42 (s, 1H, -OH), 6.53 (d, 1H, Ar-H), 6.43 (d, 1H, Ar-H), 6.37 (dd, 1H, Ar-H), 2.40 (t, 2H, Ar-CH$_2$), 1.23-1.46 (m, 26H, -CH$_2$), 0.85 (t, 3H, -CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$and DMSO-d$_6$): δ (ppm) 148.54, 146.54, 128.80, 115.45, 114.43, 111.67, 30.60, 29.04, 28.72, 28.42, 28.38, 28.33, 28.03, 21.38, 13.0.

Elemental analysis: Calcd. for C$_{21}$H$_{36}$O$_2$: C, 78.69; H, 11.32. Found: C, 78.37; H, 10.98.

3.3.9   Synthesis of 4-methoxy-6-pentadecylisophthalonitrile

3.3.9.1 Synthesis of 1-methoxy-3-pentadecylbenzene

Into a 250 mL round bottom flask equipped with a magnetic stirring bar were taken 3-pentadecylphenol (10.0 g, 32.8 mmol), potassium hydroxide (7.35 g, 131 mmol), methyl iodide (9.32 g, 66 mmol) and dimethyl sulfoxide (150 mL). The reaction mixture was stirred overnight at room temperature. After the completion of the reaction, water (100 mL) was added and reaction mixture was extracted with dichloromethane (2 x 100 mL). The organic layer was

washed with water (2 x 75 mL); dried over sodium sulfate and filtered. The evaporation of solvent afforded crude product which was purified by silica gel (60-120 mesh) column chromatography (pet ether as an eluent) to obtain pure 1-methoxy-3-pentdecylbenzene.

Yield: 9.93 g (95 %).

M.P.: 28-29 ^{o}C (Lit. M.P.: 27-28 ^{o}C).[10]

IR (CHCl$_3$, cm^{-1}): 1150 (-C-O-C- stretching)

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 7.20 (dd, 1H, Ar-H), 6.69- 6.79 (m, 3H, Ar-H), 3.80 (s, 3H, -OCH$_3$), 2.57 (t, 2H, Ar-CH$_2$), 1.25-1.60 (m, 26 H, -CH$_2$), 0.88 (t, 3H,-CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$): δ (ppm) 159.55, 144.55, 129.09, 12081, 114.15, 110.72, 54.98, 36.04, 31.94, 31.42, 29.71, 29.38, 22.70, 14.11.

Elemental analysis: Calcd. for C$_{22}$H$_{38}$O: C, 82.95; H, 12.02. Found: C, 82.75; H, 11.86.

3.3.9.2 Synthesis of 1,5-dibromo-2-methoxy-4-pentadecylbenzene

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a reflux condenser, a dropping funnel and a thermometer were placed 1-methoxy 3-pentadecyl benzene (29.24 g, 0.092 mol) and dichloromethane (150 mL). The reaction mixture was stirred and bromine (10 mL, 0.195 mol) was added in dropwise manner at a temperature between -5 ^{o}C to 0 ^{o}C over a period of 30 min. The top of the condenser was equipped with a trap to absorb the hydrogen bromide released during the reaction. After completion of 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 % ammonia solution (100 mL). Two phases formed in the reaction mixture were separated and the organic layer was washed with water (2 x 100 mL). The organic layer was separated, dried over anhydrous sodium sulfate and filtered. Removal of solvent on a rotary evaporator afforded crude product which was chromatographed on silica gel (60-120 mesh) column with pet ether: ethyl acetate (95:5, v/v) as an eluent to obtain pure 1,5-dibromo-2-methoxy-4-pentadecylbenzene.

Yield: 40 g (92 %).

M.P.: 38 ^{o}C

IR (CHCl$_3$, cm^{-1}): 670 cm^{-1}.

^{1}H-NMR (200 MHz, CDCl$_3$): δ (ppm) 7.65 (s, 1H, Ar-H), 6.72 (s, 1H, Ar-H), 3.86 (s, 3H, -OCH$_3$), 2.65 (t, 2H, Ar-CH$_2$), 1.25-1.57 (m, 26 H, -CH$_2$), 0.87 (t, 3H, -CH$_3$).

^{13}C-NMR (50 MHz, CDCl$_3$): δ (ppm) 155.10, 142.50, 135.94, 114.81, 113.26, 109.20, 56.28, 36.32, 31.90, 29.66, 29.34, 22.67, 14.10.

Elemental analysis: Calcd. for C$_{22}$H$_{36}$Br$_2$O: C, 55.47; H, 7.62; Br, 33.55. Found: C, 54.85; H, 7.50; Br, 33.48.

3.3.9.3 Synthesis of 4-methoxy-6-pentadecylisophthalonitrile

Into a 250 mL three-necked round bottom flask containing 1,5-dibromo-2-methoxy-4-pentadecylbenzene (10.0 g, 21 mmol) was added copper cyanide (9.40 g, 105 mmol) followed by CuSO$_4$ (0.20 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). The organic layer was successively washed with water (2 x 100 mL), brine (2 x 100 mL) and water (2 x 100 mL). The organic layer was separated, dried over sodium sulphate and filtered. Removal of solvent on a rotary evaporator afforded crude 4-methoxy-6-pentadecylisophthalonitrile which was purified by silica gel (60-120 mesh) column chromatography (pet ether: ethyl acetate, 98:2, v/v).

Yield: 5.4 g (70 %).

M.P.: 82 ^{o}C.

IR (CHCl$_3$, cm^{-1}): 2225 (-CN)

^{1}H-NMR (400 MHz, CDCl$_3$): δ (ppm) 7.79 (s, 1H, Ar-H), 6. 87 (s, 1H, Ar-H), 3.99 (s, 3H, -OCH$_3$), 2.85 (t, 2H, Ar-CH$_2$), 1.24-1.67 (m, 26 H, -CH$_2$), 0.86 (t, 3H,-CH$_3$).

^{13}C-NMR (100 MHz, CDCl$_3$): δ (ppm) 163.43, 154.50, 137.89, 116.27, 114.36, 112.30, 105.00, 100.78, 56.49, 35.43, 31.80, 30.56, 29.54, 29.48, 29.36, 29.24, 29.18, 22.57, 14.01.

Elemental analysis: Calcd. for C$_{24}$H$_{36}$N$_2$O: C, 78.21; H, 9.85; N, 7.60. Found: C, 78.04; H, 9.65; N, 7.48.

3.4   Results and discussion

One of the approaches to improve processability of high temperature /high performance polymers is the attachment of flexible chains as pendent groups. It is reported that the use of monomers bearing pendent flexible groups greatly reduces strong intermolecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. In general, such pendent groups not only bring about improved solubility but also help lower the melting and glass transition temperatures.[8,11] 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 diamines, diacid, diisocyanate, diphenol and dinitrile were designed and synthesized.

The following difunctional monomers were synthesized starting from CNSL:

   a.   4-Pentadecylbenzene-1,3-diamine,

   b.   *N,N'*-(4-Pentadecyl-1,3-phenylene) bis(4-aminobenzamide) (PDP-4AB),

c. *N,N'*-(4-Pentadecyl-1,3-phenylene) bis(3-aminobenzamide) (PDP-3AB),

d. 2,4-Diisocyanato-1-pentadecylbenzene,

e. 3,5-Diamino-4'-pentadecylbenzophenone,

f. 3,5-Diamino-*N*-(4-pentadecylphenyl)benzamide,

g. 2,2'(4-Pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid),

h. 2-Pentadecylbenzene-1,4-diol, and

i. 4-Methoxy-6-pentadecylisophthalonitrile

3.4.1   Synthesis of 4-pentadecylbenzene-1,3-diamine

Aromatic diamines are an important class of starting materials for the preparation of a variety of high performance polymers such as aromatic polyimides, polyamides, poly(amideimide)s, poly(azomethine)s, etc. Phenylene diamines are one of the most widely used aromatic diamines for the synthesis of polymers. Among phenylene diamines, *meta*-phenylene diamines are most suitable for improving the solubility of the resulting polymers because the *meta*-linkages act as kinks, and help in the disruption of symmetry and hence the synthesis of substituted *meta*-phenylene diamines has gained importance.

Scheme 3.1 depicts route for the synthesis of 4-pentadecylbenzene-1,3-diamine.
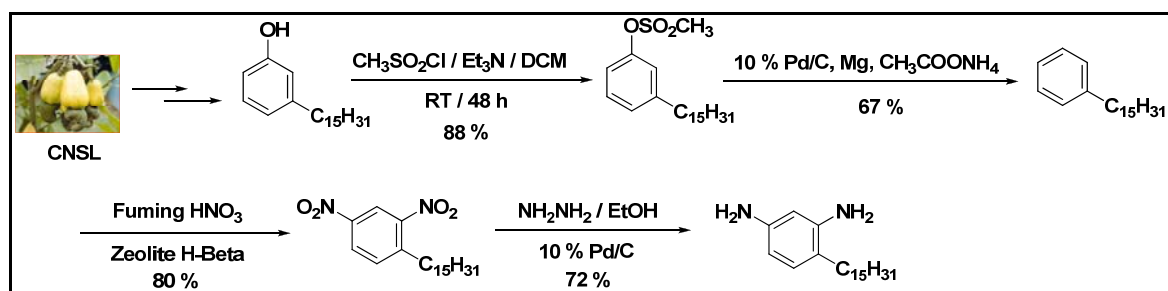
Scheme 3.1 Synthesis of 4-pentadecylbenzene-1,3-diamine

A new unsymmetrical aromatic diamine *viz*., 4-pentadecylbenzene-1,3-diamine (PBDA) was synthesized in four steps starting from 3-pentadecylphenol (3-PDP) which in turn is obtainable from CNSL- a renewable resource material.

In the first step, 3-PDP was reacted with methanesulfonyl chloride. In this reaction, hydroxyl group of 3-PDP was converted into corresponding mesyl ester. 1-Methyl sulfonyloxy-3-pentadecylbenzene was purified by recrystallization from methanol.

In the second step, 1-methyl sulfonyloxy-3-pentadecylbenzene was converted to pentadecyl benzene by using Pd-C catalyzed deoxygenation method.[12] The crude product was purified by column chromatography (eluent: pet ether). Pentadecylbenzene acts as an intermediate compound and can undergo various electrophilic substitution reactions like nitration, bromination, Friedel-Crafts acylation, etc.

In the next step, nitration of pentadecylbenzene using nitrating mixture comprising of fuming nitric acid and trifluoroacetic anhydride and acetic anhydride in the presence of zeolite

H-β was carried out as per the reported procedure.[13] This method gives 2,4-dinitro-1-pentadecylbenzene as a major product. The crude product was chromatographed on silica gel column with pet ether as an eluent to obtain pure 2,4-dinitro-1-pentadecylbenzene which was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 2,4-dinitro-1-pentadecylbenzene (**Figure 3.2**) exhibited absorption bands at 1530 and 1345 cm^{-1} corresponding to the asymmetric -NO_2 stretching and symmetric -NO_2 stretching, respectively.
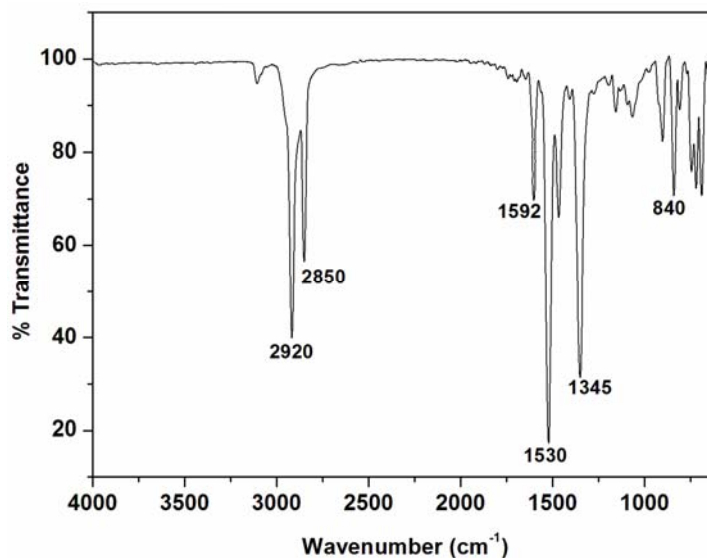
Figure 3.2 FT-IR spectrum (CHCl₃) of 2,4-dinitro-pentadecylbenzene

^{1}H-NMR spectrum of 2,4-dinitro-1-pentadecylbenzene is reproduced in **Figure 3.3.**
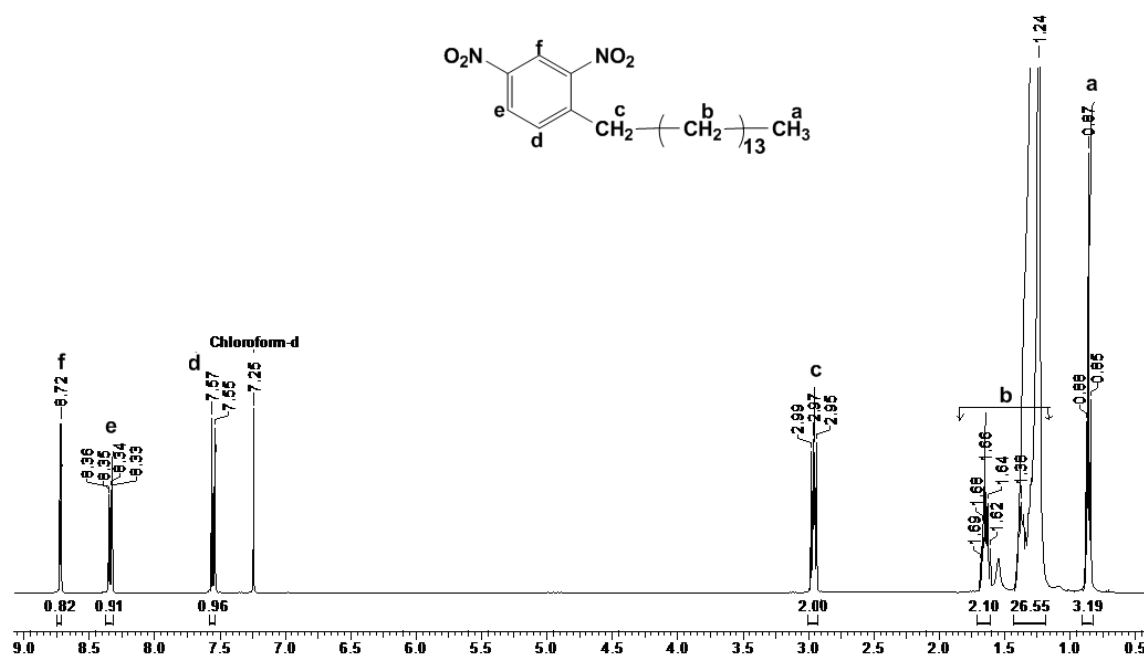
Figure 3.3 ^{1}H-NMR spectrum (CDCl₃) of 2,4-dinitro-pentadecylbenzene

The aromatic proton 'f' flanked by two nitro groups displayed a doublet at 8.72 δ, ppm and the aromatic proton 'e' *ortho* and *para* to the nitro group appeared as doublet of doublet at

8.33 δ, ppm. The aromatic proton 'd' *ortho* to the pentadecyl chain displayed a doublet at 7.54 δ, ppm. The benzylic methylene protons 'c' exhibited a triplet at 2.97 δ, ppm while the other methylene protons 'b' appeared in the range 1.24 - 1.69 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.87 δ, ppm.

^{13}C-NMR spectrum of 2,4-dinitro-1-pentadecylbenzene is reproduced in **Figure 3.4** and the peak assignments were confirmed by DEPT spectrum.
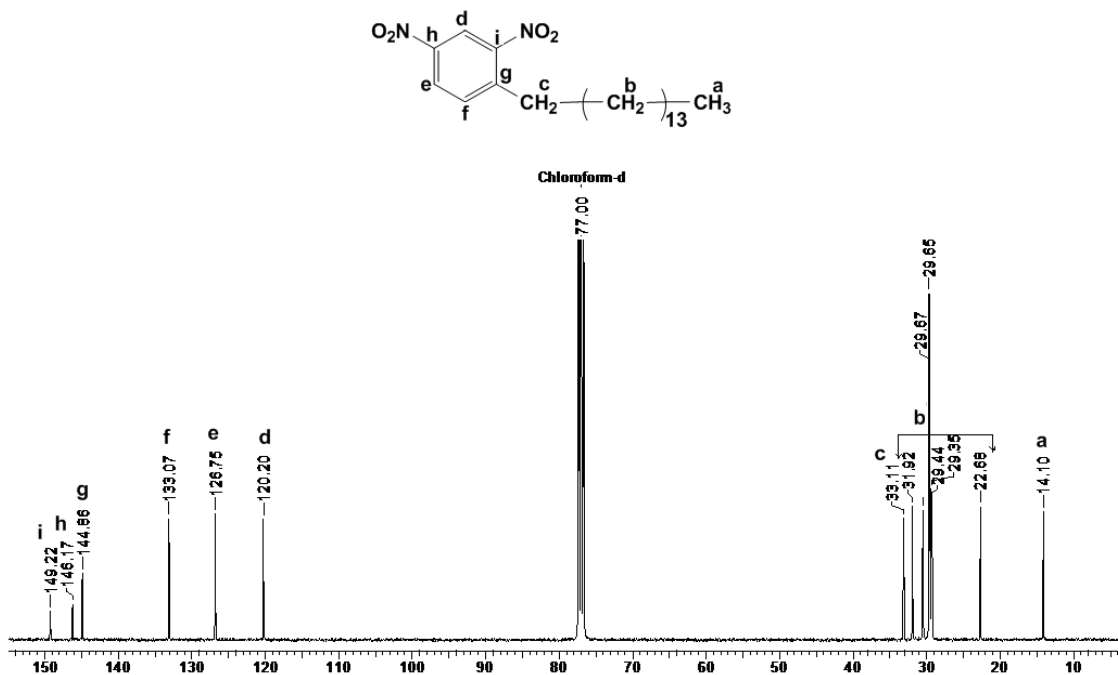
Figure 3.4 ^{13}C-NMR spectrum (CDCl$_3$) of 2,4-dinitro-pentadecylbenzene

The quaternary aromatic carbon 'i' and 'h' appeared at 149.22 and 146.17 δ, ppm, respectively. The quaternary aromatic carbon 'g' attached to pentadecyl chain displayed a peak at 144.86 δ, ppm. The aromatic carbons 'd', 'e' and 'f' appeared at 133.07, 126.75 and 120.20 δ, ppm, respectively. The methylene carbon 'c' displayed a peak at 33.11 δ, ppm and other methylene carbons 'b' appeared in the range 22.68- 31.92 δ, ppm. The methyl carbon 'a' of pentadecyl chain showed a signal at 14.10 δ, ppm.

The reduction of 2,4-dinitro-1-pentadecylbenzene using hydrazine hydrate / Pd-C (10 wt %) reagent system afforded the desired 4-pentadecylbenzene-1,3-diamine. The crude diamine was chromatographed over neutral alumina with dichloromethane as an eluent to obtain pure 4-pentadecylbenzene-1,3-diamine which was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

In FT-IR spectrum of 4-pentadecylbenzene-1,3-diamine (**Figure 3.5**) absorption bands at 3200, 3320 and 3400 cm^{-1} were observed which correspond to the –N-H stretching of amino group.
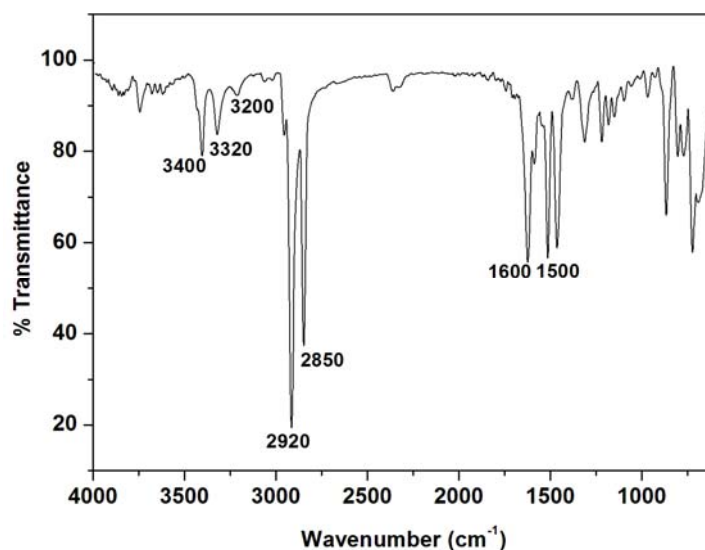
Figure 3.5 FT-IR spectrum (CHCl₃) of 4-pentadecylbenzene-1,3-diamine

^{1}H-NMR spectrum of 4-pentadecylbenzene-1,3-diamine is depicted in **Figure 3.6.**
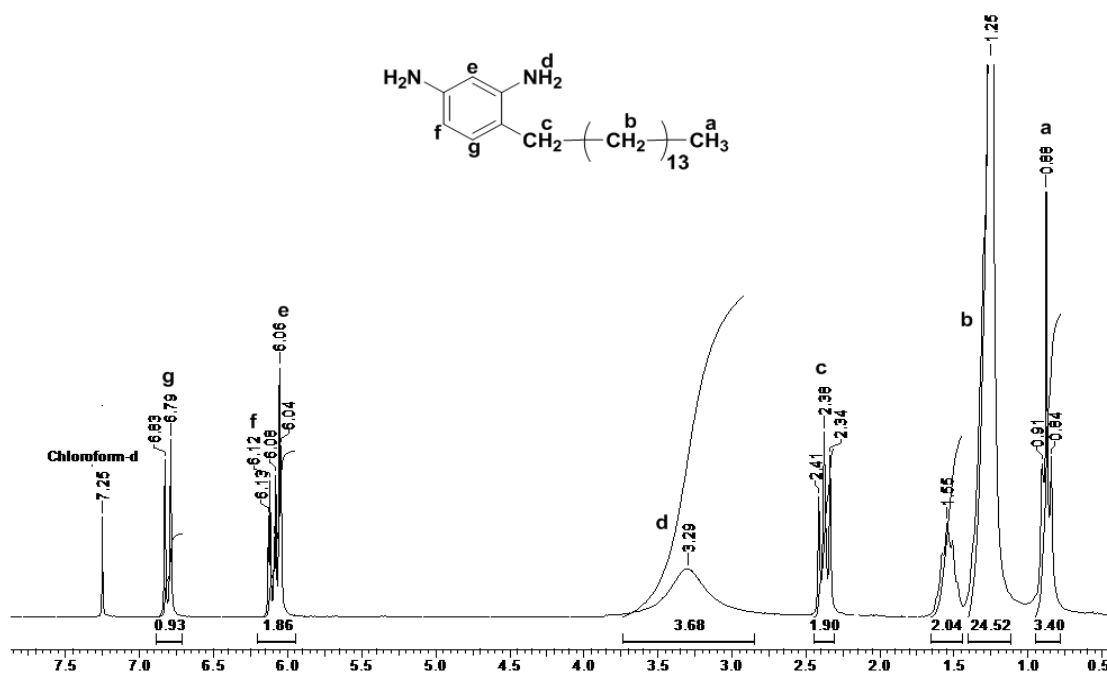
Figure 3.6 ^{1}H-NMR spectrum (CDCl₃) of 4-pentadecylbenzene-1,3-diamine

A doublet at 6.81 δ, ppm is ascribed to aromatic proton 'g' *meta-* to the amino group. A doublet of doublet observed at 6.12 δ, ppm is due to aromatic proton 'f' *ortho-* and *para-* to the amino group. A doublet at 6.06 δ, ppm is assignable to the aromatic proton 'e' flanked by two amino groups. A broad peak at 3.29 δ, ppm is due to amino group protons 'd'. The benzylic methylene protons 'c' exhibited a triplet at 2.38 δ, ppm while the other methylene protons 'b' appeared in the range 1.25 - 1.38 δ, ppm. Methyl group protons 'a' exhibited a triplet at 0.88 δ, ppm.

^{13}C-NMR spectrum of 4-pentadecylbenzene-1,3-diamine alongwith the assignments is presented in **Figure 3.7**
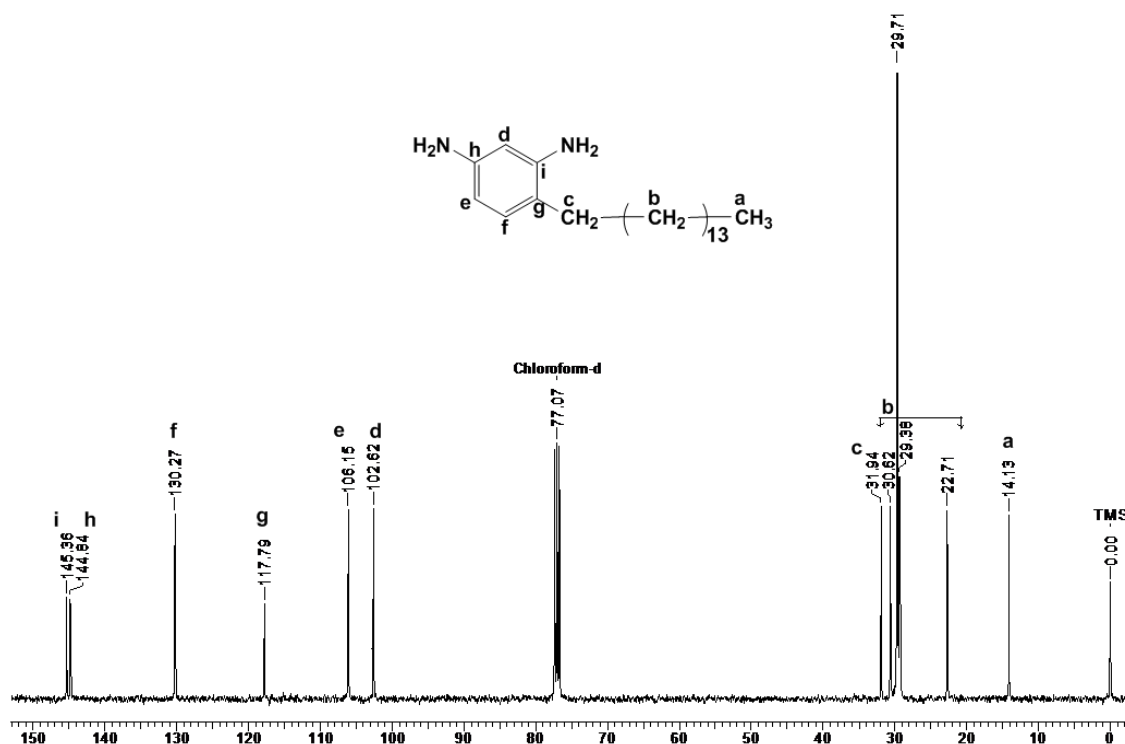
Figure 3.7 ^{13}C-NMR spectrum (CDCl$_3$) of 4-pentadecylbenzene-1,3-diamine

The quaternary aromatic carbons 'i' and 'h' attached to amino groups appeared at 145.36 and 144.84 δ, ppm and the quaternary aromatic carbon 'g' attached to pentadecyl chain displayed a peak at 117.79 δ, ppm. The aromatic carbon 'd' flanked by amino groups showed a signal at 102.62 δ, ppm and other aromatic carbons 'f' and 'e' appeared at 130.27 and 106.15 δ, ppm, respectively. The bezylic carbon 'c' displayed peak at 31.94 δ, ppm and other methylene carbons 'b' appeared in the range 22.71- 30.62 δ, ppm. The methyl carbon 'a' of pentadecyl chain showed signal at 14.13 δ, ppm.

3.4.2   Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) (PDP-4AB) (I)

Scheme 3.2 outlines the route for the synthesis of diamines containing preformed amide linkages.

I = -4-NH₂ , R = C₁₅H₃₁ ;   II = -3-NH₂ , R = C₁₅H₃₁

Ref I = -4-NH₂ , R = H   ;   Ref II = -3-NH₂ , R = H
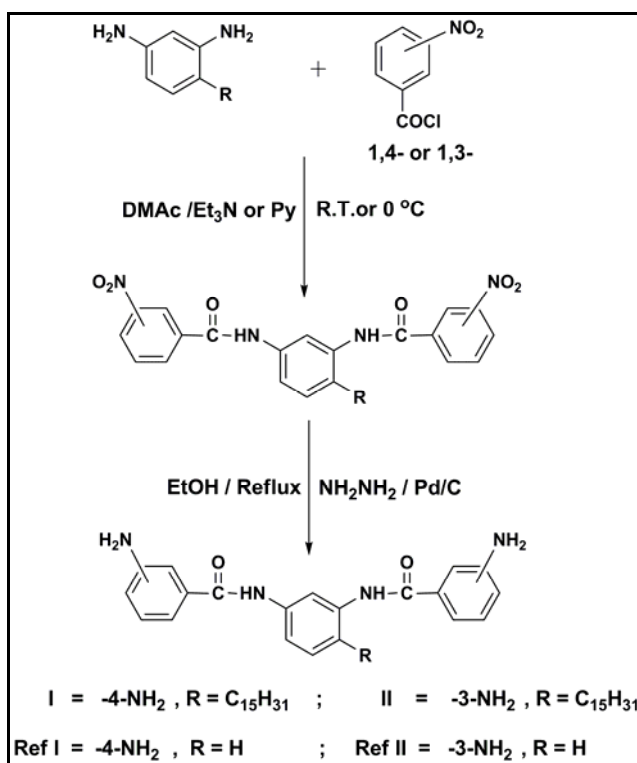
Scheme 3.2 Synthesis of diamines containing preformed amide linkages

In the first step, 4-pentadecylbenzene-1,3-diamine was reacted with 4-nitro benzoyl chloride in DMAc, in the presence of triethylamine as catalyst to obtain the intermediate dinitro compound *viz.*, *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-nitrobenzamide) (PDP-4NB). Pure PDP-4NB was obtained by recrystallization from a mixture of DMAc and ethanol (1:2, v/v) and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of PDP-4NB (**Figure 3.8**) exhibited characteristic absorption bands at 1524 cm^{-1} (asymmetric -NO$_2$ stretching) and 1346 cm^{-1} (symmetric -NO$_2$ stretching). The band at 3280 and 1678 cm^{-1} were assigned to –N-H and C=O of amide linkage, respectively.
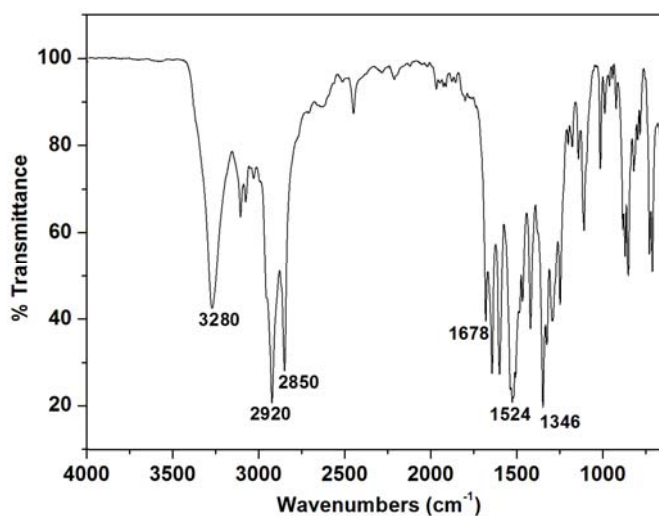
Figure 3.8 FT-IR spectrum (KBr) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-nitrobenzamide)

¹H-NMR spectrum of PDP-4NB is depicted in **Figure 3.9.**
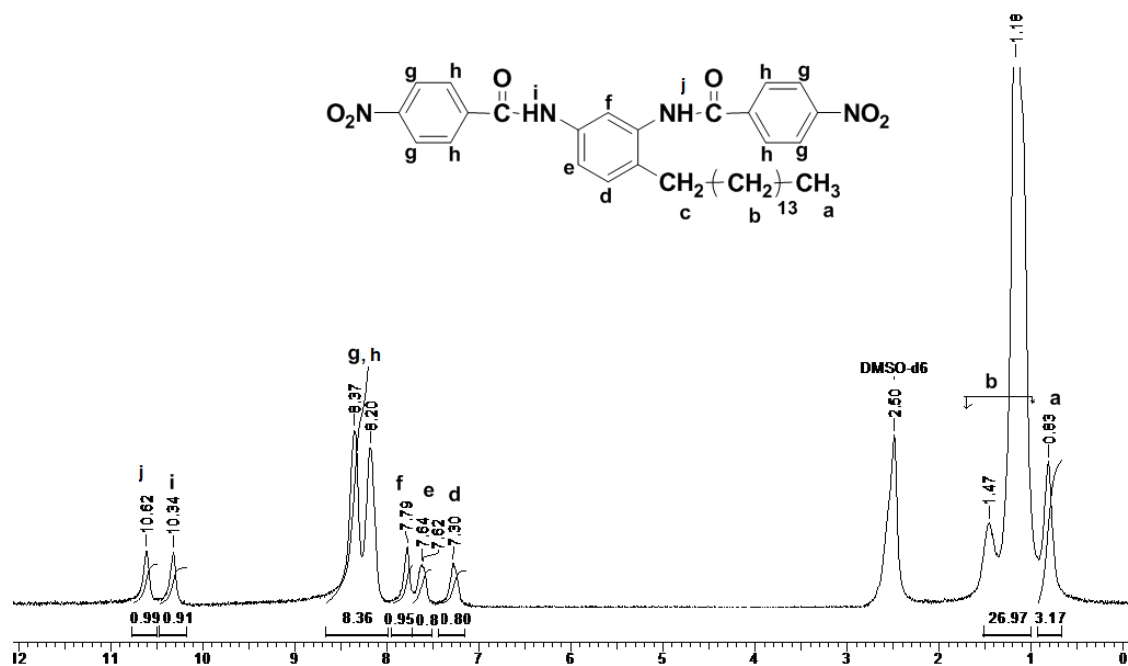
Figure 3.9 ¹**H-NMR spectrum (DMSO-d₆) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-nitro benzamide)**

Interestingly, two separate peaks 'i' and 'j' were observed for –NH of amide linkage at 10.34 and 10.62 δ, ppm. This magnetic non-equivalance of protons 'i' and 'j' is due to asymmetry introduced by the presence of pentadecyl chain. The aromatic protons 'g' and 'h' appeared in the range 8.20-8.37 δ, ppm. The aromatic proton 'f' flanked by two amide groups displayed a peak at 7.79 δ, ppm and the aromatic protons 'e' and 'd' appeared as two doublets at 7.63 and 7.30 δ, ppm, respectively. The peak corresponding to benzylic protons 'c' was overlapped with a signal due to DMSO-d₆. The other methylene protons 'b' displayed peaks in the range 1.18-1.47 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.83 δ, ppm.

¹³C-NMR spectrum of PDP-4NB along with the assignments of the carbon atoms is depicted in **Figure 3.10**.
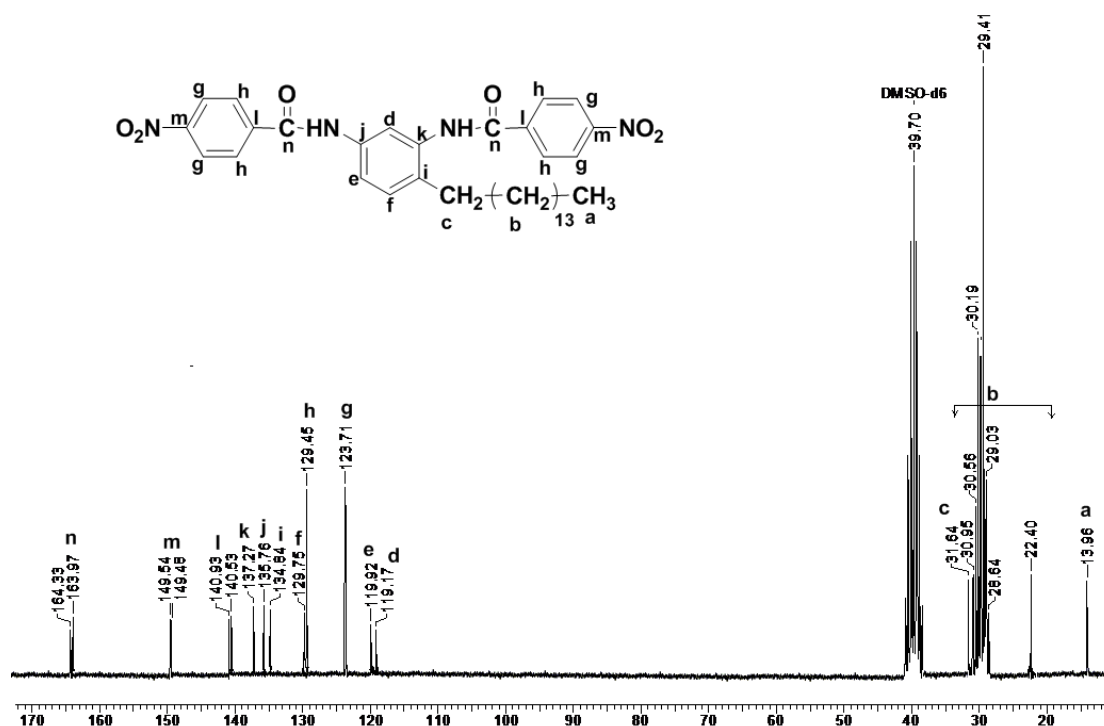
Figure 3.10 **^{13}C-NMR spectrum (DMSO-d$_6$) of *N,N'*-(4-pentadecyl-1,3-phenylene)bis(4-nitrobenzamide)**

The carbonyl carbons 'n' of amide groups gave rise to two distinct resonances at 163.97 and 164.33 δ, ppm. The quaternary carbons 'm' attached to the nitro groups appeared at 149.54 and 149.48 δ, ppm and the quaternary carbons 'l' attached to the carbonyl group displayed peaks at 140.53 and 140.93 δ, ppm. Other quaternary carbons appeared at 137.27, 135.76 and 134.84 δ, ppm.

In the next step, PDP-4NB was reduced to the diamine *viz.*, *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) (PDP-4AB) by catalytic hydrogenation using hydrazine hydrate and Pd-C (10 wt.%). The crude diamine was purified by recrystallization from methanol and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of PDP-4AB (**Figure 3.11**) exhibited N-H stretching absorption bands at 3429 (asymmetric N-H stretching) and 3346 cm^{-1} (symmetric N-H stretching) and C=O stretching at 1635 cm^{-1}.
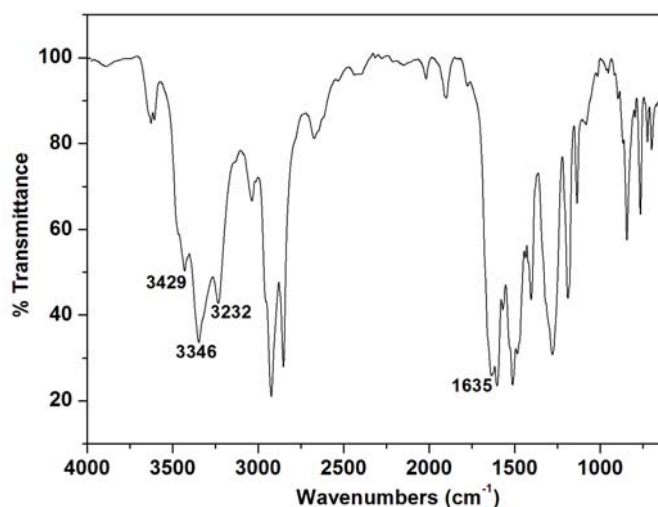
Figure 3.11 FT-IR spectrum (KBr) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-amino benzamide)

^{1}H-NMR spectrum of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) is reperesented in **Figure 3.12**.
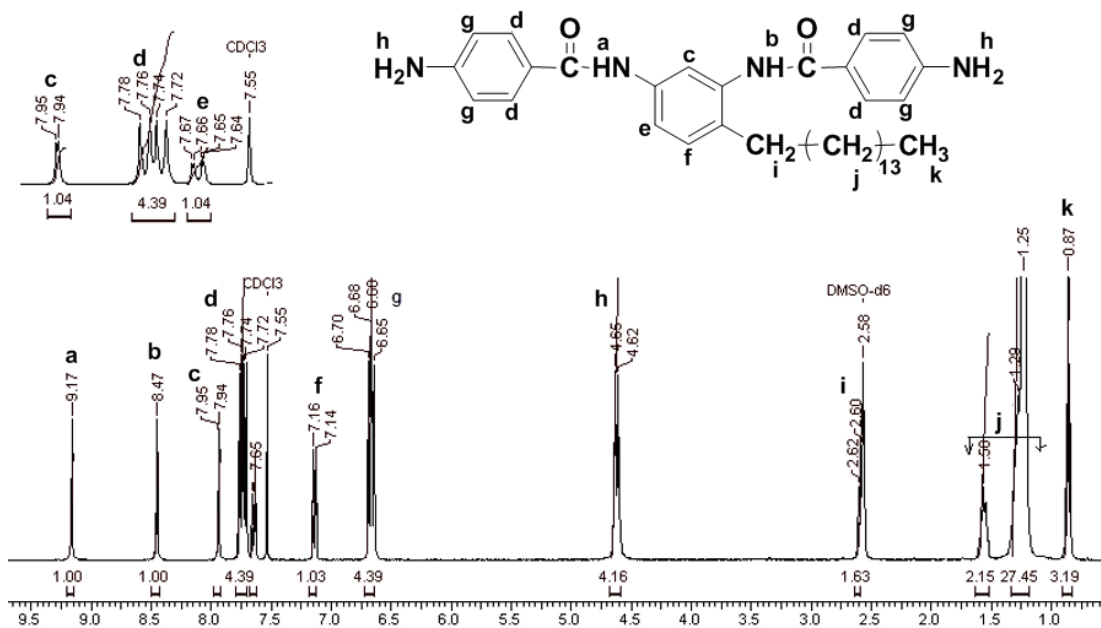
Figure 3.12 ^{1}H-NMR spectrum (CDCl$_3$ and DMSO-d$_6$) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide)

Two separate peaks 'a' and 'b' were observed for amide protons at 9.17 and 8.47 δ, ppm. The aromatic proton 'c' flanked by amide groups appeared as a doublet at 7.95 δ, ppm. The aromatic protons 'd' and 'g' displayed peaks at 7.74 and 6.60 δ, ppm, respectively. The aromatic proton 'e' appeared as a doublet of doublet at 7.66 δ, ppm and 'f' appeared as a doublet at 7.15 δ, ppm. The signal at 4.63 δ, ppm is due to –NH$_2$ protons 'h'. The benzylic methylene protons 'i' appeared at 2.61 δ, ppm and other methylene protons displayed peaks in the range 1.25- 1.58 δ, ppm. The terminal –CH$_3$ protons 'k' appeared as a triplet at 0.87 δ, ppm.

^{13}C-NMR spectrum of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) along with assignments is presented in **Figure 3.13**.
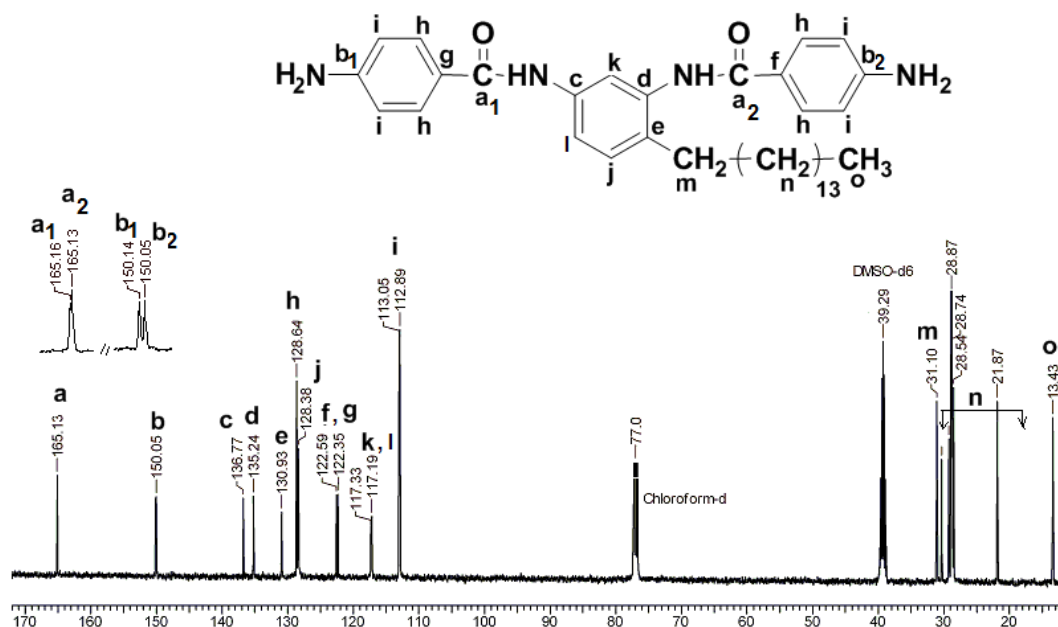
Figure 3.13 [13]**C-NMR spectrum (CDCl₃ and DMSO-d₆) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide)**

The model compound *viz.*, *N,N'*-(1,3-phenylene) bis(4-aminobenzamide) (**Ref I**) was synthesized as per the procedure reported in the literature by condensing *m*-PDA with 4-nitro benzoyl chloride, followed by the reduction of dinitro compound, *viz.*, *N,N'*-(1,3-phenylene) bis(4-nitrobenzamide).[7]

3.4.3   Synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-aminobenzamide) (PDP-3AB)

Scheme 3.2 outlines the route for the synthesis of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-aminobenzamide).

In the first step, PBDA was reacted with 3-nitro benzoyl chloride in DMAc at 0 °C, in the presence of pyridine as catalyst to obtain the intermediate dinitro compound *viz.*, *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-nitrobenzamide)   (PDP-3NB)   which   was   purified   by recrystallization from a mixture of DMAc and ethanol (1:2, v/v) and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of PDP-3NB (**Figure 3.14**) exhibited characteristic absorption bands at 1529 (asymmetric –NO₂ stretching) and 1350 cm⁻¹ (symmetric –NO₂ stretching).
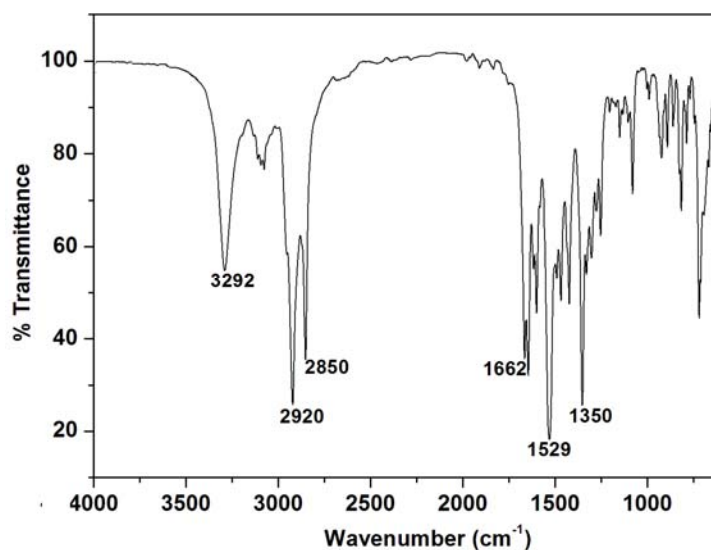
Figure 3.14 FT-IR spectrum (KBr) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-nitrobenzamide)

^{1}H-NMR spectrum of 3PDP-3NB is depicted in **Figure 3.15**.
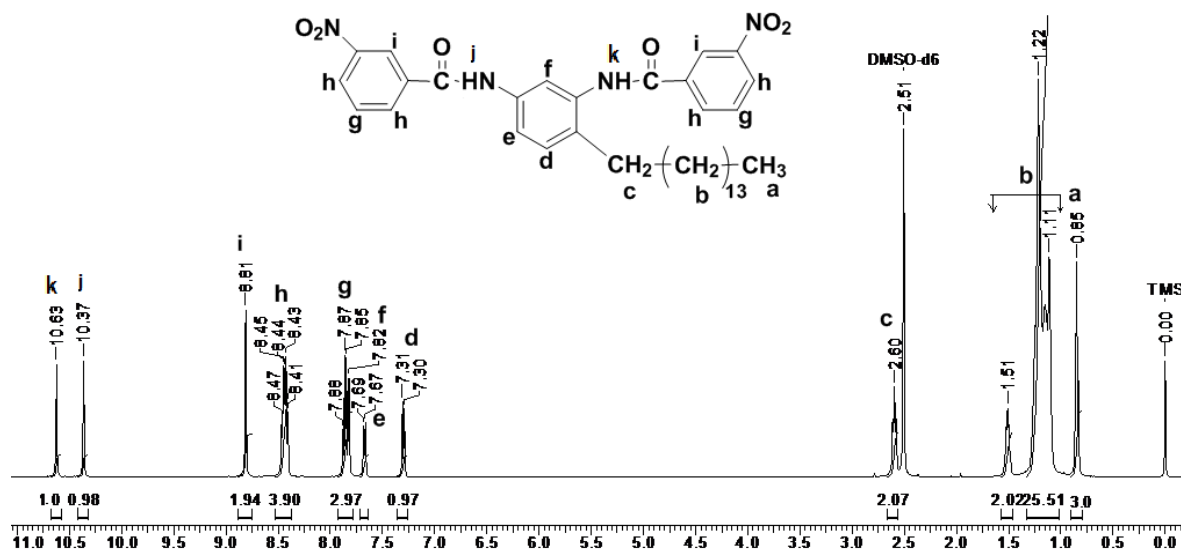
Figure 3.15 ^{1}H-NMR spectrum (DMSO-d$_6$) of *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-nitro benzamide)

Two separate peaks 'k' and 'j' were observed for amide protons at 10.37 and 10.63 δ, ppm. The aromatic protons 'i' flanked by C=O and –NO$_2$ groups exhibited a signal at 8.91 δ, ppm. The aromatic protons 'h' appeared in the range 8.41 – 8.47 δ, ppm. The aromatic protons 'g' and 'f' appeared together in the range 7.82 – 7.88 δ, ppm. The aromatic protons 'd' and 'e' exhibited two doublets at 7.31 and 7.68 δ, ppm, respectively. The benzylic –CH$_2$ protons 'c' displayed a triplet at 2.60 δ, ppm and other methylene protons 'b' displayed peaks in the range 1.22 – 1.51 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.85 δ, ppm.

^{13}C-NMR spectrum of *N,N*-(4-pentadecyl-1,3-phenylene) bis(3-nitrobenzamide) (PDP-3NB) along with assignments is presented in **Figure 3.16**.
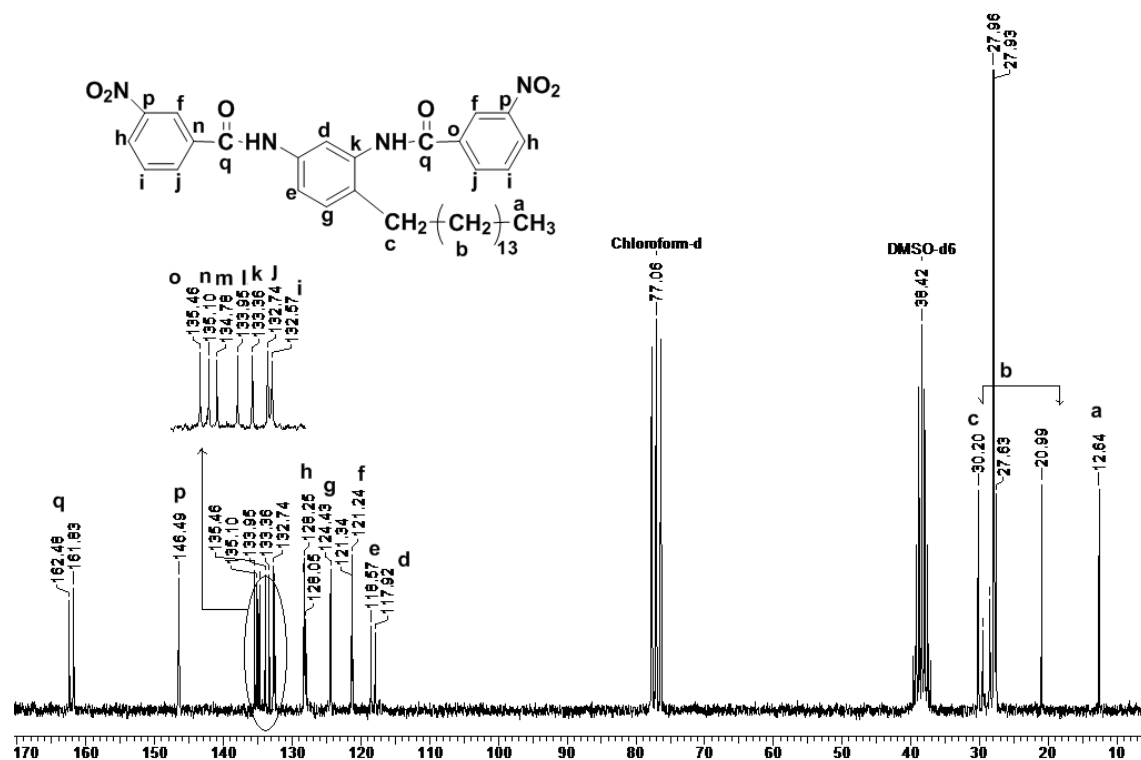
Figure 3.16 ^{13}C-NMR spectrum (CDCl₃ and DMSO-d₆) of *N,N*-(4-pentadecyl-1,3-phenylene) bis(3-nitrobenzamide)

PDP-3AB was obtained by reducing PDP-3NB using hydrazine hydrate and Pd-C (10 wt %). Pure PDP-3AB was obtained after recrystallization from methanol and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of PDP-3AB (**Figure 3.17**) exhibited N-H stretching absorption bands at 3219, 3310 and 3415 cm^{-1}.
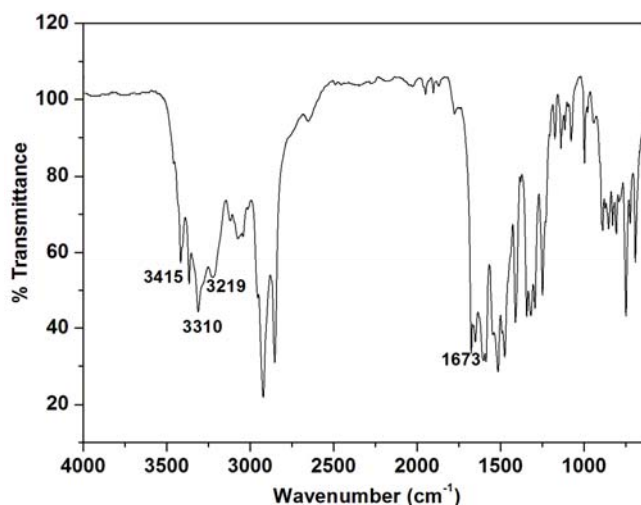
Figure 3.17 FT-IR spectrum (KBr) of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-amino benzamide)

¹H-NMR spectrum of *N,N*-(4-pentadecyl-1,3-phenylene) bis(3-nitrobenzamide) is reperesented in **Figure 3.18**.
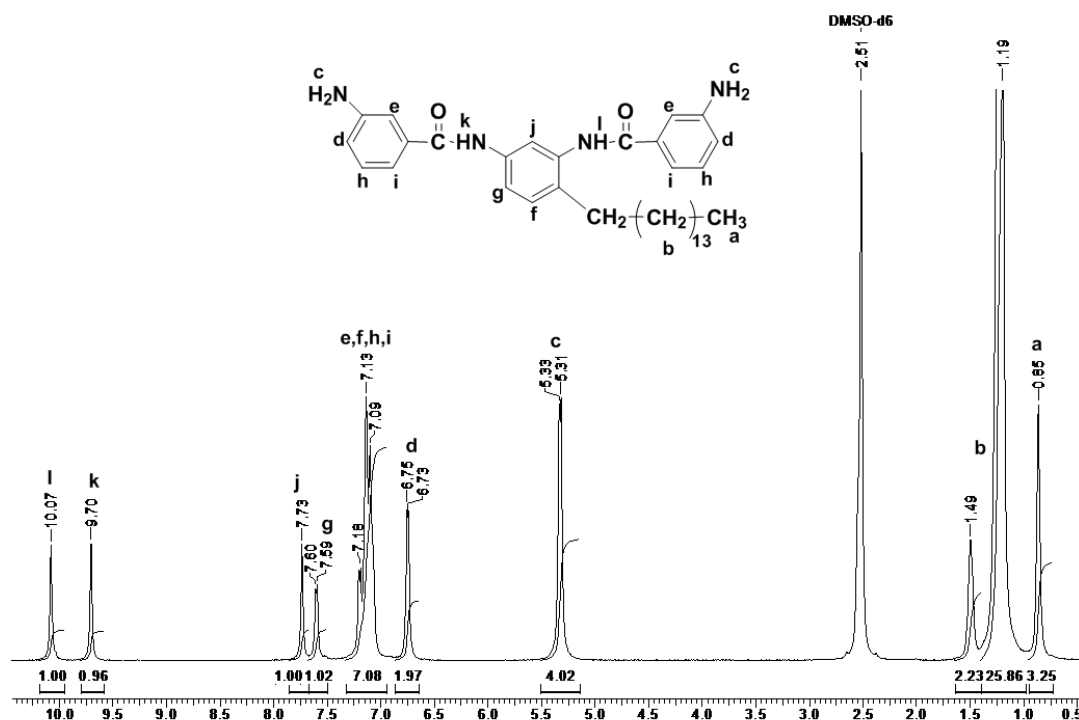
Figure 3.18 ¹H-NMR spectrum (DMSO-d₆) of *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-aminobenzamide)

Two separate peaks 'k' and 'l' were observed for amide protons at 10.07 and 9.70 δ, ppm. The aromatic proton 'j' flanked by amide groups appeared at 7.73 δ, ppm. The aromatic proton 'g' displayed a doublet at 7.59 δ, ppm. The aromatic protons 'e', 'f', 'g', 'h' and 'i' appeared in the range 7.09- 7.18 δ, ppm. The aromatic proton 'd' appeared as a doublet at 6.74 δ, ppm. The signal at 5.32 δ, ppm is due to –NH₂ protons 'c'. The signal due to benzylic methylene protons was overlapped by solvent peak at 2.51 δ, ppm and other methylene protons 'b' displayed peaks in the range 1.19- 1.49 δ, ppm. The terminal –CH₃ protons 'a' appeared as a triplet at 0.85 δ, ppm.

¹³C-NMR spectrum of *N,N*-(4-pentadecyl-1,3-phenylene) bis(3-nitrobenzamide) along with assignments is presented in **Figure 3.19**.
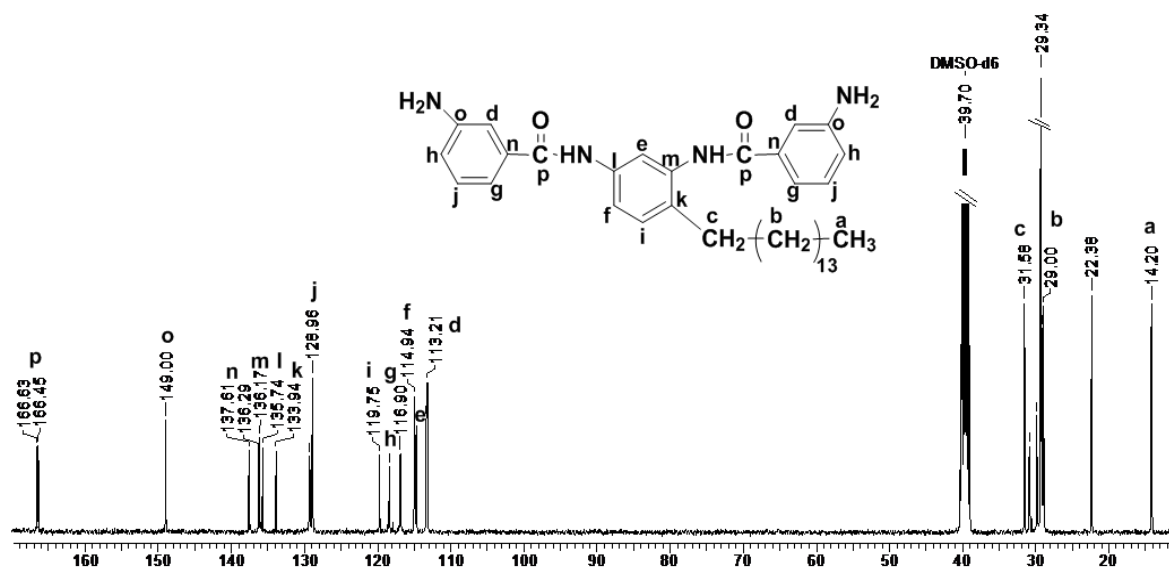
Figure 3.19 ^{13}C-NMR spectrum (DMSO-d[6]) *N,N'*-**(4-pentadecyl-1,3-phenylene)bis(3-amino benzamide)**

The model compound *viz.*, *N,N'*-(1,3-phenylene)bis(3-aminobenzamide) **(Ref II)** was synthesized as per the procedure reported in the literature by condensing *m*-PDA with 3-nitro benzoyl chloride, followed by the reduction of dinitro compound, *viz.*, *N,N'*-(1,3-phenylene) bis(3-nitrobenzamide).[7]

3.4.4   Synthesis of 2,4-diisocyanato-1-pentadecylbenzene

Aromatic diisocyanates are important raw materials in polymer chemistry since they are valuable precursors for the synthesis of polyurethanes, polyureas, polyimides, polyamides, etc. Diisocyanates can be prepared by a variety of methods.[14] The phosgenation of an amine or its salt is the method of great importance.[15] The reaction of a nitro compound with carbon monoxide,[16] the reaction of isocyanic acid with an olefin,[17] Curtius rearrangement,[18] Lossen rearrangement[19] are some of the methods generally employed for the synthesis of diisocyanates.

Scheme 3.3 depicts synthesis of 2,4-diisocyanato-1-pentadecylbenzene starting from 4-pentadecylbenzene-1,3-diamine.
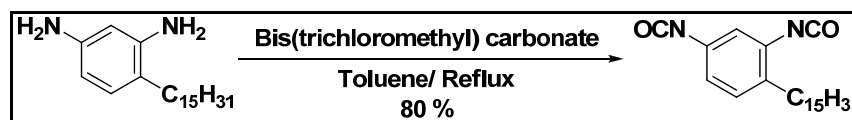
Scheme 3.3 Synthesis of 2,4-diisocyanato-1-pentadecylbenzene

The synthesis of 2,4-diisocyanato-1-pentadecylbenzene was carried out starting from PBDA in a single step reaction using the well-known method, i.e. phosgenation of an amine with bis(trichloromethyl) carbonate (triphosgene).[7] The phosgenation reaction of diamine was carried out in an inert atmmosphere with excess of bis(trichloromethyl) carbonate. The structure of 2,4-diisocyanato-1-pentadecylbenzene was confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR

spectroscopy.   FT-IR spectrum of 2,4-diisocyanato-1-pentadecylbenzene is presented in **Figure 3.20**. A strong absorption band at 2262 cm^{-1} characteristic of the asymmetric stretching vibration of the isocyanate group was observed.
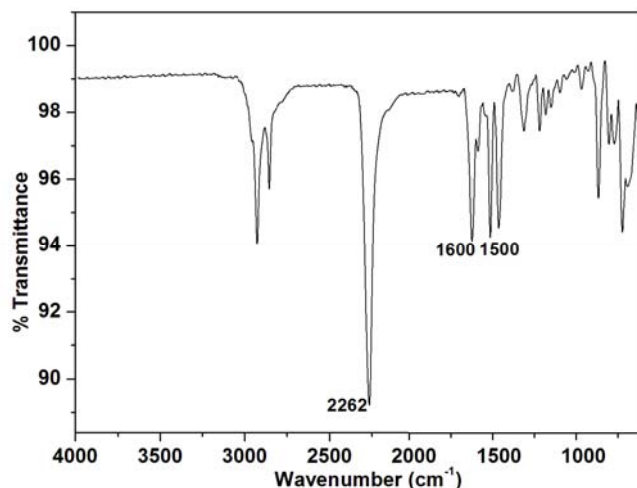
Figure 3.20 FT-IR spectrum (CHCl$_3$) of 2,4-diisocyanato-1-pentadecylbenzene

^{1}H-NMR spectrum of 2,4-diisocyanato-1-pentadecylbenzene is shown in **Figure 3.21.**
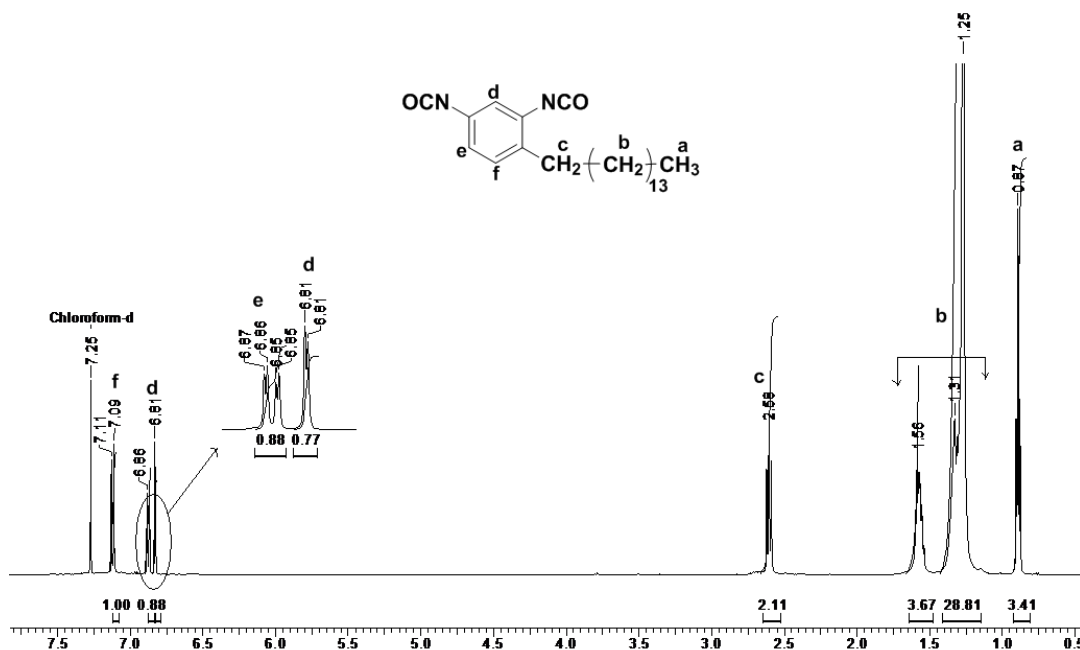
Figure 3.21 ^{1}H-NMR spectrum (CDCl$_3$) of 2,4-diisocyanato-1-pentadecylbenzene

       The aromatic proton 'f' *ortho* to the pentadecyl chain displayed a doublet at 7.10 δ, ppm. The aromatic proton 'e' *ortho*-and *para* to the isocyanate group exhibited a doublet of doublet at 6.86 δ, ppm. The aromatic proton 'd' flanked by two isocyanate groups appeared as a doublet at 6.81 δ, ppm. The bezylic methylene proton 'c' appeared as a triplet at 2.58 δ, ppm while other methylene protons 'b' displayed a triplet at 1.56 and a multiplet in the region 1.25- 1.56 δ, ppm. Terminal methyl group protons 'a' appeared as a triplet at 0.87 δ, ppm.

^{13}C-NMR spectrum of 2,4-diisocyanato-1-pentadecylbenzene along with the assignments of carbon atoms is presented in **Figure 3.22**
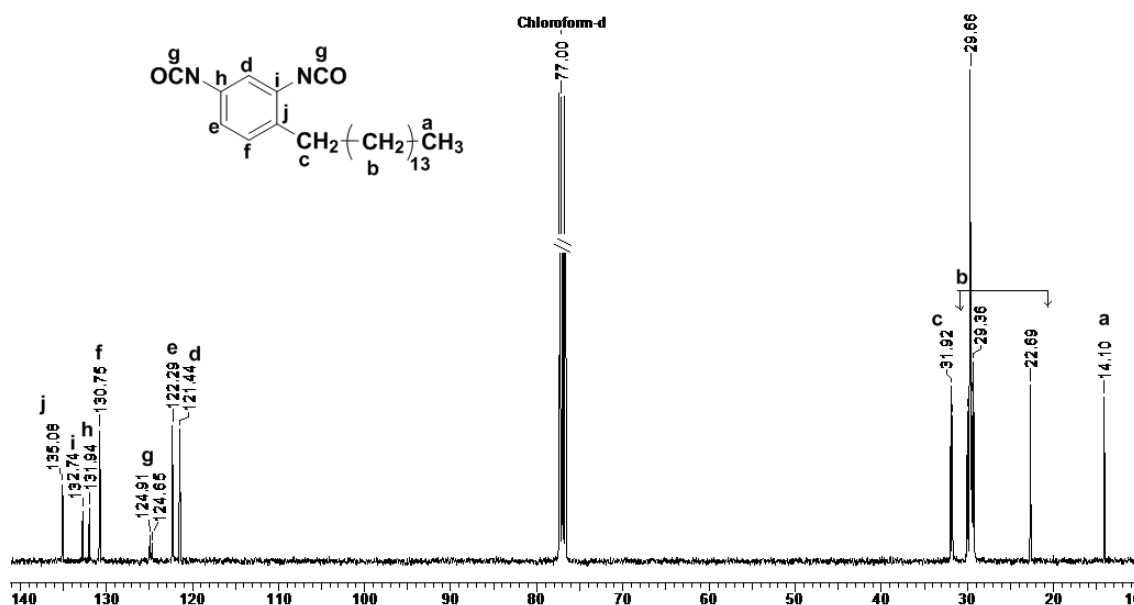
Figure 3.22 ^{13}C-NMR spectrum (CDCl₃) of 2,4-diisocyanato-1-pentadecylbenzene

In ^{13}C-NMR of 2,4-diisocyanato-1-pentadecylbenzene the peaks at 124.91 and 124.65 δ, ppm were assigned to the carbon atoms of the –NCO group.

3.4.5   Synthesis of 3,5-diamino-4'-pentadecylbenzophenone

Scheme 3.4 depicts the route for synthesis of 3,5-diamino-4'-pentadecylbenzophenone starting from pentadecylbenzene.
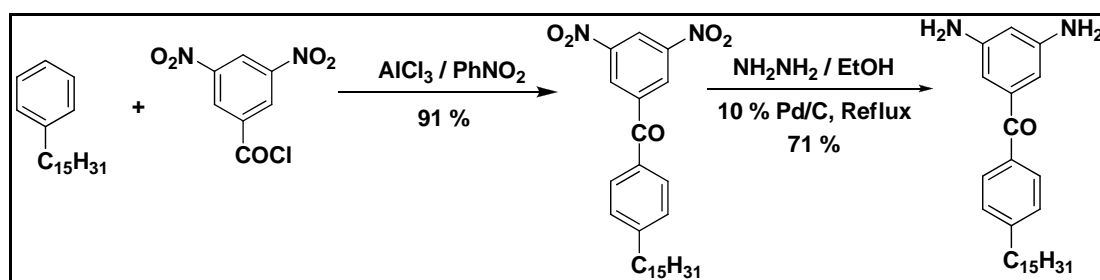
Scheme 3.4 Synthesis of 3,5-diamino-4'-pentadecylbenzophenone

In the first step, Friedel-Crafts acylation of pentadecylbenzene was carried out using 3,5-dinitrobenzoylchloride in the presence of a Lewis acid such as AlCl₃ and nitrobenzene as solvent.[20] The obtained 3,5-dinitro-4'-pentadecylbenzophenone was recrystallized from ethanol and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 3,5-dinitro-4'-pentadecylbenzophenone (**Figure 3.23**) displayed characteristics absorption bands at 1546 (asymmetric NO₂ stretching) and 1346 cm⁻¹ (symmetric NO₂ stretching). The band at 1667 cm⁻¹ was assigned to the –C=O stretching.
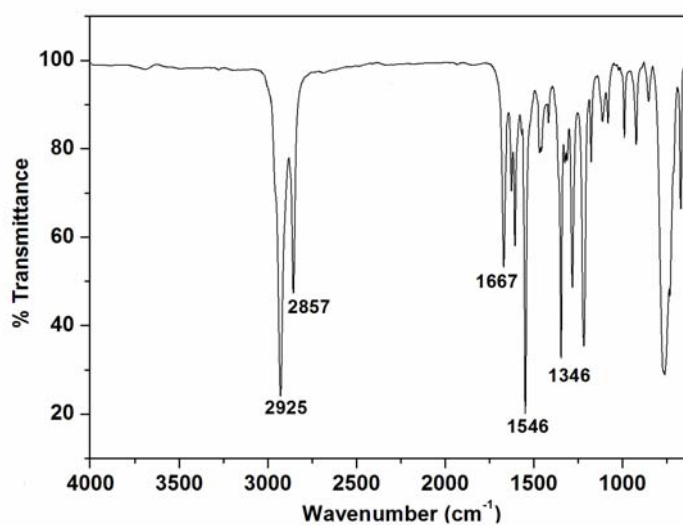
Figure 3.23 FT-IR spectrum (CHCl$_3$) of 3,5-dinitro-4'-pentadecylbenzophenone

^{1}H-NMR spectrum of 3,5-dinitro-4'-pentadecylbenzophenone is presented in **Figure 3.24.**
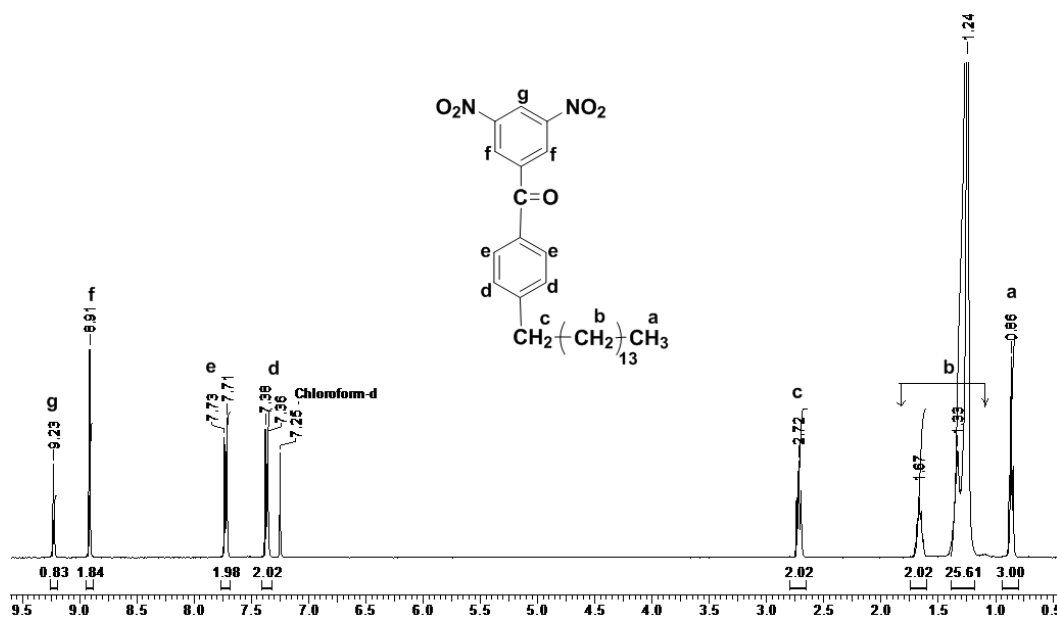
Figure 3.24 ^{1}H-NMR spectrum (CDCl$_3$) of 3,5-dinitro-4'-pentadecylbenzophenone

The aromatic proton 'g' flanked by –NO$_2$ groups appeared as a singlet at 9.23 δ, ppm. The aromatic proton 'f' exhibited a singlet at 8.91 δ, ppm and the aromatic proton 'e' appeared as a doublet at 7.72 δ, ppm. The aromatic protons 'd' *ortho* to pentadecyl chain displayed a doublet at 7.37 δ, ppm. The benzylic –CH$_2$ protons 'c' appeared as atriplet at 2.72 δ, ppm while methylyne protons 'b' appeared in the range 1.24- 1.67 δ, ppm. The terminal –CH$_3$ protons 'a' appeared as a triplet at 0.86 δ, ppm.

^{13}C-NMR specrum of 3,5-dinitro-4'-pentadecylbenzophenone along with assignments of the carbon atoms is presented in **Figure 3.25.**
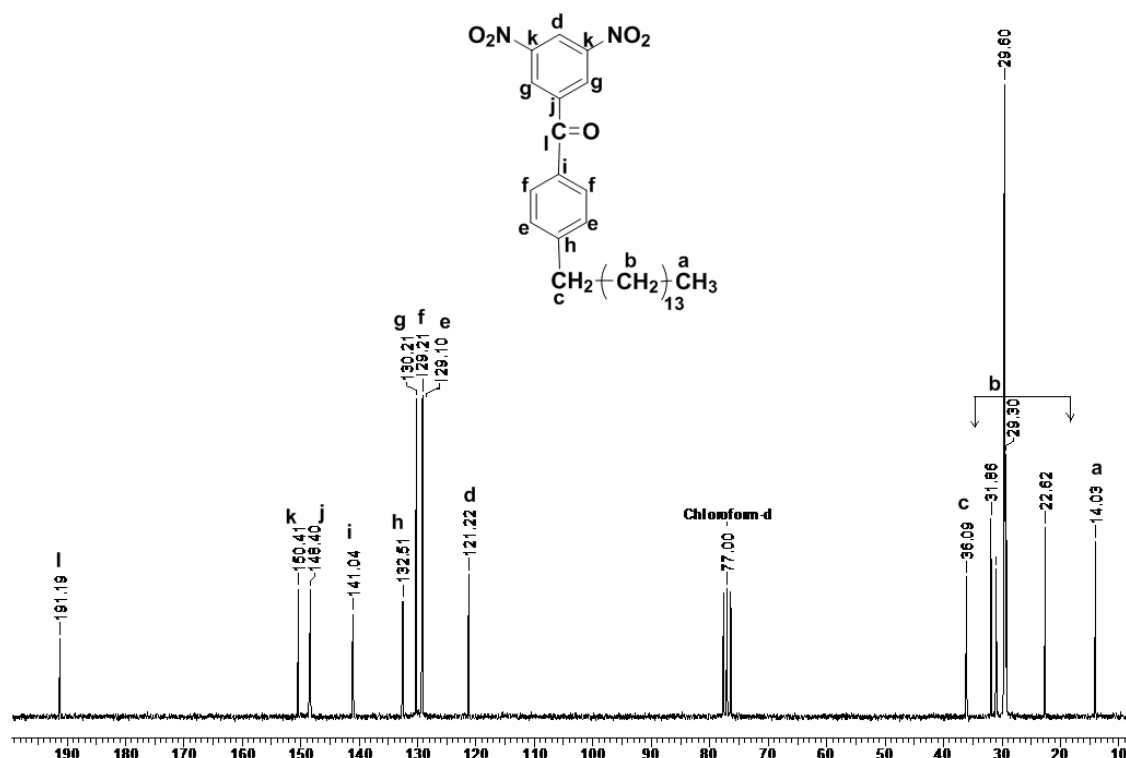
Figure 3.25 ^{13}C-NMR spectrum (CDCl$_3$) of 3,5-dinitro-4'-pentadecylbenzophenone

The carbonyl carbon 'l' exhibited a signal at 161.19 δ, ppm. The quaternary aromatic carbons 'k' attached to –NO$_2$ groups displayed a signal at 150.41 δ, ppm while quaternary carbons attached to the carbonyl group 'j' and 'i' appeared at 148.40 and 141.04 δ, ppm, respectively. The other quaternary aromatic carbon 'h' showed a signal at 132.51 δ, ppm. The aromatic carbons appeared in the range 121.22- 130.21 δ, ppm. The benzylic carbon 'c' displayed peak at 36.09 δ, ppm while other methylene carbons 'b' appeared in the range 22.62-31.86 δ, ppm. Methyl carbon 'a' of pentadecyl chain showed a signal at 14.03 δ, ppm.

In the next step, reduction of 3,5-dinitro-4'-pentadecylbenzophenone was carried out using hydrazine hydrate / Pd-C (10 wt %) reagent system to obtain 3,5-diamino-4'-pentadecyl benzophenone.[21] Pure compound was obtained by recrytallization from methanol and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 3,5-diamino-4'-pentadecylbenzophenone (**Figure 3.26**) exhibited the characteristic absorption bands for –NH stretching at 3450, 3355 and 3220 cm^{-1}. The band at 1733 cm^{-1} was assigned to –C=O linkage.
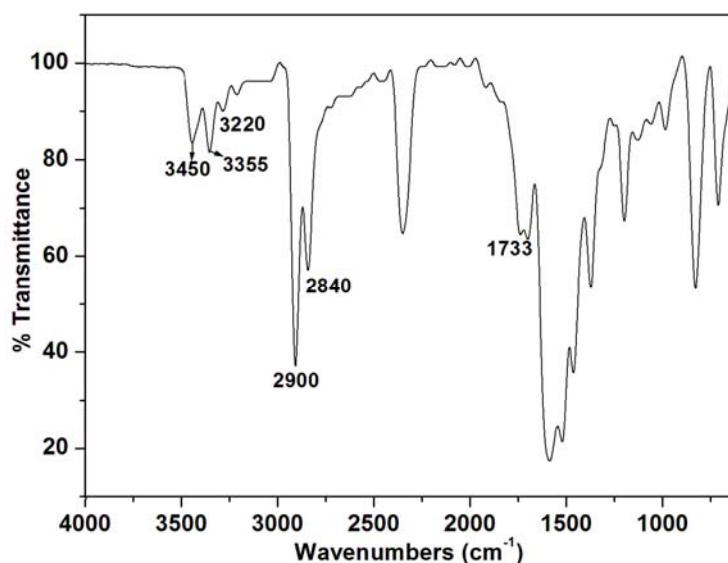
Figure 3.26 FT-IR spectrum (CHCl₃) of 3,5-diamino-4'-pentadecylbenzophenone

^{1}H-NMR spectrum of 3,5-diamino-4'-pentadecylbenzophenone is presented in **Figure 3.27**
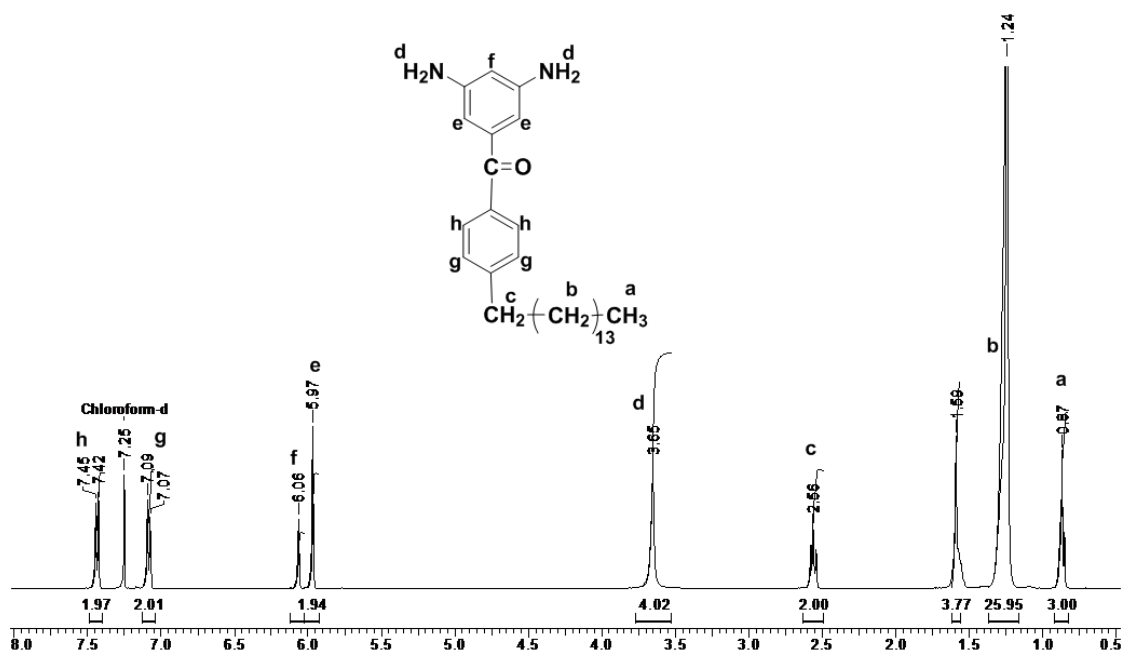
Figure 3.27 ^{1}H-NMR spectrum (CDCl₃) of 3,5-diamino-4'-pentadecylbenzophenone

The aromatic protons 'h' and 'g' appeared as doublets at 7.43 and 7.08 δ, ppm, respectively. The aromatic proton 'f' flanked by amino groups showed a signal at 6.06 δ, ppm while other aromatic protons 'e' appeared at 5.97 δ, ppm. A broad singlet at 3.65 δ, ppm is ascribed to the amino protons 'd'. The bezylic protons 'c' appeared as a triplet at 2.58 δ, ppm while other methylene protons 'b' displayed peaks in the range 1.24- 1.59 δ, ppm. Methyl group protons 'a' exhibited a triplet at 0.87 δ, ppm.

^{13}C-NMR spectrum of 3,5-diamino-4'-pentadecylbenzophenone along with assignments of carbon atoms is presented in **Figure 3.28**
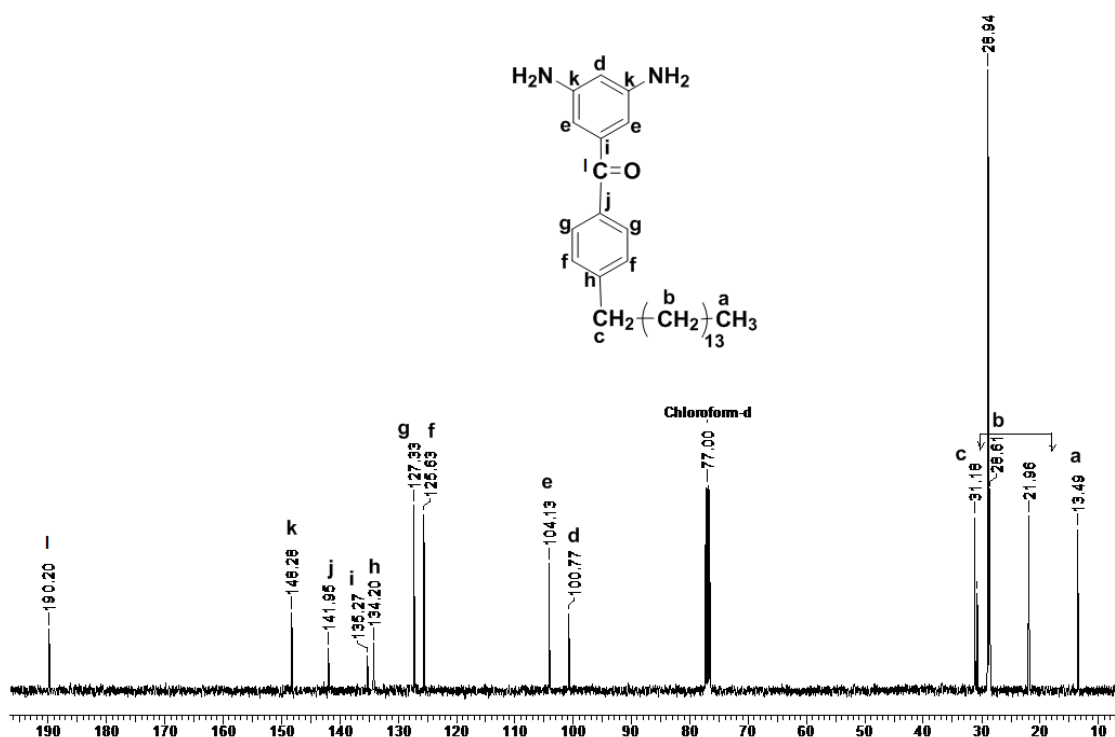
Figure 3.28 ^{13}**C-NMR spectrum (CDCl$_3$) of 3,5-diamino-4'-pentadecylbenzophenone**

3.4.6 Synthesis of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide

  Scheme 3.5 depicts route for the synthesis of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide starting from pentadecylbenzene.
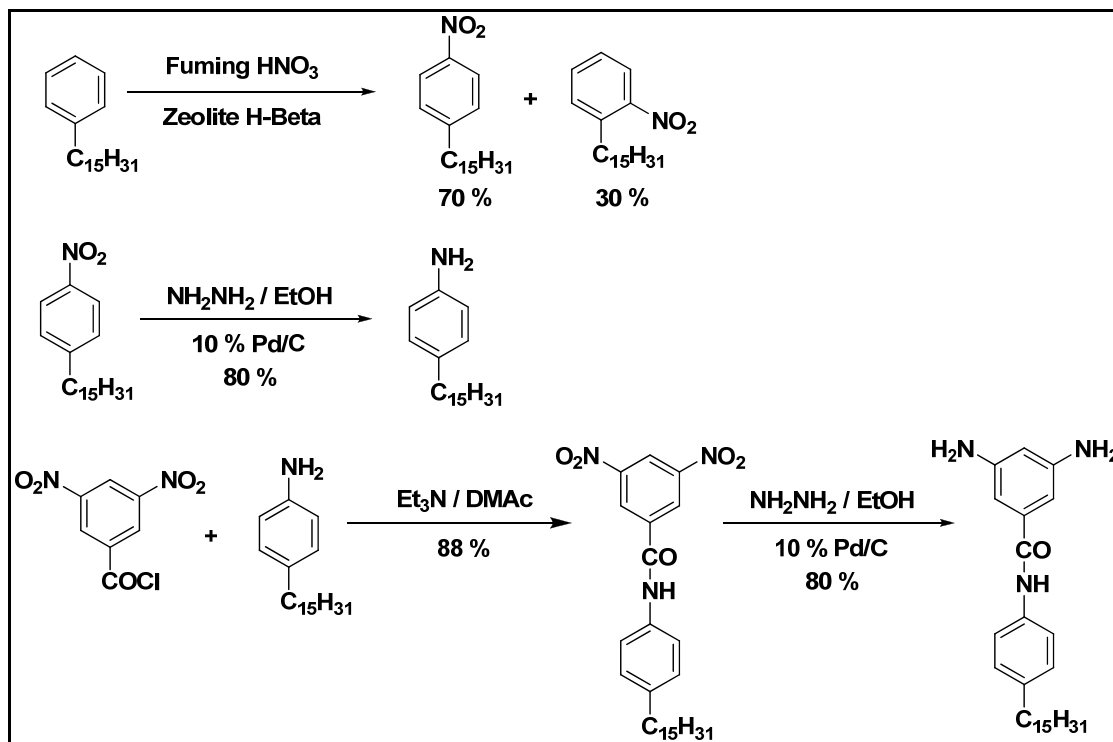
Scheme 3.5 Synthesis of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide

In the first step, pentadecylbenzene was nitrated using the nitrating mixture consisting of fuming HNO_3 and acetic anhydride in the presence of zeolite- H-β.[13] The mixture of *ortho-* and *para*-isomers was obtained in which *para*-isomer was in major proportion (≈ 70 %). The use of zeolite-H-β has found to provide improved selectivity towards the *para-* position over traditional mixed acid system.[13] The *para*-isomer was isolated using column chromatography on silica gel with pet ether as an eluent to obtain pure 1-nitro-4-pentadecylbenzene which was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. FT-IR spectrum of 1-nitro-4-pentadecylbenzene (**Figure 3.29**) exhibited the characteristic stretching bands for nitro group at 1520 and 1342 cm^{-1}.
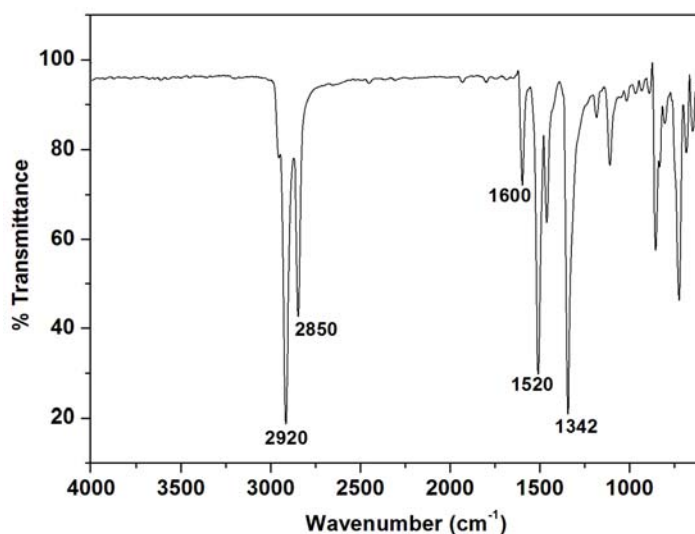
Figure 3.29 FT-IR (CHCl₃) spectrum of 1-nitro-4-pentadecylbenzene

^{1}H-NMR spectrum of 1-nitro-4-pentadecylbenzene (**Figure 3.30**) exhibited the presence of a doublet at 8.13 δ, ppm whcih corresponds to protons 'e' *ortho* to –NO₂ group.
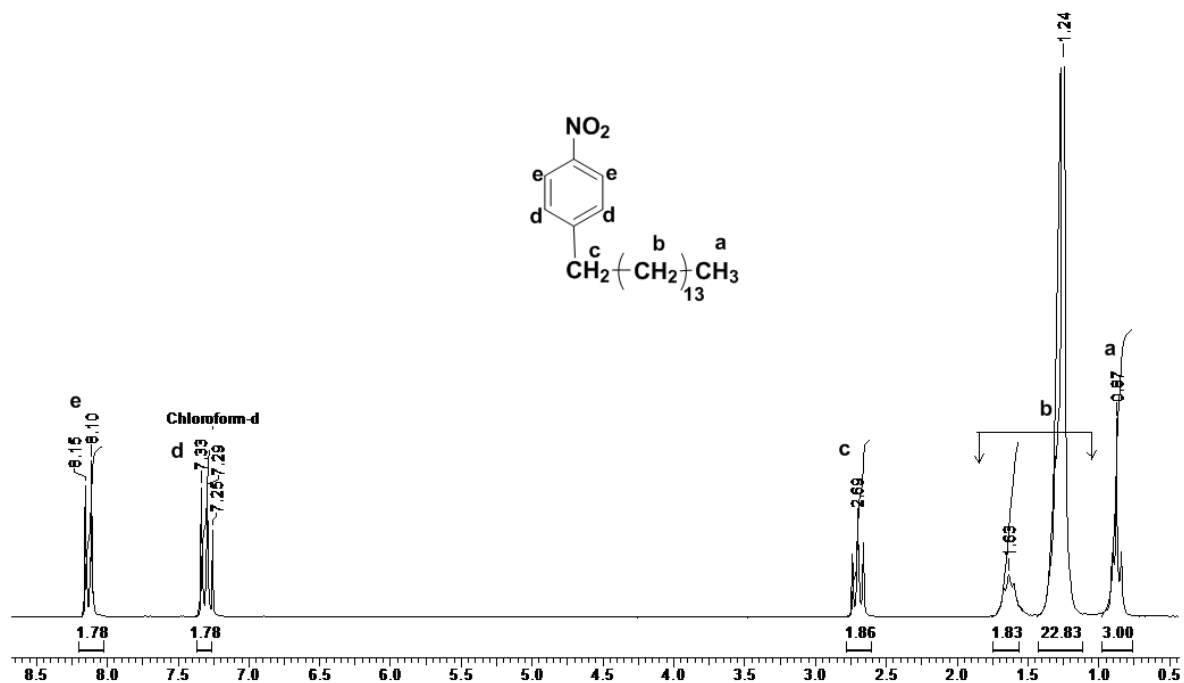
Figure 3.30 ^{1}H-NMR spectrum (CDCl₃) of 1-nitro-4-pentadecylbenzene

The doublet at 7.30 δ, ppm was assigned to aromatic protons 'd' *ortho* to pentadecyl chain. The benzylic –CH$_2$ protons 'c' appeared as atriplet at 2.69 δ, ppm while methylyne protons 'b' appeared in the range 1.24- 1.63 δ, ppm. The terminal –CH$_3$ protons 'a' appeared as a triplet at 0.87 δ, ppm.

^{13}C-NMR specrum of 1-nitro-4-pentadecylbenzene along with assignments of the carbon atoms is presented in **Figure 3.31.**
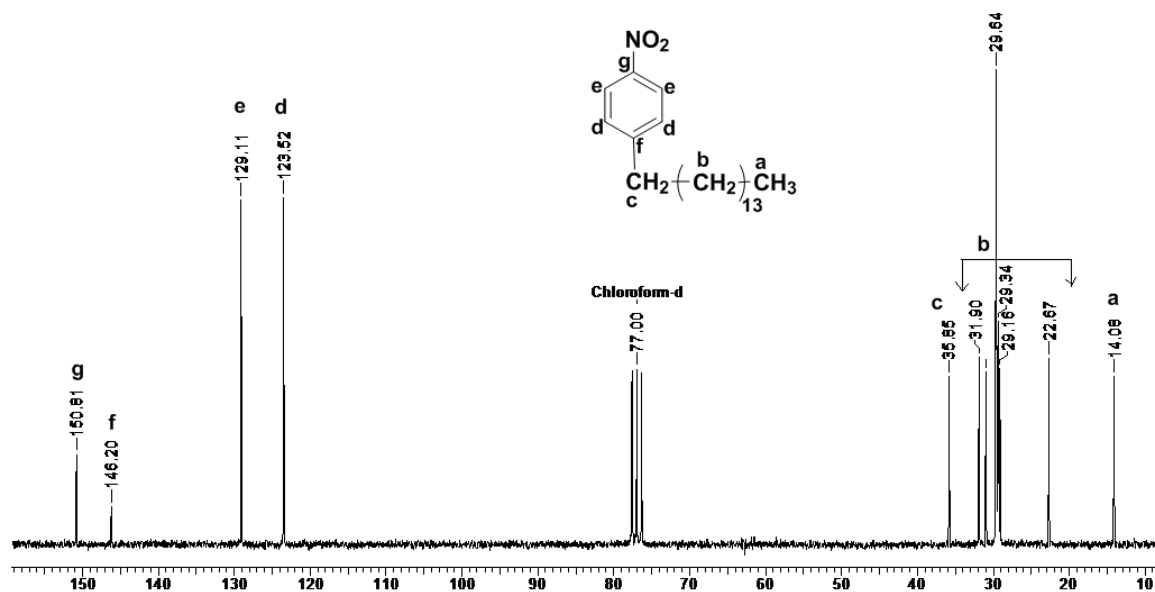
Figure 3.31 ^{13}C-NMR spectrum (CDCl$_3$) of 1-nitro-4-pentadecylbenzene

In the second step, reduction of 1-nitro-4-pentadecylbenzene using hydrazine hydrate /Pd-C (10 wt %) reagent system afforded the desired 4-pentadecylaniline which was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 4-pentadecylaniline (**Figure 3.32**) exhibited the characteristic absorption bands for –NH stretching at 3220, 3320 and 3400 cm^{-1}.
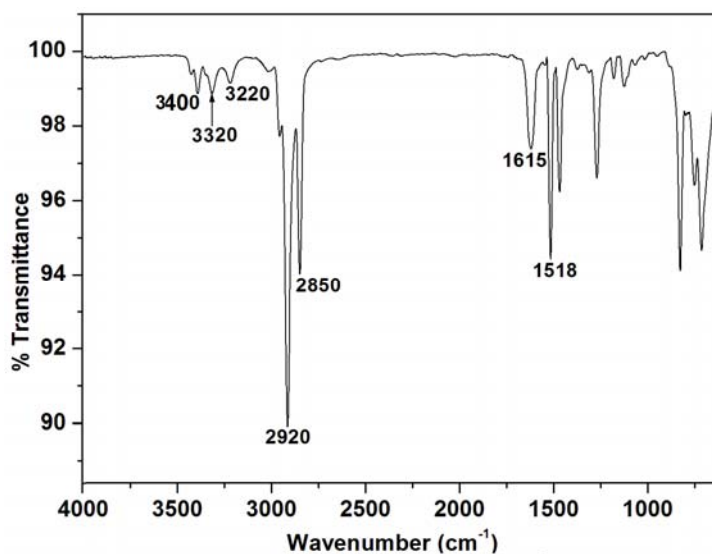
Figure 3.32 FT-IR spectrum (CHCl$_3$) of 4-pentadecylaniline

^{1}H-NMR spectrum of 4-pentadecylaniline is depicted in **Figure 3.33.**
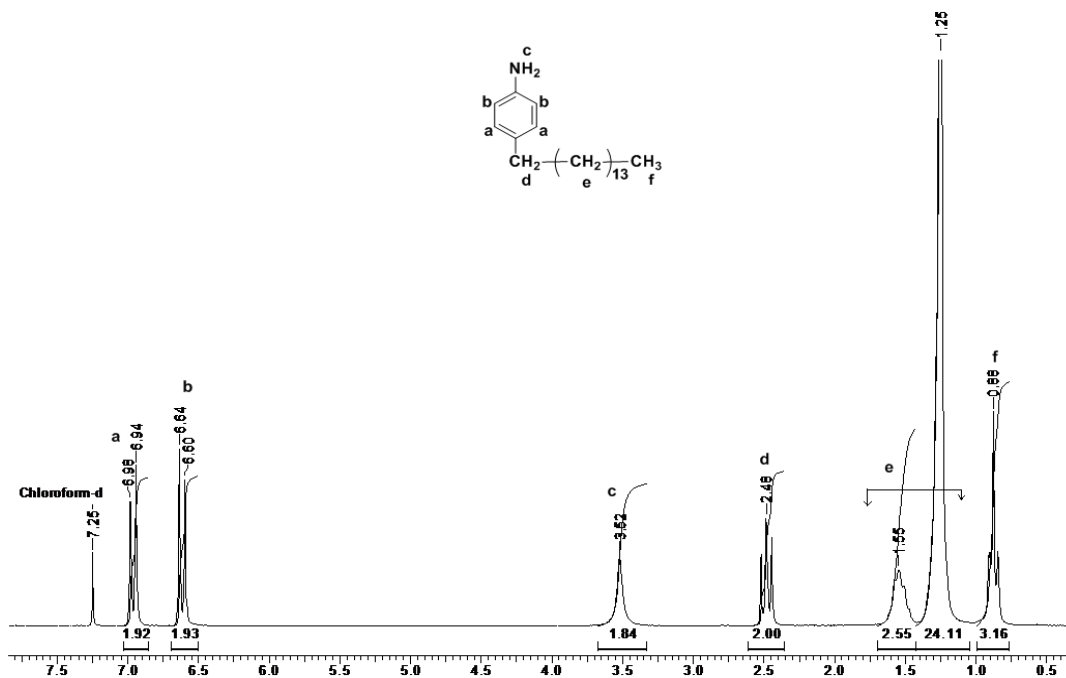
Figure 3.33 ^{1}H-NMR spectrum (CDCl$_3$) of 4-pentadecylaniline

The aromatic protons 'a' *ortho* to pentadecyl chain appeared as a doublet at 6.96 δ, ppm and aromatic protons 'b' *ortho* to –NH$_2$ group displayed a doublet at 6.62 δ, ppm. A broad singlet at 3.52 δ, ppm is ascribed to the amino group. The benzylic –CH$_2$ protons 'd' appeared as atriplet at 2.48 δ, ppm while methylyne protons 'e' appeared in the range 1.25- 1.55 δ, ppm. The terminal –CH$_3$ protons 'f' appeared as a triplet at 0.88 δ, ppm.

^{13}C-NMR spectrum of 4-pentadecylaniline along with assignments of carbon atoms is presented in **Figure 3.34.**
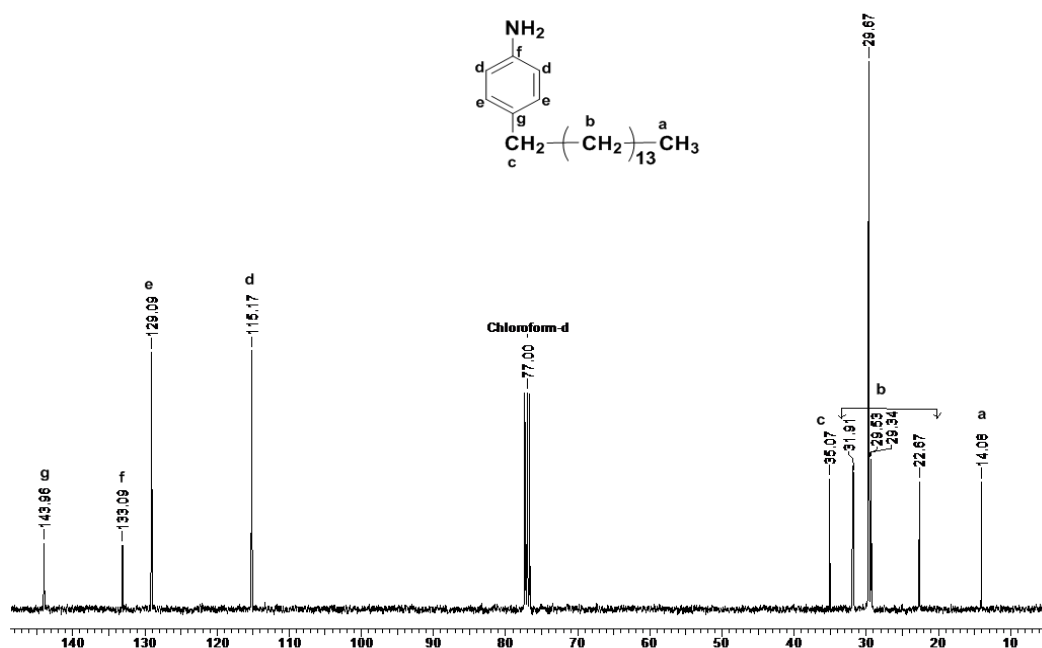
Figure 3.34 ^{13}C-NMR spectrum (CDCl$_3$) of 4-pentadecylaniline

In the third step, 4-pentadecylaniline was reacted with 3,5-dinitro benzoyl chloride in the presence of triethylamine as hydrogen chloride scavenger in DMAc at room temperature. The obtained 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide was purified by recrystallization from a mixture of DMAc and ethanol (1:2, v/v) to obtain pure compound which was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide (**Figure 3.35**) exhibited characteristic bands for the nitro group at 1525 (asymmetric -NO$_2$ stretching) and 1340 cm^{-1} (symmetric -NO$_2$ stretching). The absorption band at 1655 cm^{-1} corresponds to the carbonyl group.
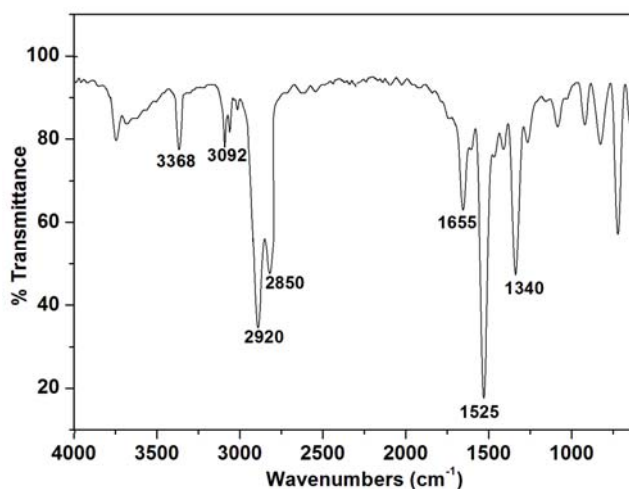
Figure 3.35 FT-IR spectrum (KBr) of 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide

^{1}H-NMR spectrum of 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide in acetone-d$_6$ is reproduced in **Figure 3.36.**
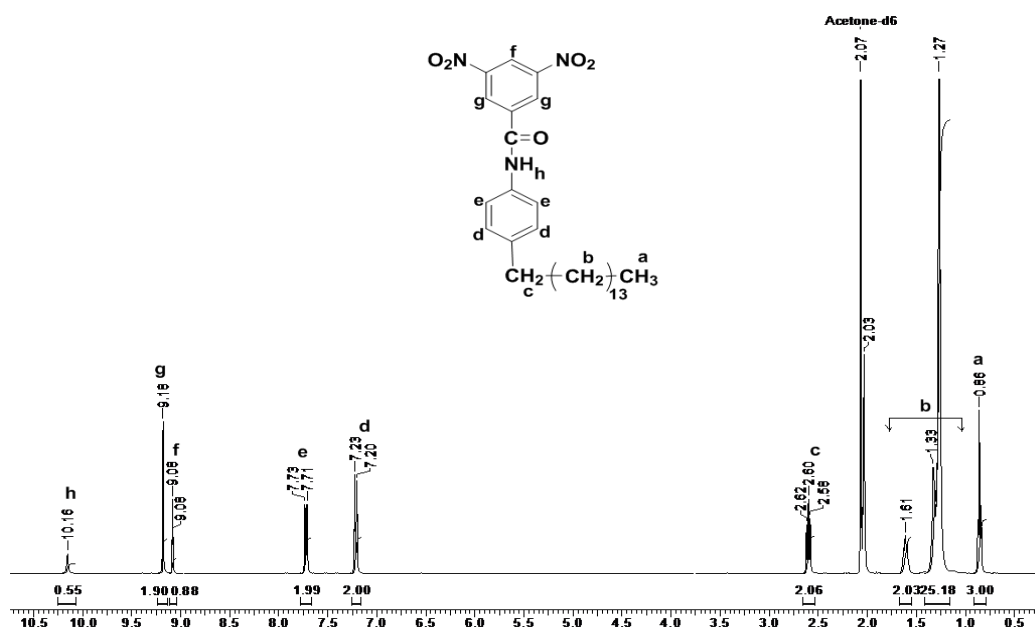
Figure 3.36 ^{1}H-NMR spectrum (Acetone-d$_6$) of 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide

The amide proton 'h' appeared as a singlet at 10.16 δ, ppm. The aromatic proton 'f' flanked by two nitro groups appeared as a doublet at 9.08 δ, ppm and aromatic protons 'g' displayed a doublet at 9.18 δ, ppm. The aromatic protons 'e' appeared as a doublet at 7.72 δ, ppm and aromatic protons 'd' *ortho* to pentadecyl chain exhibited a doublet at 7.21 δ, ppm. The benzylic methylene protons 'c' displayed a triplet at 2.60 δ, ppm while methylene protons 'b' appeared in the range 1.27- 1.61 δ, ppm. Methyl protons 'a' displayed a triplet at 0.86 δ, ppm.

^{13}C-NMR specrum of 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide along with assignments of the carbon atoms is presented in **Figure 3.37.**
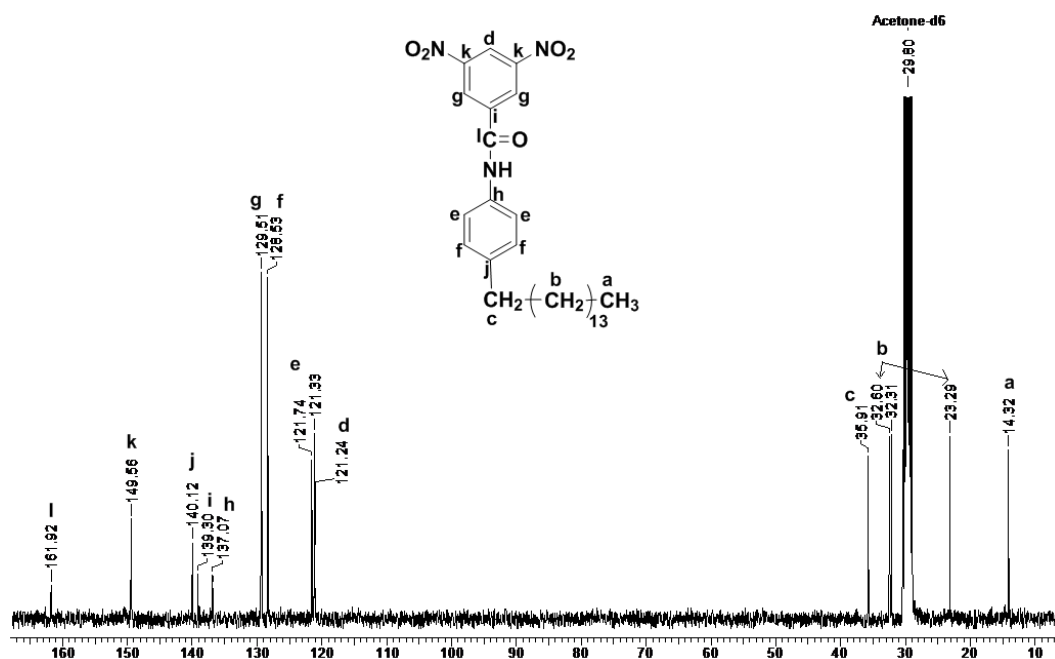
Figure 3.37 ^{13}C-NMR spectrum (acetone-d$_6$) of 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide

In the last step, 3,5-dinitro-*N*-(4-pentadecylphenyl) benzamide was reduced to the diamine *viz.*, 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide using hydrazine hydrate /Pd-C (10 wt %) reagent system. The crude diamine was purified by recrystallization from methanol and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. **Figure 3.38** represents FT-IR spectrum of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide.
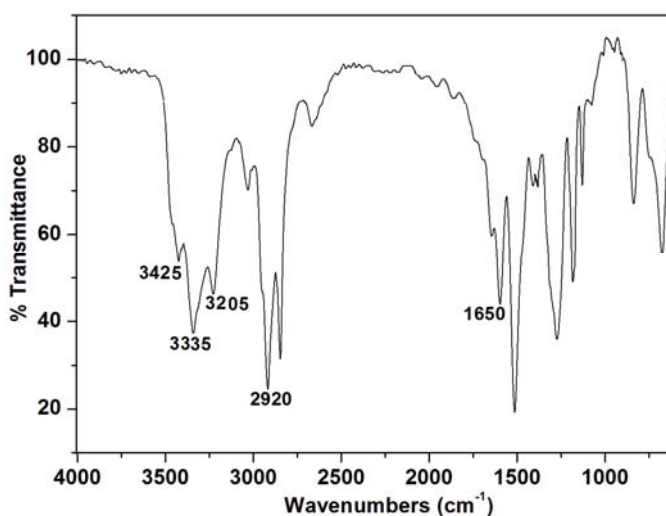
Figure 3.38 FT-IR spectrum (KBr) of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide

The bands between 3205 to 3425 cm^{-1} are characteristic of the amino group and –NH of the amide group. The band at 1650 cm^{-1} is assigned to the carbonyl of the amide group. The characteristic absorption bands of the nitro group were not observed indicting complete reduction of the nitro compound to the amine.

^{1}H-NMR spectrum of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide is reproduced in **Figure 3.39.**
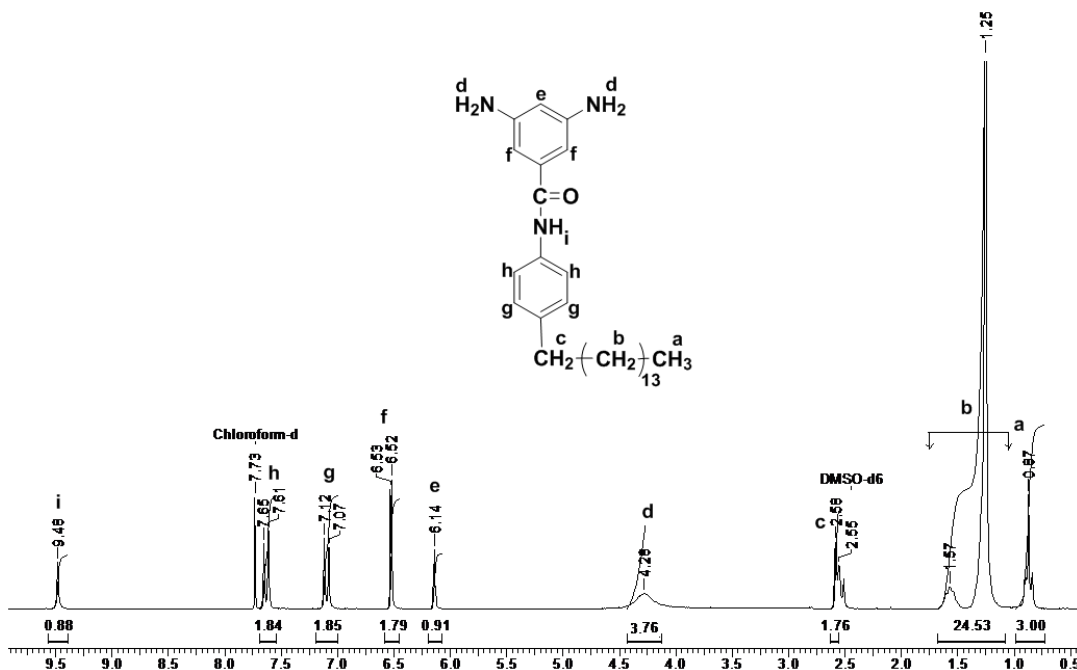
Figure 3.39 ^{1}H-NMR spectrum (CDCl$_3$ and DMSO-d$_6$) of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide

The amide protons 'i' appeared as a singlet at 9.48 δ, ppm. The aromatic protons 'h' adjacent to –NH of amide group appeared as a doublet at 7.63 δ, ppm while aromatic protons 'g' *ortho* to pentadecyl chain displayed a doublet at 7.10 δ, ppm. The aromatic protons 'f' adjacent

to carbonyl group exhibited a doublet at 6.52 δ, ppm and the aromatic proton 'e' flanked by amine groups showed a singlet at 6.14 δ, ppm. The –NH$_2$ protons 'd' exhibited a broad singlet at 4.26 δ, ppm. The benzylic methylene protons 'c' showed a signal along with reference protons (DMSO-d$_6$) while other methylene protons 'b' appeared in the range 1.25-1.57 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.87 δ, ppm.

^{13}C-NMR spectrum of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide along with assignments of carbon atoms is presented in **Figure 3.40.**
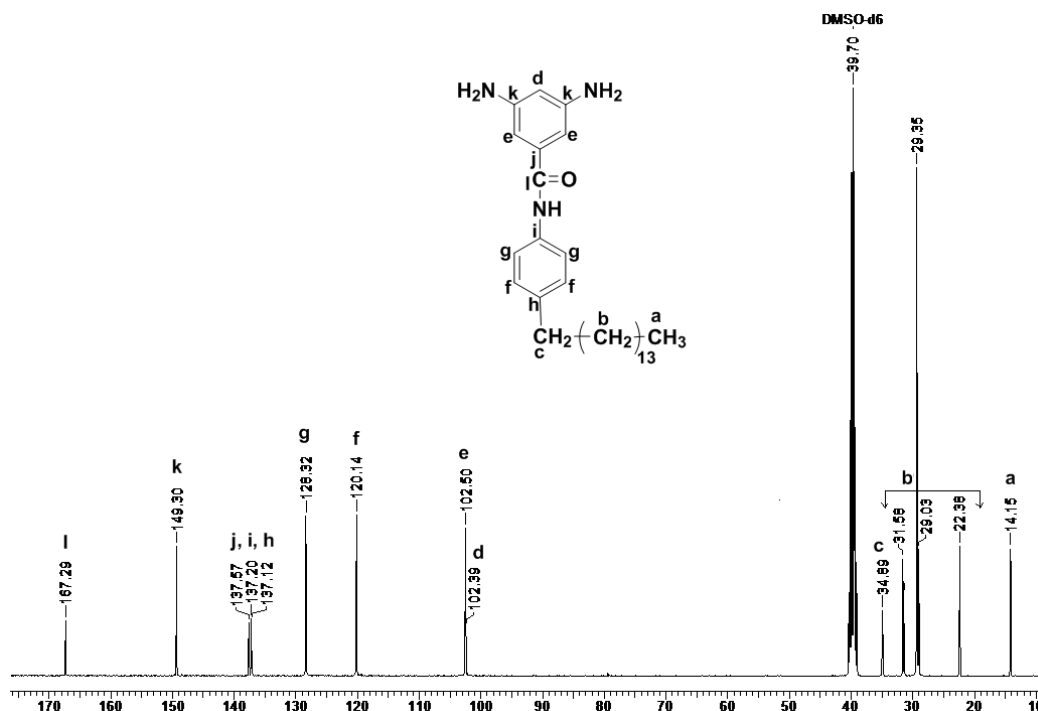
Figure 3.40 ^{13}C-NMR spectrum (DMSO-d$_6$) of 3,5-diamino-*N*-(4-pentadecylphenyl) benzamide

3.4.7 Synthesis of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid) (PDPDA)

A new diimide-dicarboxylic acid containing pentadecyl chain was designed and synthesized in a single step reaction starting from 4-pentadecylbenzene-1,3-diamine. **Scheme 3.6** depicts route for synthesis of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid)
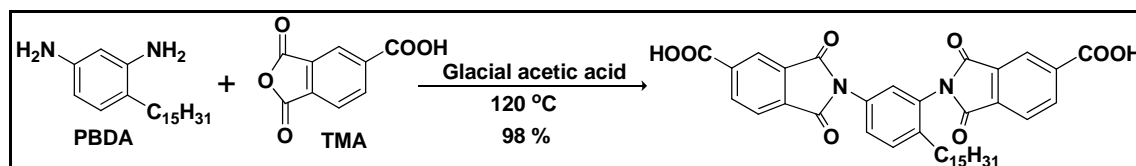
Scheme 3.6 Synthesis of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid)

4-Pentadecyl benzene-1,3-diamine was condensed with two molar equivalents of trimellitic dianhydride in glacial acetic acid at 120 °C.[22] The crude product was purified by recrystallization from a mixture of DMF and water (7:1, v/v) to obtain pure PDPDA. The structure of PDPDA was confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy. FT-IR spectrum of PDPDA is depicted in **Figure 3.41**.
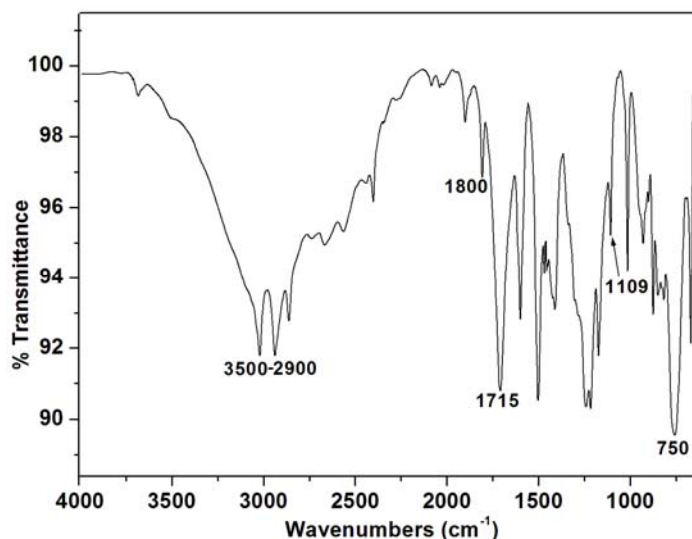
Figure 3.41 FT-IR spectrum (KBr) of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxo isoindoline-5-carboxylic acid)

A broad absorption band at 3500-2900 cm^{-1} corresponds to –OH of acid group. The imide C=O symmetric stretching appeared at 1800 cm^{-1}. There was overlapping in the C=O frequency of acid and imide asymmetric stretching at 1715 cm^{-1}. Absorption bands at 1390 (imide-II) and 750 cm^{−1} (imide-IV) correspond to the C–N–C stretching and bending vibrations of the imide, respectively. The absorption at 1109 cm^{−1} (imide-III) corresponds to imide ring deformation.

^{1}H-NMR spectrum of PDPDA along with the assignments is depicted in **Figure 3.42**.
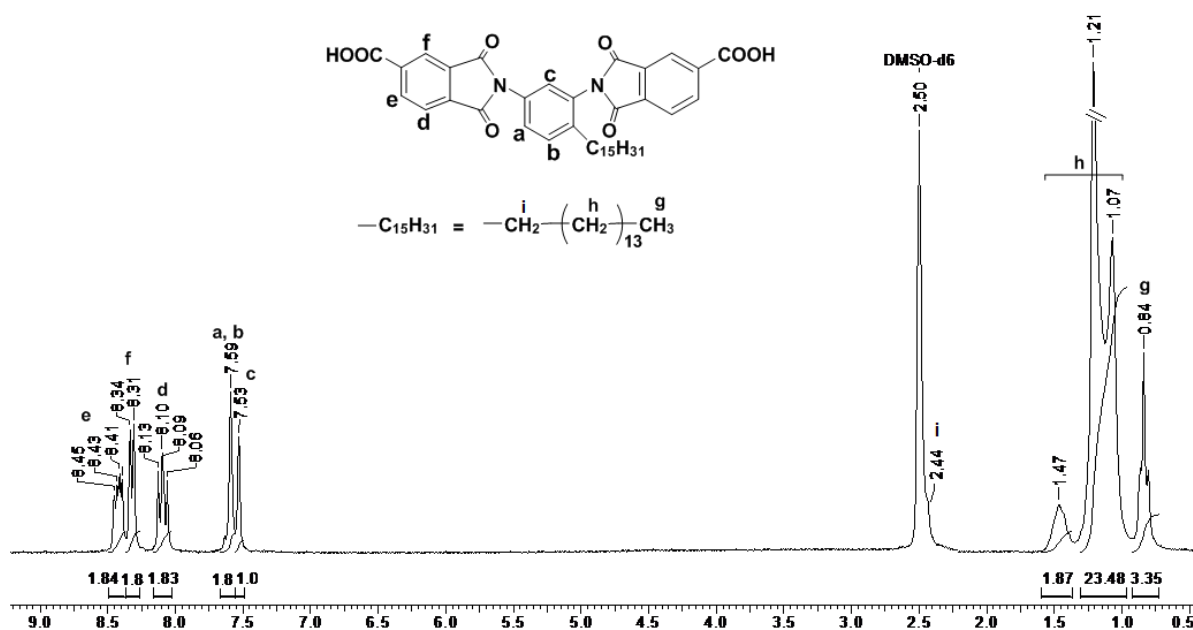
Figure 3.42 ^{1}H-NMR spectrum (DMSO-d$_6$) of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid)

The aromatic protons of trimellitimido ring appeared in the downfield region 8.45- 8.06 δ, ppm. The aromatic protons 'a, b' and 'c' of the diamine moiety appeared in the region 7.59- 7.53 δ, ppm. The benzylic methylene protons 'i' and DMSO-d$_6$ protons merged together and appeared in the region 2.50- 2.44 δ, ppm while other methylene protons 'h' displayed peaks in the range 1.47 - 1.07 δ, ppm. Methyl group protons 'g' appeared as a triplet at 0.84 δ, ppm. The signal due to the carboxylic acid proton was not observed probably due to the fast exchange of this proton with trace amount of moisture associated with the solvent.

^{13}C-NMR spectra of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid) is reproduced in **Figure 3.43** and the peak assignments were confirmed by DEPT spectrum.
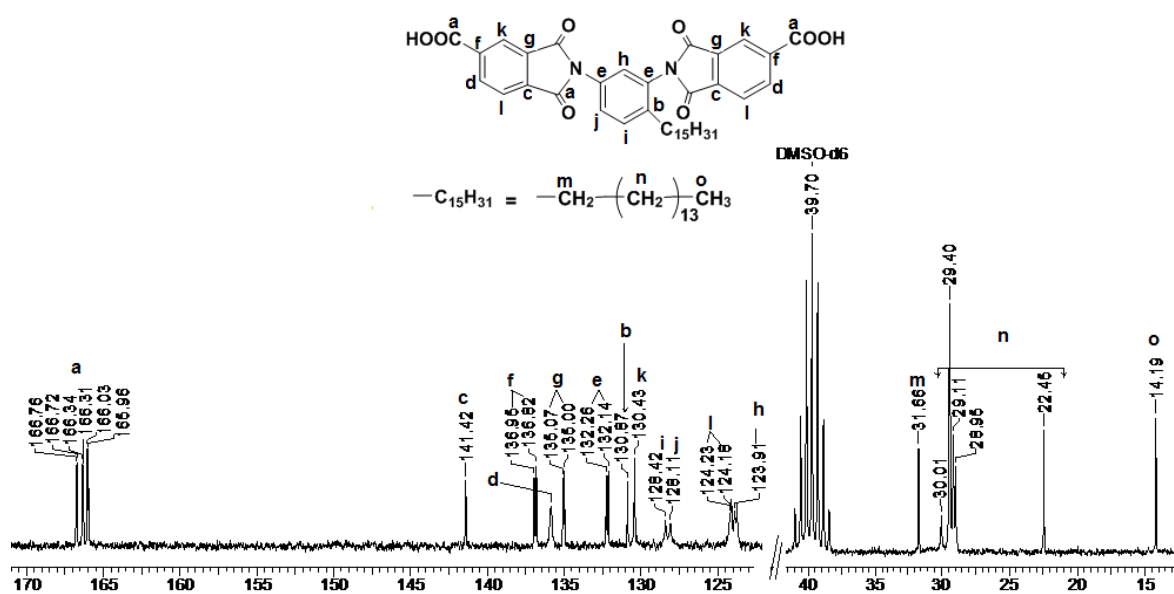
Figure 3.43 ^{13}**C-NMR spectrum (DMSO-d$_6$) of 2,2'(4-pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid)**

The peaks corresponding to carbonyl carbons of imide rings and acid 'a' were observed in the range 166.76- 165.96 δ, ppm. The quaternary aromatic carbons 'c' displayed peak at 141.42 δ, ppm and the quaternary aromatic carbons 'f' attached to carboxyl groups appeared at 136.95 and 136.82 δ, ppm. The quaternary aromatic carbons attached to imide ring 'e' displayed peaks at 132.26 and 132.14 δ, ppm. The other quaternary aromatic carbons 'g' appeared at 135.07 and 135.00 δ, ppm and the quaternary carbon attached to pentadecyl chain 'b' appeared at 130.87 δ, ppm. The peaks appeared in the region 130.43- 123.91 δ, ppm were assigned to the aromatic carbons h, i, j, k and l. The peak observed at 31.66 δ, ppm was assigned to the carbon 'm' and the peaks appeared in the region 30.01- 22.45 δ, ppm could be assigned to the methylene carbons 'n' of pentadecyl chain. The peak observed at 14.19 δ, ppm was due to methyl carbon 'o' of pentadecyl chain.

3.4.8   Synthesis of 2-pentadecylbenzene-1,4-diol

Scheme 3.7 depicts route for synthesis of 2-pentadecylbenzene-1,4-diol starting from 3-pentadecylphenol. The synthesis of 2-pentadecylbenzene-1,4-diol comprised of three steps; diazotization followed by reduction, oxidation and again reduction.
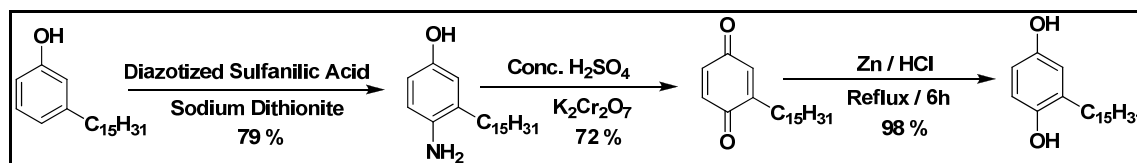
Scheme 3.7 Synthesis of 2-pentadecylbenzene-1,4-diol

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 FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy and the data was in good agreement with the structure.[8]

The second step involved oxidation of 4-amino-3-pentadecyl phenol using potassium dichromate as an oxidizing agent in acidic medium to obtain 2-pentadecyl-2,5-cyclohexadiene-1,4-dione which was purified by recrystallization from acetone.[9] FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy data was in good agreement with the structure.

In the next step, reduction of 2-pentadecyl-2,5-cyclohexadiene-1,4-dione was accomplished using Zn/HCl. Pure 2-pentadecylbenzene-1,4-diol was obtained by recrystallization from ethanol and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 2-pentadecylbenzene-1,4-diol (**Figure 3.44**) showed a broad band at 3265 cm^{-1} corresponding to -OH stretching.
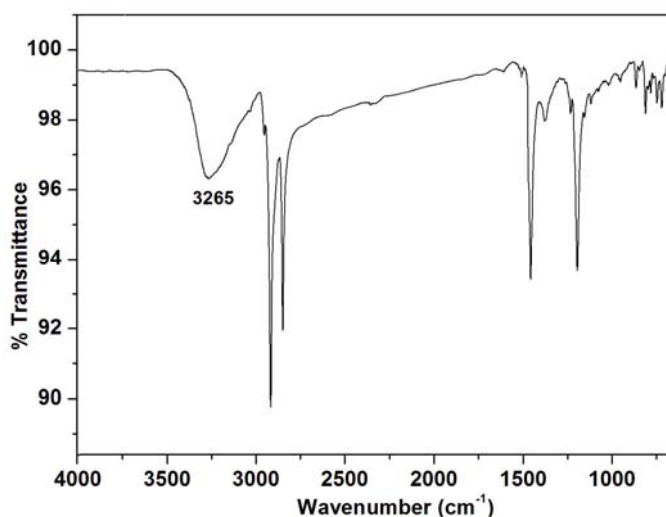
Figure 3.44 FT-IR spectrum (CHCl$_3$) of 2-pentadecylbenzene-1,4-diol

^{1}H-NMR spectrum of 2-pentadecylbenzene-1,4-diol is depicted in **Figure 3.45**.
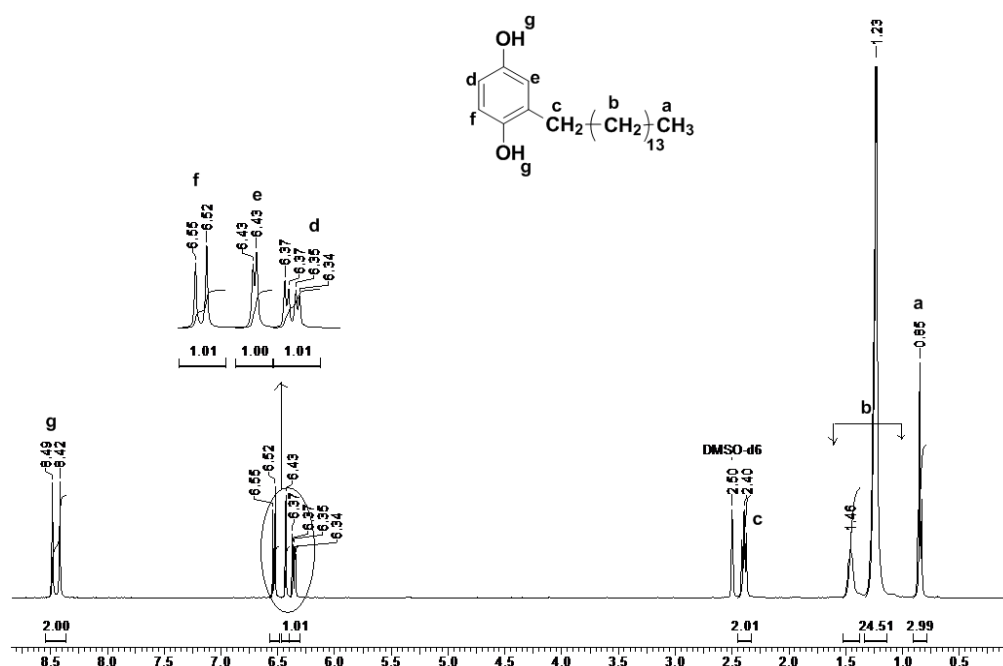
Figure 3.45 ¹H-NMR spectrum (CDCl₃) of 2-pentadecylbenzene-1,4-diol

Two separate singlets were observed at 8.42 and 8.49 δ, ppm corresponding to two -OH groups. The aromatic proton 'f' *ortho* to –OH group and *meta* to pentadecyl chain appeared as a doublet at 6.53 δ, ppm while the aromatic proton 'e' *ortho* to pentadecyl chain displayed a doublet at 8.43 δ, ppm. The aromatic proton 'd' *para* to pentadecyl chain exhibited a doublet of doublet at 6.36 δ, ppm. The benzylic –CH₂ 'c' appeared as a triplet at 2.40 δ, ppm while other methylene protons 'b' appeared as a multiplet in the range 1.23- 1.46 δ, ppm. Methyl group protons 'a'exhibited a triplet at 0.85 δ, ppm.

¹³C-NMR spectrum of 2-pentadecylbenzene-1,4-diol along with assignments of carbon atoms is presented in **Figure 3.46.**
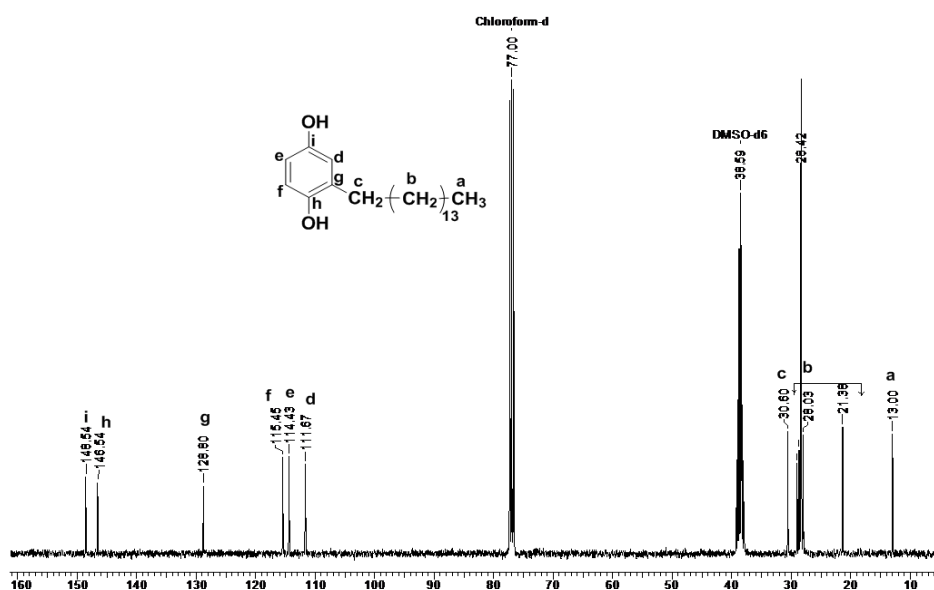

Figure 3.46 ¹³C-NMR spectrum (CDCl₃ and DMSO-d₆) of 2-pentadecylbenzene-1,4-diol

3.4.9   Synthesis of 4-methoxy-6-pentadecylisophthalonitrile

Aromatic dicyano / dinitrile compounds are useful precursors for the synthesis of various monomers and polymers. For example, dicyano compound upon hydrolysis gives diacid from which polyamides, poly(oxadiazole)s, polyesters, etc. can be synthesized.[7] Aromatic dinitriles undergoes hydroboration polymerization,[23, 24] and polybenzimidazoles,[25] polybenzoxazoles,[26] polyamides,[27] poly(1,3,4-oxadiazole)s,[28] etc. can be obtained using aromatic dinitriles as monomer.

Scheme 3.8 depicts route for the synthesis of 4-methoxy-6-pentadecylisophthalonitrile.
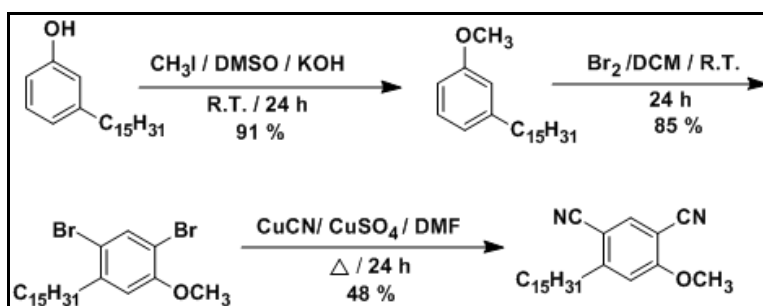
Scheme 3.8 Synthesis of 4-methoxy-6-pentadecylisophthalonitrile

A new aromatic dinitrile monomer containing pendent pentadecyl chain, *viz.,* 4-methoxy-6-pentadecylisophthalonitrile was designed and synthesized starting from 3-pentadecyl phenol making use of simple organic transformations like etherification, electrophilic aromatic substitution such as bromination, followed by cyanation.

In the first step, 1-methoxy-3-pentadecylbenzene was prepared by reaction of 3-pentadecyl phenol with methyl iodide in the presence of potassium hydroxide. The product was purified using column chromatography and was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.[10]

FT-IR spectrum of 1-methoxy-3-pentadecylbenzene displayed band at 1220 cm^{-1} corresponding to –C-O-C- stretching. **(Figure 3.47)**
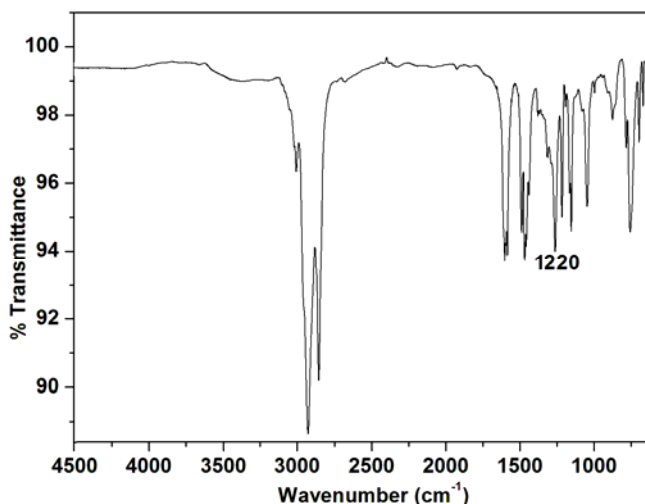
Figure 3.47 FT-IR spectrum (CHCl$_3$) of 1-methoxy-3-pentadecylbenzene

^{1}H-NMR spectrum of 1-methoxy-3-pentadecylbenzene is depicted in **Figure 3.48**
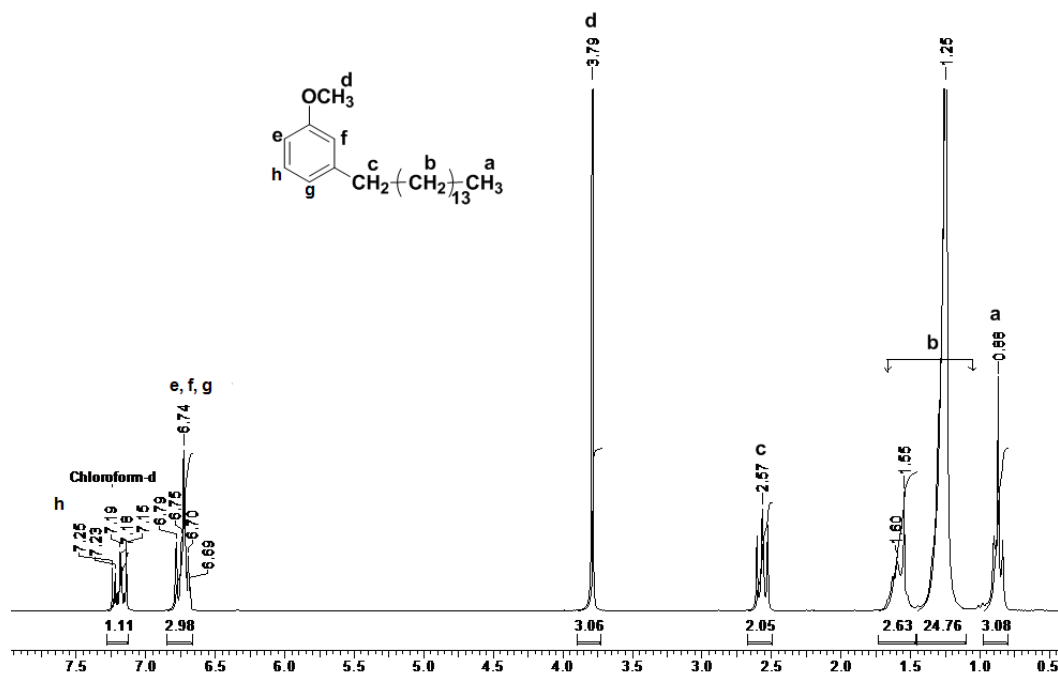
Figure 3.48 ^{1}H-NMR spectrum (CDCl$_3$) of 1-methoxy-3-pentadecylbenzene

A doublet of doublet at 7.20 δ, ppm corresponds to the aromatic proton 'f'. The aromatic protons 'e', 'f' and 'g' displayed peaks in the region 6.69 -6.79 δ, ppm. The methoxy group protons 'd' displayed a singlet at 3.79 δ, ppm. The bezylic methylene protons 'c' appeared as a triplet at 2.57 δ, ppm and other methylene protons displayed peaks in the range 1.25- 1.60 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.88 δ, ppm.

^{13}C-NMR spectrum of 1-methoxy-3-pentadecylbenzene is presented in **Figure 3.49**
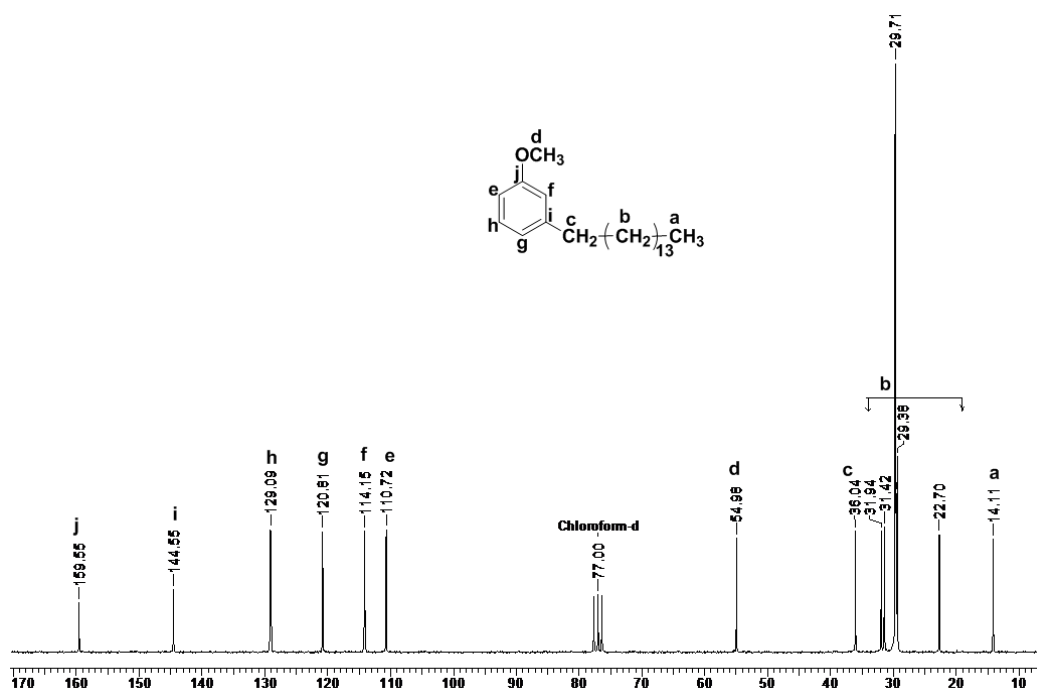
Figure 3.49 ^{13}C-NMR spectrum (CDCl$_3$) of 1-methoxy-3-pentadecylbenzene

In the second step, bromination of 1-methoxy-3-pentadecylbenzene was carried out to obtain the crude product which was purified by column chromatography (pet ether: ethyl acetate, 95:5, v/v). Pure 1,5-dibromo-2-methoxy-4-pentadecyl benzene was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

In the FT-IR spectrum of 1,5-dibromo-2-methoxy-4-pentadecyl benzene **(Figure 3.50)** the band at 670 cm^{-1} was assigned to C-Br stretching.
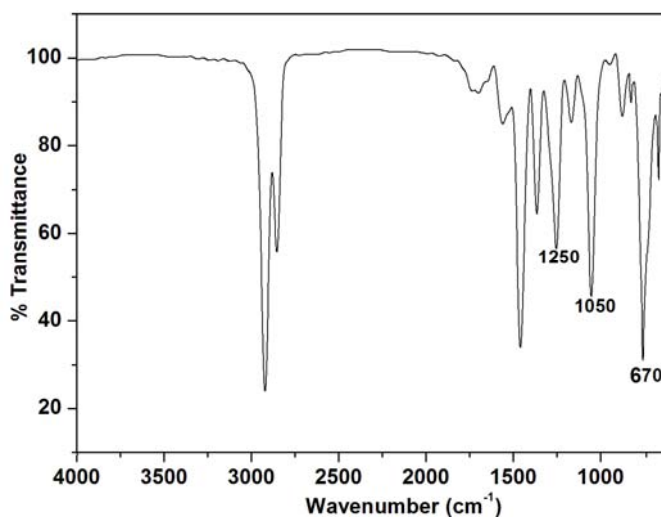
Figure 3.50 FT-IR spectrum (CHCl$_3$) of 1,5-dibromo-2-methoxy-4-pentadecylbenzene

^{1}H-NMR spectrum of 1,5-dibromo-2-methoxy-4-pentadecyl benzene is depicted in **Figure 3.51.**
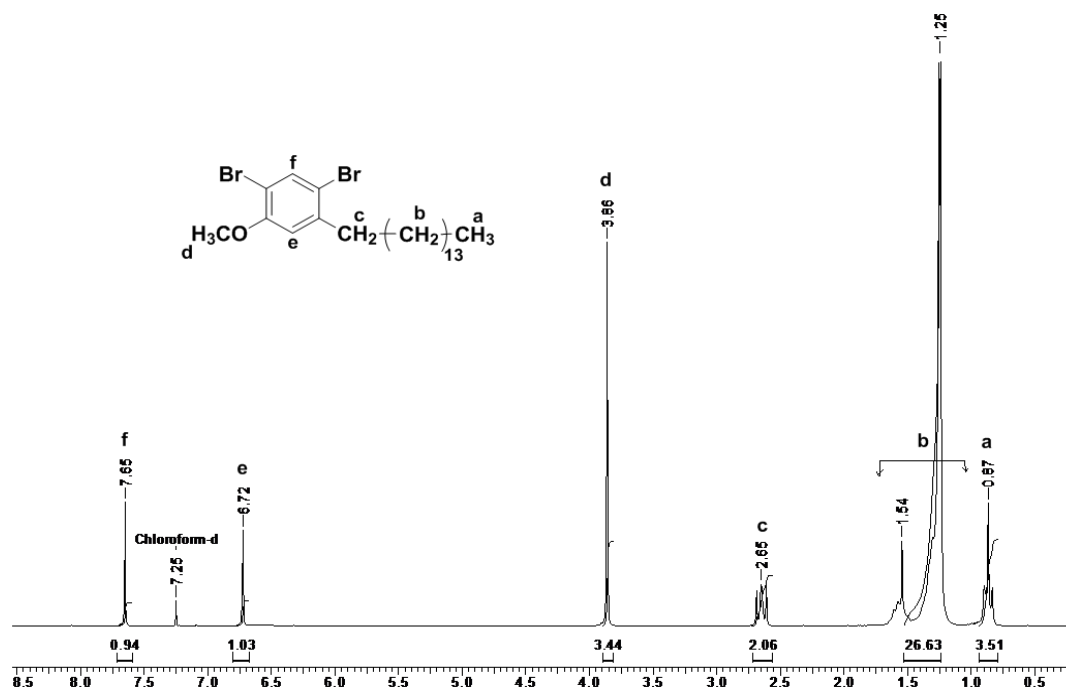
Figure 3.51 ^{1}H-NMR spectrum (CDCl$_3$) of 1,5-dibromo-2-methoxy-4-pentadecylbenzene

The aromatic proton 'f' flanked by two bromine atoms displayed a singlet at 7.86 δ, ppm and the aromatic proton 'e' appeared as a singlet at 7.65 δ, ppm. The methoxy group protons 'd'

appeared as a singlet at 3.86 δ, ppm. The benzylic methylene protons 'c' exhibited a triplet at 2.65 δ, ppm and other methylene protons displayed peaks in the range 1.25- 1.54 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.87 δ, ppm.

^{13}C-NMR spectrum of 1,5-dibromo-2-methoxy-4-pentadecyl benzene along with assignments is presented in **Figure 3.52.**
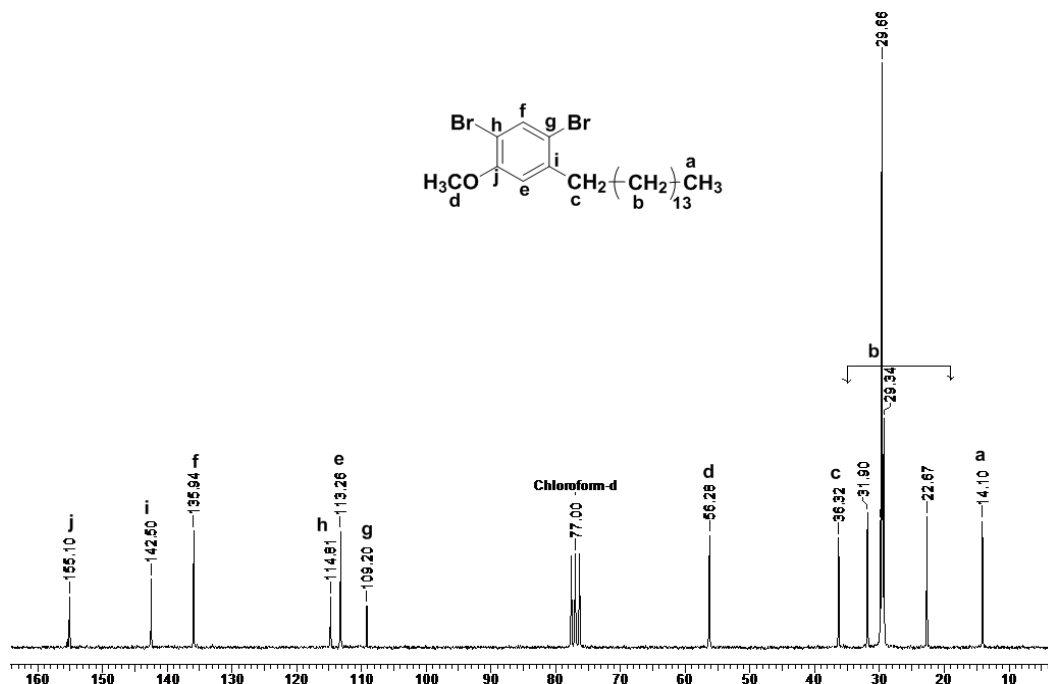
Figure 3.52 ^{13}C-NMR spectrum (CDCl$_3$) of 1,5-dibromo-2-methoxy-4-pentadecylbenzene

The quaternary carbons 'j' and 'i' attached to methoxy group and pentadecyl chain appeared at 155.10 and 142.50 δ, ppm, respectively. Other quaternary carbons 'h' and 'g' attached to bromine displayed peaks at 114.81 and 109.20 δ, ppm. The aromatic carbon 'f' flanked by bromine atoms exhibited a signal at 135.94 δ, ppm and aromatic carbon 'e' appeared at 113.26 δ, ppm.

In the third step, 1,5-dibromo-2-methoxy-4-pentadecylbenzene was treated with copper cyanide in the presence of copper sulfate in DMF as a solvent to obtain 4-methoxy-6-pentadecylisophthalonitrile. A variety of methods for the preparation of aryl nitriles have been developed,[29] The direct cyanation of aryl halides by copper(I) cyanide is known as Rosenmund–von Braun reaction.[30] Recently, several palladium- or nickel-catalyzed aryl cyanation[31] approaches were reported. However, many of these methods require special reagents such as expensive and toxic phosphines as ligands, etc. [31,32] Rosenmund–von Braun reaction remains one of most useful methods for the synthesis of aryl nitriles because of its cost efficiency and easy operation.[30,33]

4-Methoxy-6-pentadecylisophthalonitrile was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FT-IR spectrum of 4-methoxy-6-pentadecylisophthalonitrile **(Figure 3.53)** exhibited the characteristic stretching band for the -CN at 2225 cm⁻¹.
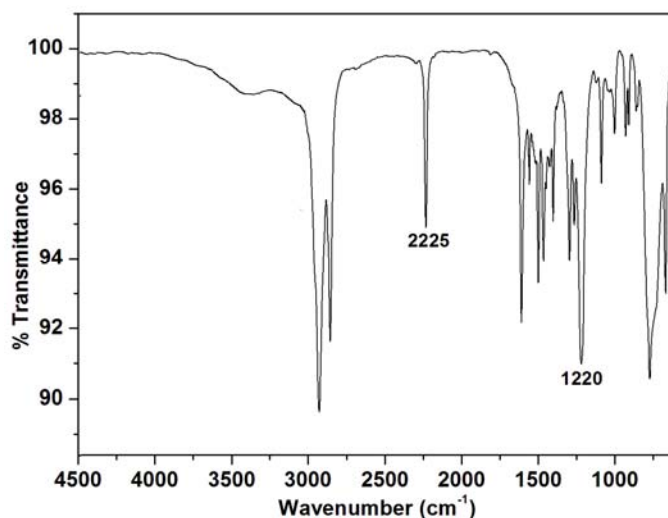
Figure 3.53 FT-IR spectrum (CHCl₃) of 4-methoxy-6-pentadecylisophthalonitrile

¹H-NMR spectrum of 4-methoxy-6-pentadecylisophthalonitrile is depicted in **Figure 3.54**.
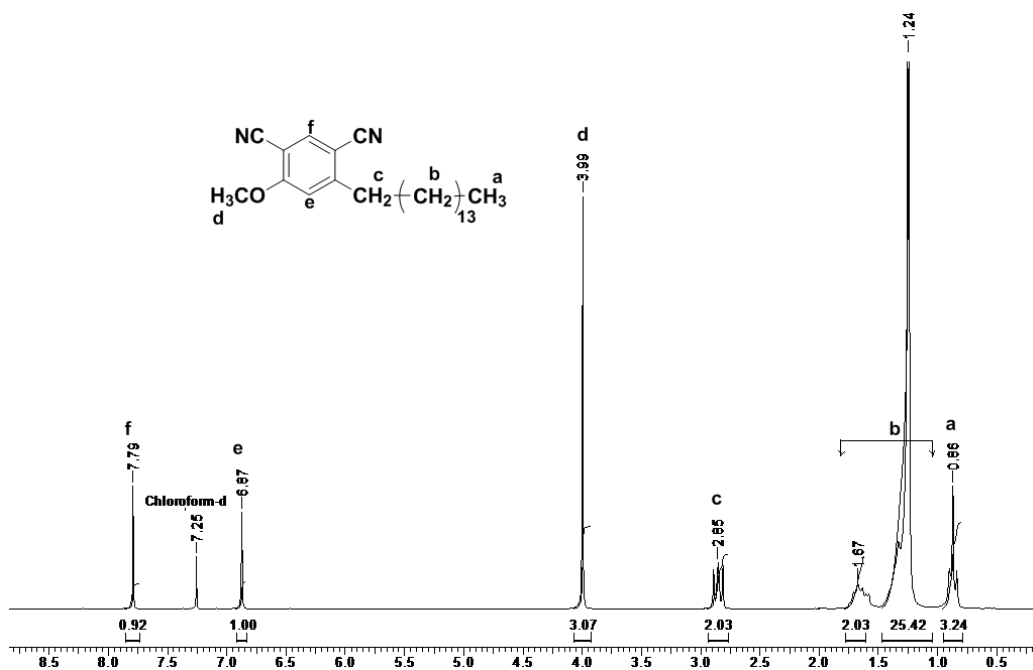
Figure 3.54 ¹H-NMR spectrum (CDCl₃) of 4-methoxy-6-pentadecylisophthalonitrile

The aromatic proton 'f' flanked by two cyano groups exhibited a singlet at 7.79 δ, ppm and the aromatic proton 'e' *ortho* to methoxy group displayed a singlet at 6.87 δ, ppm. The methoxy protons 'd' appeared as a singlet at 3.99 δ, ppm. The benzylic methylene protons 'c' exhibited a ttriplet at 2.85 δ, ppm and other methylene protons displayed peaks in the range 1.24-1.67 δ, ppm. Methyl group protons 'a' appeared as a triplet at 0.86 δ, ppm.

^{13}C-NMR spectrum of 4-methoxy-6-pentadecylisophthalonitrile along with assignments is presented in **Figure 3.55**.
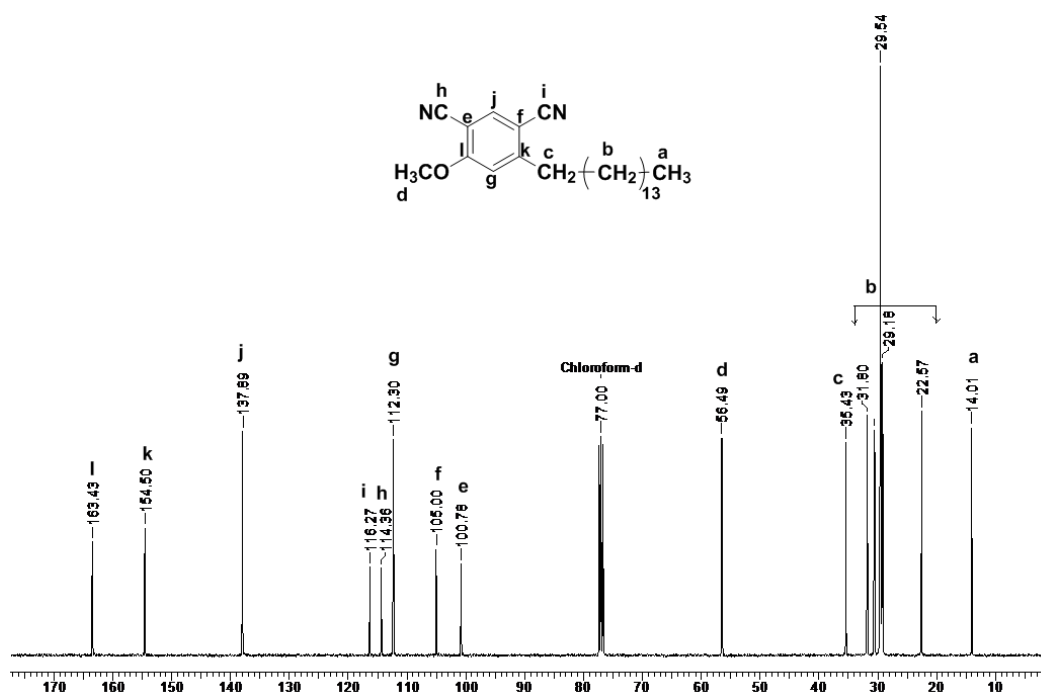
Figure 3.55 ^{13}C-NMR spectrum (CDCl$_3$) of 4-methoxy-6-pentadecylisophthalonitrile

The quaternary carbons 'k' and 'l' attached to methoxy group and pentadecyl chain, appeared at 154.50 and 163.43 δ, ppm. The quaternary carbons 'e' and 'f' containing cyano groups exhibited signals at 100.78 and 105.0 δ, ppm. The aromatic carbons 'g'and 'j' displayed peaks at 112.30 and 137.89 δ, ppm. The methoxy carbon 'd' displayed a signal at 56.49 δ, ppm and the benzylic carbon 'c' appeared at 35.43 δ, ppm while the other methylene carbons 'b' exhibited peaks in the range 22.57 – 31.80 δ, ppm. The terminal methyl carbon 'a' appeared at 14.01 δ, ppm.

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 a variety of new value-added condensation monomers *viz*; aromatic diamines, diacid, diphenol, diisocyanate and dinitrile was explored. Nine new difunctional monomers containing pendent pentadecyl chain were synthesized starting from CNSL, *viz*;

   a. 4-Pentadecylbenzene-1,3-diamine,

   b. *N,N*-(4-Pentadecyl-1,3-phenylene)bis(4-aminobenzamide),

   c. *N,N*-(4-Pentadecyl-1,3-phenylene)bis(3-aminobenzamide),

   d. 2,4-Diisocyanato-1-pentadecylbenzene,

   e. 3,5-Diamino-4'-pentadecylbenzophenone,

   f. 3,5-Diamino-*N*-(4-pentadecylphenyl)benzamide,

   g. 2,2'(4-Pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid),

   h. 2-Pentadecylbenzene-1,4-diol, and

   i. 4-Methoxy-6-pentadecylisophthalonitrile

2. Difunctional monomers are potentially useful for the synthesis of a host of high performance polymers.

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Chapter 4

Synthesis and Characterization of Polyimides Based on 4-Pentadecylbenzene-1,3-diamine

4.1   Introduction

Aromatic polyimides are an important class of high performance polymers due to their excellent thermo-oxidative stability, mechanical strength, electrical properties, and high radiation and solvent resistance[1-3]. However, most of the aromatic polyimides are insoluble in organic solvents and exhibit high softening temperatures, which present serious processing difficulties. The key reasons for insolubility and non-melting character in wholly aromatic polyimides are the lack of chain flexibility and strong interchain interactions.[4,5] The interchain interactions in polyimides are charge transfer complexes whose strength is dependent on the electron affinity of the dianhydrides and the ionization potential of the diamine. In the last few decades, many studies have been conducted to control these interactions in order to produce more tractable polyimides, which can be processed by conventional techniques such as melt processing or casting from volatile organic solvents while maintaining thermooxidative stability. The majority of these studies involved three main structural modifications to tailor the properties (i) incorporation of thermally stable but flexible or nonsymmetrical linkages in the backbone, (ii) introduction of large polar or non-polar substituents pendent from the polymer backbone and (iii) disruption of symmetry and recurrence of regularity through copolymerization.[6] There are several attempts, that have been reported with varying success *via* the synthesis of new diamines and dianhydrides, such as introduction of flexibilizing groups,[7-13] bulky groups,[14-16] cardo, spiro or multicyclic structures,[17-20] molecular asymmetry,[21-24] pendent flexible groups,[25-29] etc.

The approach involving synthesis of monomers containing pendent flexible groups such as alkyl group is of particular interest since the peculiar structure of the main chain of such polymers is not altered by the attachment of flexible side chains. Also, this approach not only brings about improvement in processability of polyimides[30-36] but also improves pretilt angle, making such polyimides potentially useful as films for alignment layers in liquid crystal display devices.[37-45]

It is known that molecular asymmetry induced by use of *meta*-oriented diamines, distort the linearity of the polyimide chain and this interferes with chain packing and charge transfer formation. Also, substitution ortho to the imide bond (C-N) is proposed to prevent coplanarity of the electron donor (amine) and the electron acceptor (anhydride) units, weakening the intra- and inter-chain interactions and the packing of polymer chains.[1] In general, these structural modifications lead to lowering of glass transition temperature, as well as significant improvement in solubility and processability.

In view of the above, *meta*-oriented aromatic diamine monomer *viz.*, 4-pentadecylbenzene-1,3-diamine containing pendent pentadecyl chain was considered as a useful monomer for synthesis of processable polyimides.

The objective of the present work was to synthesize a series of polyimides containing

pendent pentadecyl chains and to examine the effect of incorporation of pentadecyl chains on the polymer properties such as solubility and thermal behavior. Thus, a series of polyimides was synthesized by one-step solution polycondensation in *m*-cresol from 4-pentadecylbenzene-1,3-diamine and commercially available aromatic dianhydrides, *viz.*, 4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride.

The synthesized polyimides were characterized by inherent viscosity measurements, gel permeation chromatography (GPC), solubility tests, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetric (DSC) and UV-Vis spectroscopy studies.

4.2   Experimental

4.2.1   Materials

4-Pentadecylbenzene-1,3-diamine was synthesized as described in **Chapter 3.** 4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6-FDA) (Sigma-Aldrich) were purified by sublimation under reduced pressure. *m*-Cresol (Loba Chemie) was vacuum distilled before use.

4.2.2   Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in CHCl$_3$ at 30±0.1 $^{\circ}$C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \dfrac{2.303}{C} x \log \dfrac{t}{t_0}$

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 polyimides 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.

FT-IR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker 400 MHz spectrophotometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C using CDCl$_3$ as a solvent.

The solubility of polyimides was determined at 3 wt % concentration in various solvents at room temperature or on heating.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 10 °C/minute under nitrogen atmosphere. Sample weight taken was ~5-7 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 20 °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.

Ultraviolet–Visible (UV–Vis) spectra of polyimide solutions in chloroform were recorded on Perkin-Elmer Lambda 950 UV/Vis Spectrometer.

4.3   Synthesis of polyimides

Into a 50 ml three-necked round bottom flask equipped with a nitrogen gas inlet and a $CaCl_2$ guard tube were added 4-pentadecylbenzene-1,3-diamine (1.0 g, 3 mmol) and freshly distilled *m*-cresol (17 ml) and the mixture was stirred to get clear, homogeneous solution. To the reaction mixture, 4,4'-biphenyltetracarboxylic dianhydride (0.88 g, 3 mmol) was added in small portions with stirring under a stream of nitrogen at room temperature. The reaction mixture was stirred at room temperature for 3 h to obtain a homogeneous solution which was then heated to 200 °C and maintained at that temperature for 12 h. During the heating, water produced by the imidization reaction was removed continuously with a stream of nitrogen. The reaction mixture was then cooled to room temperature and poured into excess methanol (300 ml). The fibrous polymer obtained was filtered, washed with methanol and dried at 80 °C under vacuum overnight.

Yield: 1.7 g (97 %).

A similar procedure was followed for the synthesis of other polyimides.

4.4   Results and discussion

4.4.1   Synthesis of polyimides

Polyimides are generally synthesized by two methods (i) the two step method *via* the poly(amic acid) intermediate and (ii) the one step solution polymerization. The one step method has some advantages over the two step method. In this method, complete imidization takes place in solution itself since the reaction is carried out at high temperature (~ 200 °C).

Scheme 4.1 illustrates synthesis of polyimides from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides.
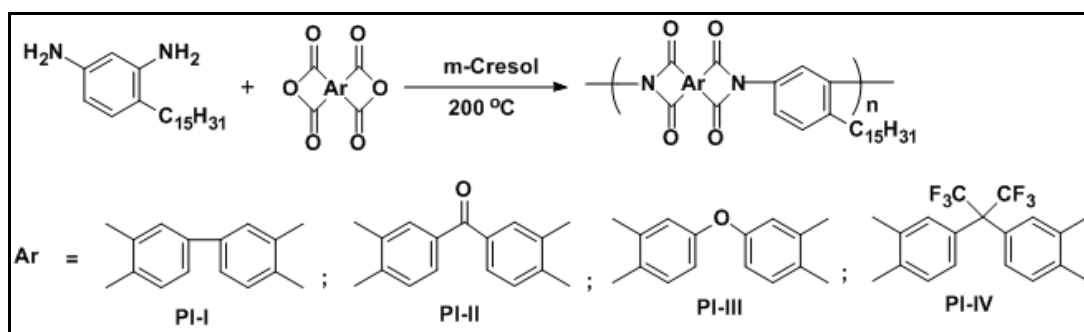
Scheme 4.1 Synthesis of polyimides from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides

The results of polymerization are summarized in **Table 4.1**. All the reaction mixtures were homogeneous throughout the course of polymerization.

Table 4.1 Synthesis of polyimides from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides

Polyimide		Yield (%)	η_{inh} (dL/g)^a	GPC^b		
				M_w	M_n	M_w/M_n
PI-I		97	0.67	1,19,000	52,200	2.2
PI-II		99	0.49	28,100	14,700	1.9
PI-III		98	0.56	76,000	38,200	2.0
PI-IV		99	0.33	95,000	48,700	1.9

a: η_{inh} was measured with 0.5% (w/v) solution of polyimides in CHCl$_3$ at 30 ± 0.1^{o}C, *b*: determined from gel permeation chromatography (mobile phase: chloroform; calibration: polystyrene standards).

Inherent viscosities of polyimides were in the range 0.33-0.67 dL/g **(Table 4.1)** indicating formation of medium to reasonably high molecular weight polymers. This was further supported by GPC measurements which gave M_n and polydispersities (M_w/M_n) in the range 14,700 – 52,200 and 1.9 - 2.2, respectively. However, molecular weights measured by GPC should not be taken as absolute as the measurements were carried out using polystyrene standards. Tough, transparent, and flexible films of polyimides could be cast from their chloroform solutions.

4.4.2   Structural characterization

The formation of polyimides was confirmed by FT-IR and ^{1}H-NMR spectroscopy.

A representative FT-IR spectrum of polyimide based on 4-pentadecylbenzene-1,3-diamine and 4,4'-biphenyltetracarboxylic dianhydride is reproduced in **Figure 4.1.**
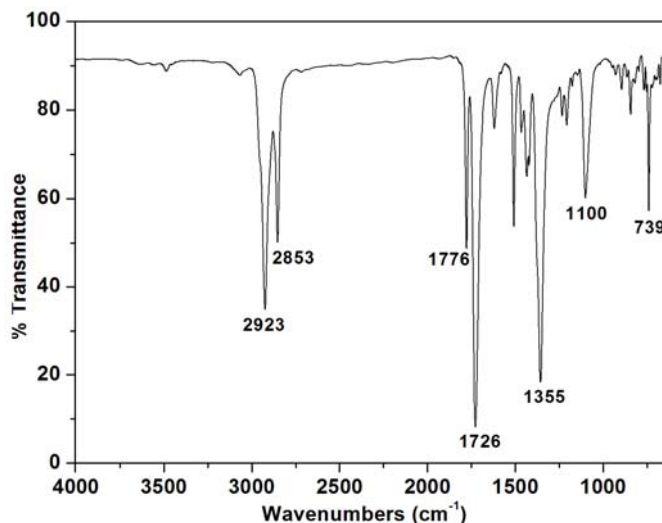
Figure 4.1 FT-IR spectrum (Film) of polyimide (PI-I) derived from 4-pentadecylbenzene-1,3-diamine and 4,4'-biphenyltetracarboxylic dianhydride

The spectrum showed characteristic absorption bands at 1776 cm^{-1} (C=O symmetric stretching of imide I) and 1726 cm^{-1} (C=O asymmetric stretching). Absorption bands at 1355 (imide-II) and 739 cm^{-1} (imide-IV) correspond to the C–N–C stretching and bending vibrations of the imide. The absorption at 1100 cm^{-1} (imide-III) corresponds to imide ring deformation.

A representative ^{1}H-NMR spectrum of polyimide derived from 4-pentadecylbenzene-1,3-diamine and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride is depicted in **Figure 4.2.**
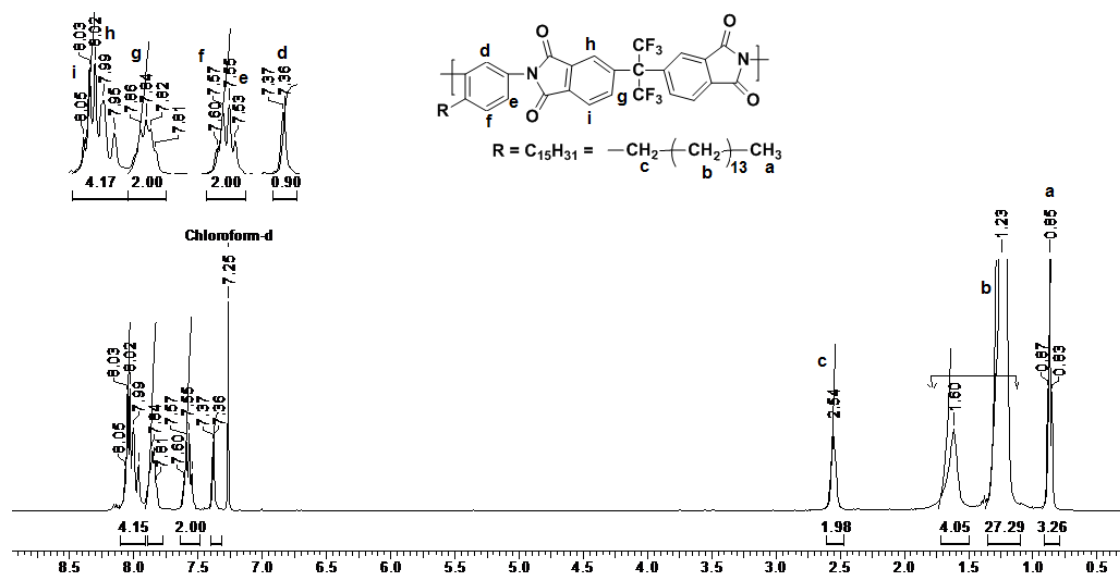
Figure 4.2 ^{1}H-NMR spectrum (CDCl$_3$) of polyimide derived from 4-pentadecylbenzene-1,3-diamine and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride

The aromatic protons of the dianhydride unit appeared in the range 7.81 - 8.05 δ, ppm while aromatic protons of the diamine moiety displayed peaks in the region 7.36 - 7.60 δ, ppm. The benzylic methylene protons exhibited a triplet at 2.54 δ, ppm while the other methylene protons appeared in the range 1.23 - 1.65 δ, ppm. Methyl group protons appeared as a triplet at 0.85 δ, ppm.

^{13}C-NMR spectrum of polyimide derived from 4-pentadecylbenzene-1,3-diamine and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride along with assignments is presented in **Figure 4.3.**
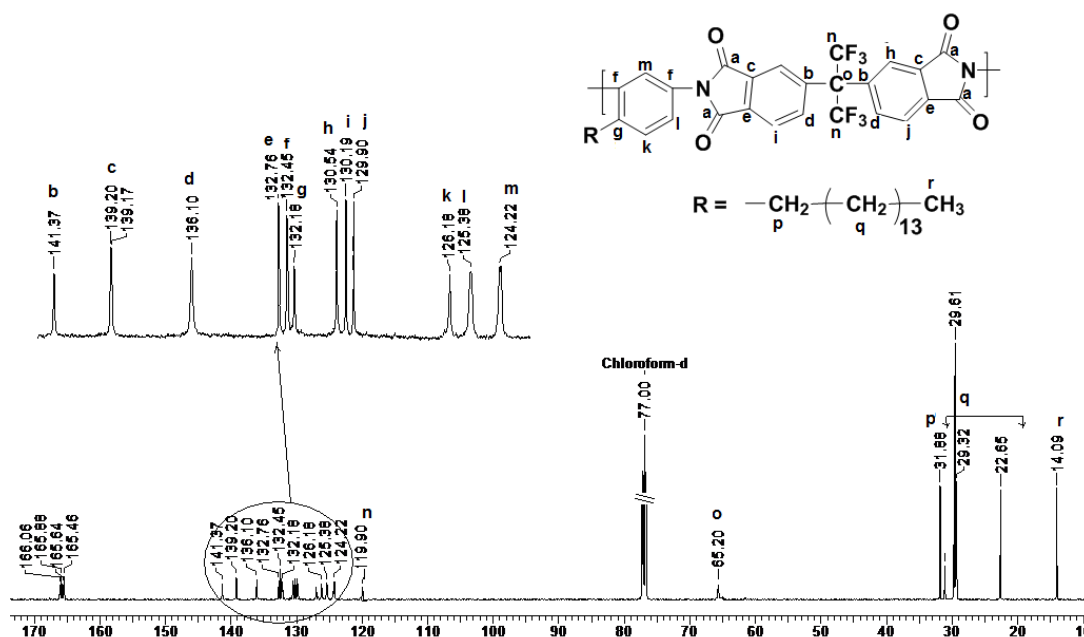
Figure 4.3 ^{13}C-NMR spectrum (CDCl₃) of polyimide derived from 4-pentadecylbenzene-1,3-diamine and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride
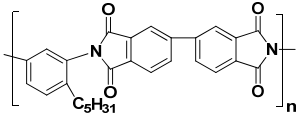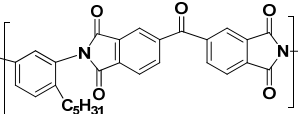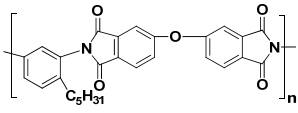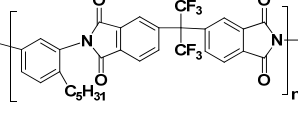
The carbonyl carbons of imide groups were appeared in the range 165.48 -166.06 δ, ppm. The peak assignments in ^{13}C-NMR spectrum were confirmed by the corresponding DEPT spectrum.

4.4.3   Solubility measurements

The solubility of polyimides was tested at 3 % (w/v) concentration in various organic solvents and the data is summarized in **Table 4.2.**

Polyimides were soluble at room temperature in polar solvents such as NMP, DMAc, *m*-cresol as well as in common organic solvent such as CHCl₃. Polyimides without pendent pentadecyl chain, i.e., polyimides obtained by polycondensation of *m*-phenylene diamine and BTDA and BPDA have been reported to be insoluble in organic solvents such as CHCl₃, *m*-cresol, and DMAc[46].

Table 4.2 Solubility data of polyimides derived from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides[a]

Polyimide		CHCl₃	THF	DMAc	NMP	Pyridine	*m*-Cresol	Nitrobenzene	Acetone
					Solvent				
PI-I		++	++	++	++	+	++	++	--
PI-II		++	--	++	+	+	++	+	--
PI-III		++	++	++	++	++	++	++	--
PI-IV		++	++	++	++	++	++	++	++

[a] --, Insoluble; +- partially soluble or swollen; + soluble on heating; ++, soluble at room temperature.

       The improved solubility of polyimides, especially that of polyimides derived from rigid dianhydrides, could be attributed to the cooperative effect of weakening of the intermolecular interactions, and entropy effect due to pentadecyl chain, and constitutional isomerism which results into head-to-head, tail-to-tail, and head-to-tail units in the main chain.[47,48]

4.4.4 X-Ray diffraction studies

       X-Ray diffractograms of polyimides derived from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides are reproduced in **Figure 4.4**.

       X-Ray diffractograms of polyimides exhibited a broad halo at about $2\theta \approx 20^{o}$ in the wide angle region indicating that the polymers are amorphous in nature. In addition to this, polyimides exhibited reflections in the small-angle region at $2\theta \approx 3^{o}$. These peaks are characteristic of typical layered structures.
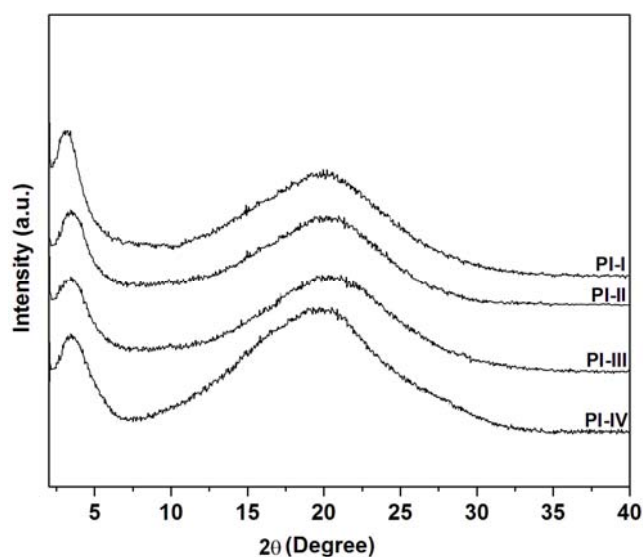
Figure 4.4 X-Ray diffractograms of polyimides derived from 4-pentadecylbenzene-1,3 diamine and aromatic dianhydrides

It is reported in the literature that polymers with flexible long chains strongly tend to form layered crystalline structure in the solid state.[49-53] 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.

4.4.5 Thermal properties

Thermal stability of polyimides was determined by TGA at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. TG curves of polyimides are reproduced in **Figure 4.5**.
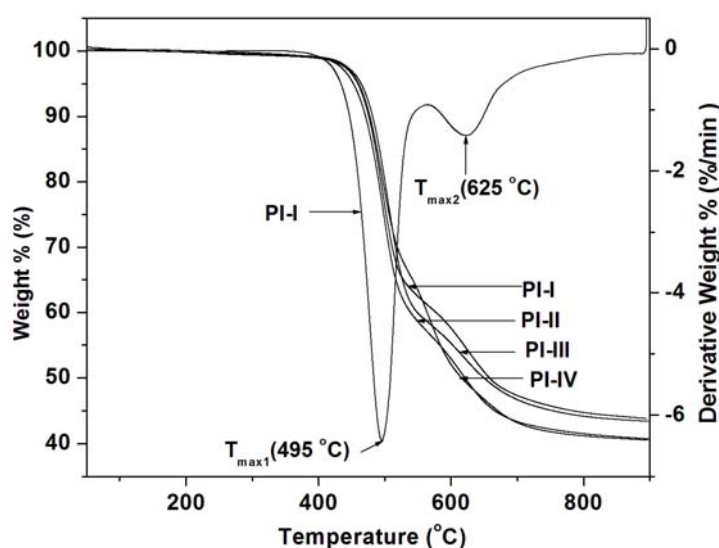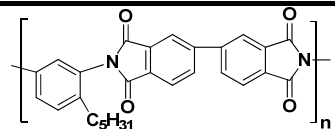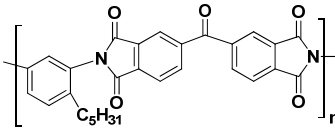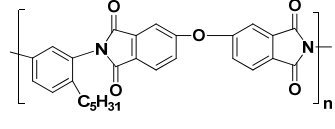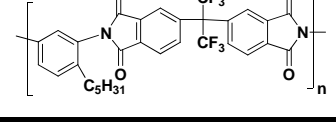
Figure 4.5 TG curves of polyimides derived from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides

Initial decomposition temperature (IDT), temperature at 10 % weight loss (T_{10}) and the weight residues at 900 ^{o}C were determined from thermograms and the data is given in **Table 4.3**.

Table 4.3 Thermal properties and UV-Visible spectral data of polyimides derived from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides

Polyimide	IDT[a] (^{o}C)	T_{10}[b] (^{o}C)	Weight residue at 900°C (%)	T_g (^{o}C)	λ_{max} (nm)[d]
PI-I	460	475	44	206 (330)[e]	324
PI-II	465	470	41	176 (320)[e]	337
PI-III	475	480	44	159 (305)[e]	290
PI-IV	465	480	41	158 (297)[e]	270

a : Initial decomposition temperature, *b* : temperature at which 10% weight loss is observed, *c*: values in the bracket are T_g values of reference polyimides based on *m*-phenylene diamine and corresponding dianhydrides and the values are taken from the literature [46,54], *d*: UV-Visible spectra of polyimides were recorded in CHCl$_3$ solution.

T_{10} values obtained from TG curves were in the range of 470-480 ^{o}C for polyimides indicating their good thermal stability. Differential thermogravimetric analysis (DTG) of polyimides showed two stage weight loss: the first stage was presumably due to decomposition of pendent alkyl groups while the second stage was due to decomposition of polyimide backbone (**Figure 4.5**). The weight residues of polyimides when heated to 900 ^{o}C, in nitrogen were in the range 41-44 %.

DSC curves of polyimides are reproduced in **Figure 4.6** and T_g values obtained from the second heating scans of polyimide samples at a heating rate of 20 ^{o}C/minute are listed in **Table 4.3**.
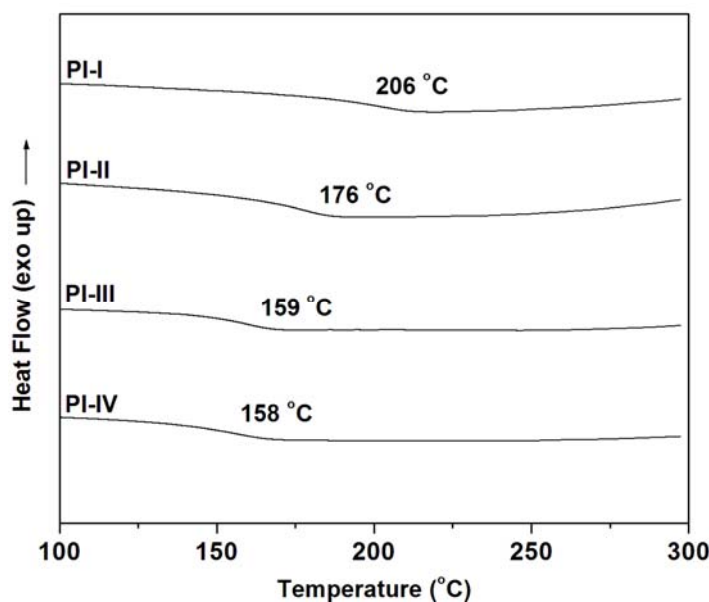
Figure 4.6 DSC curves of polyimides derived from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides

T_g values of polyimides containing pendent pentadecyl chains were in the range 158-206 ^{o}C and these values are significantly lower than those of the corresponding polyimides based on *m*-phenylene diamine which are reported to be in the range 297-330 ^{o}C.[46,54] The drop in T_g is due to introduction of flexible pentadecyl chains along the polymer backbone which decreases the rigidity of the polymer by increasing the number of degrees of freedom available. T_g values of polyimides derived from 4-pentadecylbenzene-1,3-diamine and four aromatic dianhydrides were found to be in the increasing order of 6-FDA $\cong$ ODPA < BTDA < BPDA. This result is attributed to increasing rigidity of the aromatic dianhydride. A large window between glass transition temperature and polymer degradation temperature was observed which gives an opportunity for these polyimides to be melt-processed or compression molded.

4.4.6   UV-Visible properties

The wholly aromatic polyimides strongly absorb visible light because of their aromatic conjugated structure and the intermolecular or intramolecular charge-transfer complex (CTC) formation. The coloration always obstructs their widespread applications for which colorlessness and transparency are of big concern. The colour intensity of polyimides changes from deep to pale depending on the type of anhydride used: BPDA > BTDA > ODPA > 6-FDA, when diamine structure is fixed.[55] The colour intensity of polyimides could also be elucidated from the cut-off wavelength (λ_0) observed in UV-Visible absorption spectra.

UV-Visible absorption spectra of polyimides recorded in CHCl$_3$ solutions (5 x 10^{-3} mol/L) are depicted in **Figure 4.7** and λ_0 values are listed in **Table 4**.
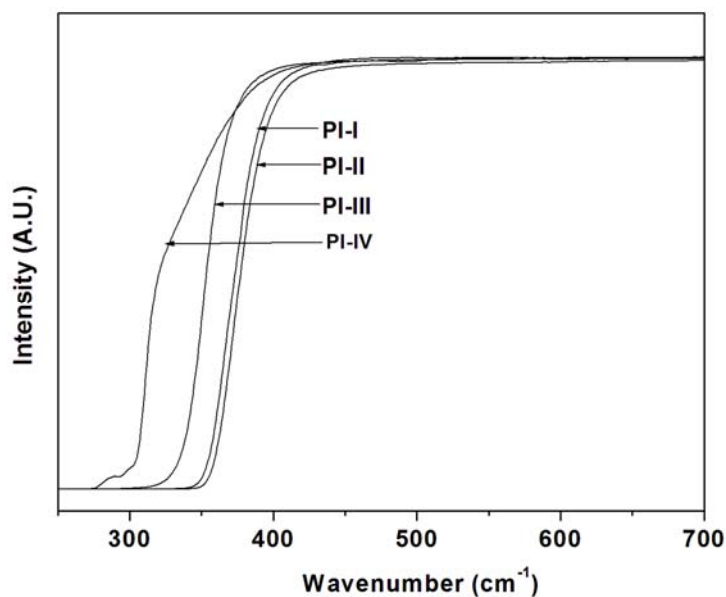
Figure 4.7 UV-Visible spectra of polyimides derived from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides in CHCl₃ solution.

The λ_0 values of polyimides containing pendent pentadecyl chains ranged from 270 to 337 nm, with the lowest λ_0 of 270 nm being that of polyimide based on 6-FDA. The presence of bulky and electron withdrawing hexafluoroisopropylidene groups reduces the intermolecular CTC formation between alternating electron donor (diamine) and electron acceptor (dianhydride) moieties.[56] The lower λ_0 (290 nm) of ODPA-based polyimide compared to that of BPDA- and BTDA-based polyimides could be attributed to the presence of ether-oxygen which functions as a separator linkage and enhances chain mobility, thereby, causing reduction in intermolecular CTC formation.

4.5   Conclusions

1. A series of new polyimides containing pendent pentadecyl chains was synthesized from 4-pentadecylbenzene-1,3-diamine and aromatic dianhydrides by a one-step solution polycondensation in *m*-cresol.

2. Inherent viscosities of polyimides were in the range 0.33-0.67 dL/g indicating formation of medium to reasonably high molecular weight polymers.

3. Polyimides were soluble at room temperature in polar solvents such as NMP, DMAc, *m*-cresol as well as in common organic solvent such as $CHCl_3$. This indicates that the incorporation of pendent flexible pentadecyl chains leads to a significant improvement in solubility of polyimides.

4. Tough, transparent and flexible films could be cast from the solution of polyimides in $CHCl_3$.

5. WAXD patterns showed that polyimides containing pendent 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 polyimides were in the range 470-480 °C indicating the good thermal stability of polymers.

7. DSC analysis showed that the attached pentadecyl side chain induced the depression of T_g (158-206 °C).

8. Overall, internal plasticization effect of the pentadecyl chain was shown to be effective in achieving processable polyimides.

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Chapter 5

Synthesis and Characterization of Polyamides and Poly(azomethine)s Containing Pendent Pentadecyl Chains

Chapter 5a

Synthesis and Characterization of Polyamides Based on 4-Pentadecyl benzene-1,3-diamine

5a.1   Introduction

Aromatic polyamides are attractive high performance polymers due to their high thermal stability and excellent mechanical strength.[1-5] However, their high softening or melting temperatures and poor solubility in organic solvents caused by the high crystallinity and high stiffness of the polymer backbone limits their processability and applications.[6,7] Several approaches have been outlined to improve the solubility and processability of aromatic polyamides with retention of their high thermal stability. These approaches include incorporation of non-coplanar groups in the main chain,[8-11] molecular asymmetry,[12-23] the use of *meta*-oriented monomers,[24,25] flexible linkages,[26-31] and bulky pendent[32-55] or cardo groups.[56-61] These modifications work by breaking chain symmetry and regularity and by destroying hydrogen bonding, generally leading to better solubility and processability.

It is reported that polymers synthesized from monomers having *m,m'*-linkages exhibit improved solubility than corresponding polymers having *p,p'*-linkages [62,63] and 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.

In view of the above, *meta*-oriented asymmetric diamine monomer *viz.*, 4-pentadecylbenzene-1,3-diamine containing a pendent 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 pendent pentadecyl chains and to investigate the effect of the incorporation of pentadecyl chains on the polymer properties such as solubility and thermal behavior. Thus, a series of polyamides was synthesized by solution polycondensation of 4-pentadecylbenzene-1,3-diamine with commercially available diacids, *viz.*, biphenyl-4,4'dicarboxylic acid, 4,4'-oxybisbenzoic acid, terephthalic acid and isophthalic acid.

The synthesized polyamides were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies.

5a.2   Experimental

5a.2.1   Materials

4-Pentadecylbenzene-1,3-diamine (PBDA) was synthesized as described in **Chapter 3**. Biphenyl-4,4'dicarboxylic acid (BDA), 4,4'-oxybisbenzoic acid (OBA), terephthalic acid (TPA) and isophthalic acid (IPA) all received from Sigma-Aldrich, were purified by sublimation under reduced pressure. Triphenyl phosphite (TPP), received from Sigma-Aldrich and 1-methyl-2-pyrrolidinone (NMP) were purified by distillation under reduced pressure. Pyridine (Merck,

India) was purified by distillation over KOH and stored over 4 Å molecular sieves. Anhydrous lithium chloride (Sigma-Aldrich) was dried at 180 $^{\circ}$C for 8 h under reduced pressure. All other chemicals were of CP grade and were used without further purification.

5a.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: $n_{inh} = \dfrac{2.303}{C} x \log \dfrac{t}{t_0}$

where *t* and *t$_0$* are flow times of polymer solution and solvent, respectively and *C* is the concentration of polymer solution.

FT-IR spectra were recorded using polymer films on a GX PerkinElmer FT-IR spectrophotometer.

NMR spectra were recorded on a Bruker NMR spectrophotometer at resonance frequency of 400 MHz for ^{1}H-NMR using pyridine-d$_5$ as a solvent.

The solubility of polymers was determined at 3 wt % concentration in various solvents at room temperature or on heating.

X-Ray diffractograms of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2 °/ minute. Dried polymer films were used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on TGA-TA5000R instrument at a heating rate of 10 °C/min in nitrogen atmosphere.

Differential scanning calorimetric (DSC) analysis was performed on Q10 TA Instrument at a heating rate of 20 $^{\circ}$C/min in nitrogen atmosphere.

5a.3   Synthesis of polyamides

A representative procedure for the synthesis of polyamides is given below:

Into a 50 mL three-necked round bottom flask equipped with a reflux condenser, a nitrogen inlet tube and a magnetic stirring bar were charged NMP (8 mL), 4-pentadecylbenzene-1,3-diamine (0.40 g, 1.25 mmol), biphenyl-4,4'dicarboxylic acid (0.31 g, 1.25 mmol), lithium chloride (0.54 g), triphenyl phosphite (0.7 mL, 2.64 mmol), and pyridine (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. Yield: 0.61 g (92 %).

A similar procedure was followed for the synthesis of other polyamides.

5a.4   Results and discussion

5a.4.1 Synthesis of polyamides

As outlined in **Scheme 5a.1,** a series of new aromatic polyamides was prepared by phosphorylation polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic diacids **(I-IV)** in NMP solution containing lithium chloride using triphenyl phosphite and pyridine as condensing agents.
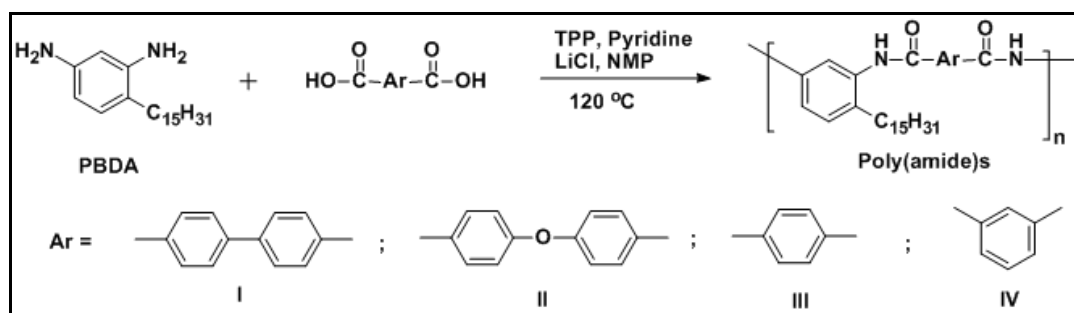
Scheme 5a.1 Synthesis of polyamides from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

The direct polycondensation technique reported by Yamazaki et al is a well accepted and very useful laboratory method for the synthesis of polyamides.[64-66] This method involves the one-pot polycondensation of aromatic diamines with aromatic diacids in the presence of an aryl phosphite such as triphenyl phosphite and an organic base such as pyridine. The addition of inorganic salts such as LiCl improves the solubility of polymer and the maximum attainable molecular weights. The advantage of this method is that it avoids the use of moisture-sensitive diacid chlorides. The polycondensation reactions were carried out at 120 $^{\circ}$C for 8 h. The polymerizations were homogeneous throughout the reaction and afforded viscous polymer solutions. The results of polymerization are summarized in **Table 5a.1**.

Table 5a.1 Synthesis of polyamides from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

	Polyamide	Diamine	Diacid	Yield (%)	η_{inh} (dL/g)^a
PA-I		PBDA	BDA	92	0.56
PA-II		PBDA	OBA	95	0.52
PA-III		PBDA	TPA	94	0.43
PA-IV		PBDA	IPA	96	0.35

a: η_{inh} was measured with 0.5 % (w/v) solution of polyamide in DMAc at 30 ± 0.1 $^{\circ}$C

Inherent viscosities of polyamides were in the range 0.35-0.56 dL/g indicating the formation of medium to reasonably high molecular weight polymers. Tough, transparent and flexible films of polyamides could be cast from their DMAc solutions.

5a.4.2   Structural characterization

The formation of polyamides was confirmed by FT-IR spectroscopy. **Figure 5a.1** depicts FT-IR spectrum of polyamide derived from 4-pentadecylbenzene-1,3-diamine and biphenyl-4,4'dicarboxylic acid
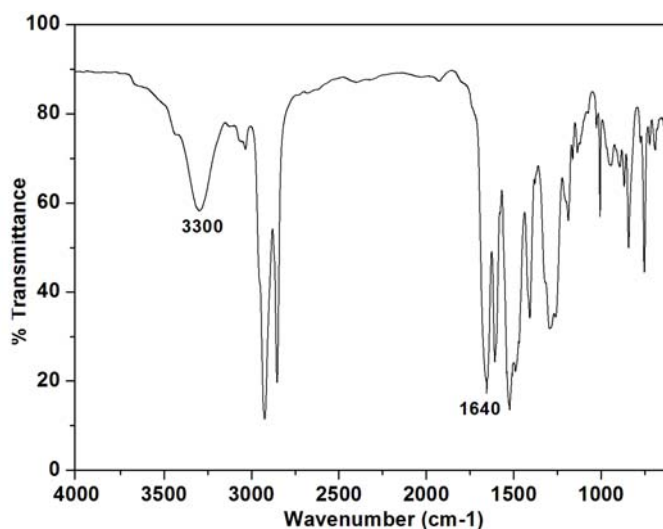
Figure 5a.1 FT-IR spectrum of polyamide (Film) derived from 4-pentadecylbenzene-1,3-diamine and biphenyl-4,4'dicarboxylic acid

Polyamide formation was characterized by the –NH stretching frequency as a broad band around 3300 cm^{-1}. Due to the hydrogen bonding, the C=O stretching vibration band shifted to lower wave number and appeared at 1640 cm^{-1}.

A representative^{1}H-NMR spectrum of polyamide (**PA-III**) derived from 4-pentadecyl benzene-1,3-diamine and terephthalic acid along with assignments and with expansion of aromatic region is shown in **Figure 5a.2**.
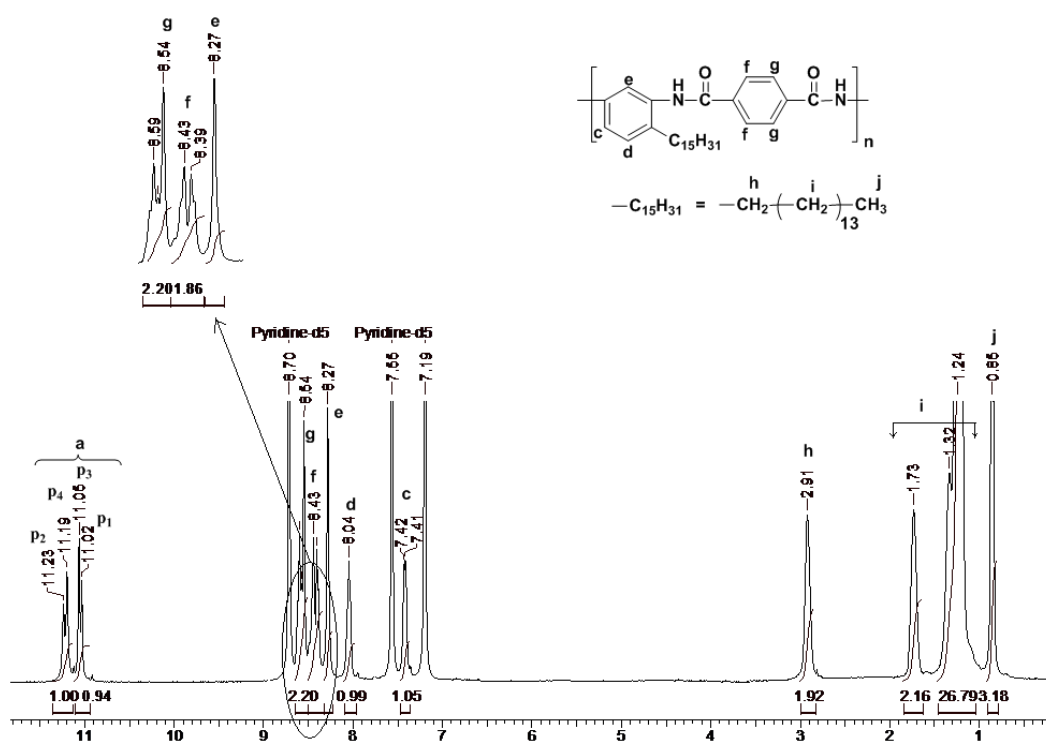
Figure 5a.2 ^{1}H-NMR spectrum of polyamide (Pyridine-d$_5$) derived from 4-pentadecyl benzene-1,3-diamine and terephthalic acid

Four different amidic proton peaks 'a' appeared at 11.23, 11.19, 11.05 and 11.02 δ, ppm. The aromatic protons of the diacid unit appeared in the range 8.39- 8.59 δ, ppm while the aromatic protons of the diamine unit appeared in the range 7.41- 8.27 δ, ppm. The benzylic methylene protons 'h' appeared as a triplet at 2.91 δ, ppm while the other methylene protons 'i' appeared in the range 1.24-1.73 δ, ppm. Methyl group protons 'j' appeared as a triplet at 0.85 δ, ppm. The appearance of four different peaks corresponding to the amide protons indicates the existence of constitutional isomerism resulting from the use of asymmetric diamine monomer (**Figure 5a.3**).
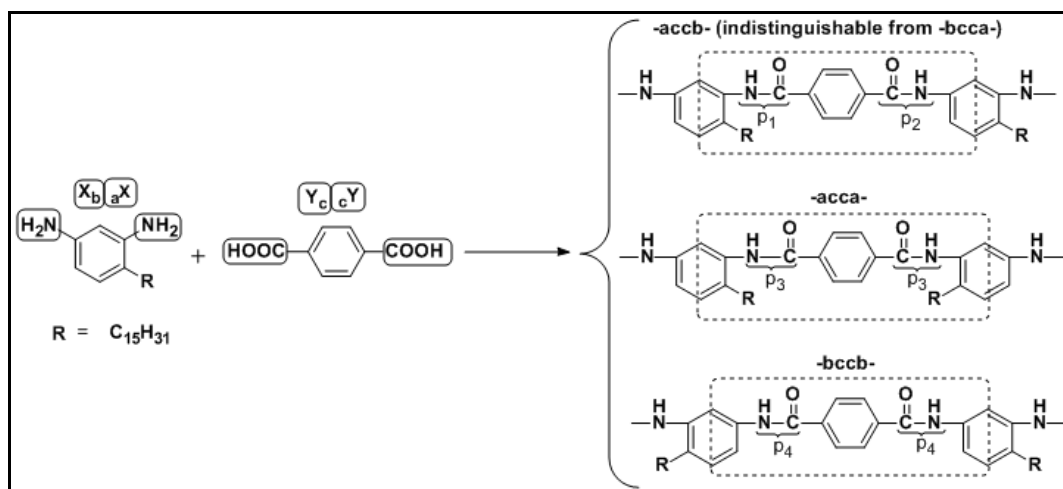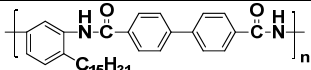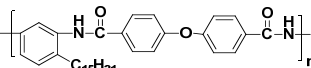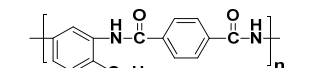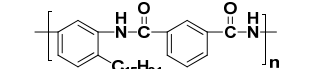
Figure 5a.3 Possible sequences in polyamide chains (PA-III) derived from 4-pentadecyl benzene-1,3-diamine and terephthalic acid

It is reported that when an asymmetric monomer reacts with a symmetric monomer, constitutional isomerism would arise.[14,67-72] Pino and coworkers 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.[73] 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. The appearance of four different amidic proton peaks in the NMR spectra could be attributed to different structural elements -accb- (p_1), -bcca- (p_2), -acca- (p_3), and -bccb- (p_4) (**Figure 5a.3**).

5a.4.3 Solubility measurements

Solubility of polyamides was tested in various organic solvents at 3 wt % concentration and data is summarized in **Table 5a.2.**

Table 5a.2 Solubility data of polyamides derived from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

Polyamide		Solvent									
		DMAc	NMP	DMF	DMSO	*m*-Cresol	CHCl$_3$	THF	Pyridine	Nitro benzene	Acetone
PA-I		+	+	+	+-	+	--	--	+	+	--
PA-II		++	++	++	+-	++	--	--	++	+	--
PA-III		++	+	+	+-	++	--	--	++	+	--
PA-IV		++	++	++	+-	++	+-	+-	++	+	--

++ : soluble at room temperature; + : soluble on heating; +- : partially soluble on heating; -- : insoluble

Polyamides were soluble in DMAc, NMP, *m*-cresol and pyridine either at room temperature or upon heating whereas reference polyamides derived from rigid diacids like biphenyl-4,4'dicarboxylic acid or terephthalic acid with 1,3-phenylene diamine were reported to be insoluble in the above solvents.[74-76] The improved solubility of polyamides containing pendent pentadecyl chains compared with that of reference polymers could be attributed to the presence of pentadecyl chains. The pendent pentadecyl chains along the polymer backbone greatly reduce strong molecular interactions of stiff chain aromatic polymers producing an effective chain separation effect which prevents their tight chain packing and increases the free volume. The

disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvent which leads to improvement in solubility.

5a.4.4 X-Ray diffraction studies

X-Ray diffractograms of polyamides derived from 4-pentadecylbenzene-1,3-diamine and aromatic diacids are shown in **Figure 5a.4**.
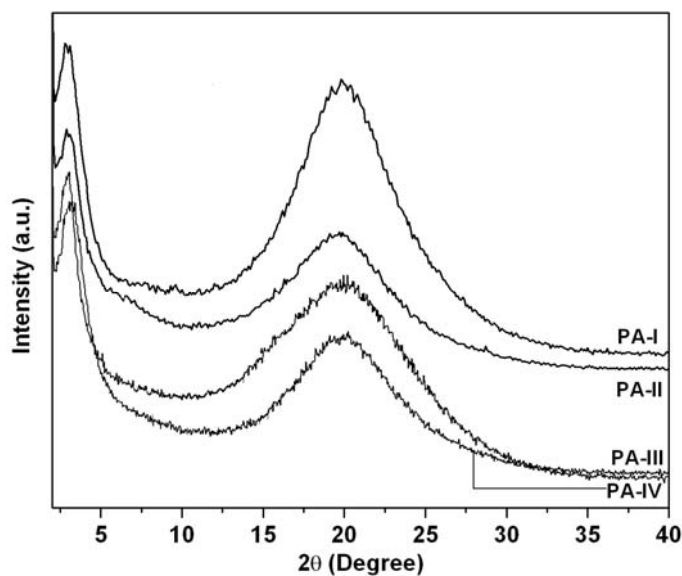
Figure 5a.4 X-Ray diffraction patterns of polyamides derived from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

X-Ray diffractograms of all polymers exhibited a broad halo in the wide angle region (at about $2\theta \approx 20^o$) indicating that the polymers were amorphous. This result could be explained in terms of the presence of the pendent pentadecyl chain in the polymer backbone which hindered packing of the polymer chains and decreased the intermolecular forces, subsequently causing a decrease in crystallinity. In addition to this, in the small angle region ($2\theta \approx 3^o$) presence of sharp peaks were observed. These peaks are characteristic of typical layered structures. It is reported in the literature that polymers with flexible pendent chains strongly tend to form layered crystalline structure in the solid state.[77,78]

5a.4.5 Thermal properties

Thermal stability of polyamides was determined by thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. TG curves of polyamides are shown in **Figure 5a.5**.
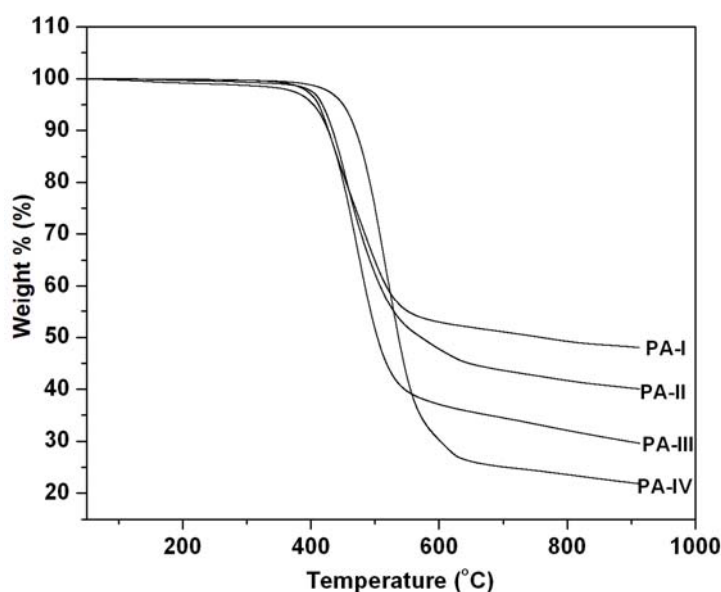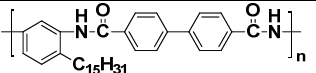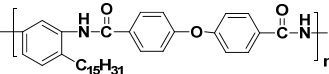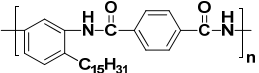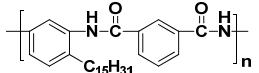
Figure 5a.5 TG curves of polyamides derived from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

Initial decomposition temperature (IDT), temperature at 10 % weight loss (T_{10}) and the weight residues at 900 °C were determined from thermograms and the data is given in **Table 5a.3**.

Table 5a.3 Thermal properties of polyamides derived from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

Polyamide		$T_{10}{}^b$ (°C)	T_g (°C)^c	Weight residue at 900°C (%)
PA-I		450 (531)^d	215 (N.D)^d	50
PA-II		435 (510)^d	169 (231)^d	40
PA-III		460 (524)^d	206 (255)^d	30
PA-IV		430	189 (250)^d	20

a : Initial decomposition temperature; *b* : temperature at which 10 % weight loss is observed; *c: g*lass transition temperature (T_g) measured on DSC at a heating rate of 20 °C/min in N_2; *d*: 1,3-phenylene diamine derived polyamides.[74,75]

T_{10} values obtained from TG curves for polyamides were in the range 430-460 °C indicating their good thermal stability. However, these polymers containing pendent pentadecyl chains were inferior in thermal stability compared to the reference polymers based on 1,3-

phenylene diamine (**Table 5a.3**) which could obviously be attributed to the presence of aliphatic side chains.[74,75] The weight residue of polyamides when heated to 900 °C in nitrogen was in the range 20-50 %. 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 20 °C / minute. DSC curves are reproduced in **Figure 5a.6** and T_g values are given in **Table 5a.3**.
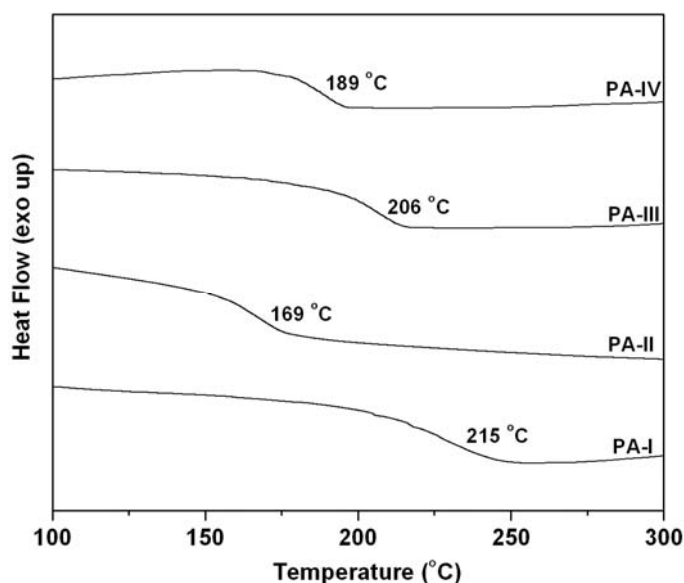
Figure 5a.6 DSC curves of polyamides derived from 4-pentadecylbenzene-1,3-diamine and aromatic diacids

T_g of polyamides containing pendent pentadecyl chains were in the range 169-215 °C. The increasing order of T_g corresponds to an increase in the rigidity of the diacid. For example, **PA-I** derived from rigid biphenyl-4,4'-dicarboxylic acid exhibited highest T_g value (215 °C) among the series of polyamides. Polyamides containing pendent pentadecyl chains showed lower glass transition temperature in comparison with those synthesized from 1,3-phenylene diamine and corresponding diacids. For example, polyamide synthesized from 1,3-phenylene diamine and 4,4'-oxybisbenzoic acid is reported to possess a T_g at 232 °C,[74] whereas when the diamine was replaced by 4-pentadecylbenzene-1,3-diamine a T_g was observed at 169 °C. Similarly, literature data for Nomex (polyamide made from 1,3-phenylene diamine and isophthalic acid) reported a T_g of 275 °C, whereas **PA-IV** showed T_g of 189 °C.[79] This result is reasonable and can be attributed to the fact that pendent 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 in T_g and decomposition temperature of polyamides offers a broad processing window.

5a.5   Conclusions

1. A series of new polyamides containing pendent pentadecyl chains was synthesized by the direct polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic diacids.

2. Inherent viscosities of polyamides were in the range 0.35-0.56 dL/g indicating formation of medium to reasonably high molecular weight polymers.

3. Polyamides were found to be soluble in DMF, DMAc, NMP, pyridine and *m*-cresol at room temperature or upon heating. This indicates that the incorporation of pendent flexible pentadecyl chains leads to a significant improvement in solubility of polyamides.

4. Tough, transparent and flexible films of the polyamides could be cast from DMAc solution.

5. Wide angle X-ray diffraction patterns indicated that polyamides containing pendent pentadecyl chains were amorphous in nature. The formation of layered structure was observed due to the packing of pentadecyl chains.

6. T_{10} values for polyamides were in the range 430-460 °C indicating good thermal stability of polyamides.

7. T_g values of polyamides were in the range 169-215 ^{o}C. The depression in T_g values of polyamides could be attributed to the presence of pendent pentadecyl chains.

8. A large difference in T_g and decomposition temperature of polyamides offers a broad processing window.

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Chapter 5b

Synthesis and Characterization of Poly(azomethine)s Based on 4-Pentadecyl benzene-1,3-diamine

5b.1   Introduction

Poly(azomethine)s known as poly(imine)s or Schiff base polymers are isolelectronic to their carbon analogues- poly(*p*-phenylene vinylene)s, making them suitable alternatives to conventional conjugated materials and are promising materials in optoelectronic and photonic applications.[1-3] Poly(azomethine)s possess good thermal stability, mechanical strength, nonlinear optical properties, ability to form metal chelates, and semiconducting properties.[4-9] The interesting properties of poly(azomethine)s are due to the presence of conjugated backbone and imine sites.[10] The imine group (-HC=N-) with a lone pair of electrons in the backbone can form intra- or inter-molecular interactions such as hydrogen bonding with other groups and has the capability for protonation and complexation with metal ions, which has a great effect on their chemical and physical properties.[11-16] Many of these polymers form mesophases on heating, but the high melting points and limited solubility due to their rigid rod-like chain structure make both their characterization and processing difficult. Several modifications of the chemical structure have been used in order to lower the transition temperature and to improve the solubility of aromatic poly(azomethine)s. These approaches include: introduction of structural irregularities such as kinks, bents or crank-shaft units,[17-20] bulky pendent groups,[21-32] flexibilizing moieties,[33-39] asymmetric substitution,[40,41] etc. An introduction of pendent alkyl chains along the polymer backbone is another approach to obtain soluble poly(azomethine)s.[42-45] The flexible side chains are thought to act as a bound solvent for the rigid polymeric backbone.[46]

In order to obtain processable poly(azomethine)s, a new diamine *viz.*, 4-pentadecylbenzene-1,3-diamine containing a pendent pentadecyl chain was considered as a useful monomer.

The objective of the present work was to synthesize a series of poly(azomethine)s containing pendent pentadecyl chains and to investigate the effect of the presence of pentadecyl chains on the polymer properties such as solubility and thermal behavior. Thus, a series of poly(azomethine)s was synthesized by solution polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic dialdehydes, *viz.*, terephthaldehyde, isophthaldehyde and a 50:50 mol % mixture of terephthaldehyde, and isophthaldehyde. The synthesized poly(azomethine)s were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-Vis and photoluminescence spectroscopy.

5b.2   Experimental

5b.2.1 Materials

4-Pentadecylbenzene-1,3-diamine (PBDA) was synthesized as described in **Chapter 3**. Terephthaldehyde (TPAld) and isophthaldehyde (IPAld) received from Aldrich, USA, were

sublimed before use. Hexamethylphosphoramide (HMPA) received from Aldrich, USA, was used as received. Anhydrous lithium chloride (Sigma-Aldrich) was dried at 180 $^{\circ}$C for 8 h under reduced pressure. 1-Methyl-2-pyrrolidinone (NMP) received from Aldrich, USA, was purified by distillation under reduced pressure.

5b.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in chloroform at 30 ± 0.1 $^{\circ}$C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \dfrac{2.303}{C} x \log \dfrac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

FT-IR spectra were recorded using polymer films on a GX PerkinElmer FT-IR spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker NMR spectrophotometer (400 MHz) in CDCl$_3$ solution at room temperature.

The solubility of polymers was determined at 3 wt % concentration in various solvents at room temperature or on heating.

X-Ray diffractograms of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films were used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on TGA-TA5000R instrument at a heating rate of 10 °C/min in nitrogen atmosphere.

Differential scanning calorimetric (DSC) analysis was performed on Q10 TA Instrument at a heating rate of 20 $^{\circ}$C/min in nitrogen atmosphere.

UV-Vis absorption spectra were recorded on Perkin Elmer spectrophotometer using 10 mm quartz cells and the photoluminescence spectra were recorded in chloroform solutions on Cary Eclipse VARIAN Fluorescence Spectrophotometer.

5b.3   Synthesis of poly(azomethine)s

A representative procedure for synthesis of poly(azomethine)s 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-pentadecylbenzene-1,3-diamine (0.50 g, 1.57 mmol), a mixture of NMP (3 mL): HMPA (3 mL) and lithium chloride (0.15 g) under nitrogen atmosphere. Terephthaldehyde (0.21 g, 1.57 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 hot water and then with methanol. The polymer was dried at 50 ^{o}C for 12 h under reduced pressure. Yield: 0.62 g (95 %).

A similar procedure was followed for the synthesis of other poly(azomethine)s.

5b.4   Results and discussion

5b.4.1 Synthesis of poly(azomethine)s

Aromatic poly(azomethine)s are usually prepared by polycondensation of an aromatic dialdehyde and a diamine in an appropriate solvent such as DMAc, DMF, HMPA, NMP, ethanol or *m*-cresol.[47,48] The reaction between diamine and dialdehyde is rapid at room temperature. However, the preparation of high molecular weight poly(azomethine)s is complicated by precipitation of the polymer during the polymerization process.[49] To improve the solubility of polymer during the polymerization process, use of different solvents and solvent mixtures as reaction media was explored.[50,51]
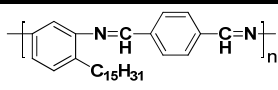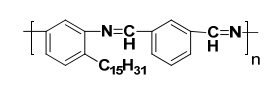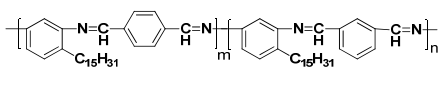
As outlined in **Scheme 5a.1,** a new series of aromatic poly(azomethine)s was prepared by polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic dialdehydes in a mixture of NMP: HMPA (1:1, v/v) containing lithium chloride.
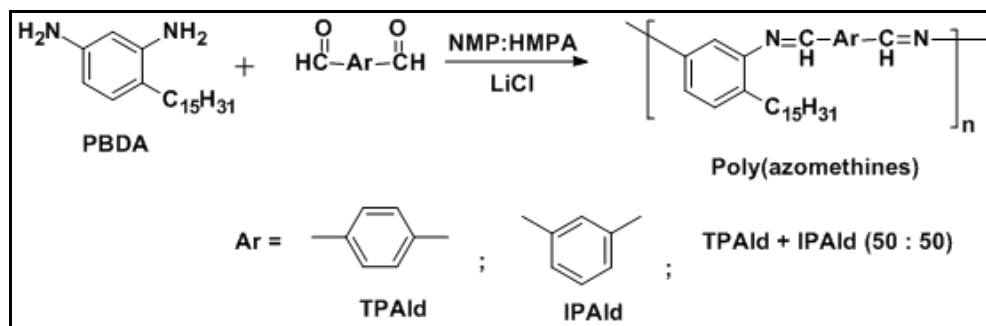
Scheme 5b.1 Synthesis of poly(azomethine)s from 4-pentadecylbenzene-1,3-diamine and aromatic dialdehydes

Lithium chloride was used to absorb water formed during the polycondensation. The polymerization reactions were homogeneous throughout. The results of polymerization are summarized in **Table 5b.1**.

Table 5b.1 Synthesis of poly(azomethine)s from 4-pentadecylbenzene-1,3-diamine and aromatic dialdehydes

Poly(azomethine)		Diamine	Dialdehyde	Yield (%)	η_{inh} (dL/g)[a]
PAZ-I		PBDA	TPAld	95	0.38
PAZ-II		PBDA	IPAld	92	0.36
PAZ-III		PBDA	TPAld:IPAld (50: 50)	94	0.33

a: η_{inh} was measured with 0.5% (w/v) solution of polyamide in CHCL$_3$ at 30 ± 0.1 ^{o}C

Inherent viscosities of poly(azomethine)s were in the range 0.33-0.38 dL/g indicating the formation of medium molecular weight polymers. Transparent, flexible and stretchable films of poly(azomethine)s could be cast from their CHCl$_3$ solutions.

5b.4.2 Structural characterization

The formation of poly(azomethine)s was confirmed by FT-IR and ^{1}H-NMR spectroscopy. A representative FT-IR spectrum of poly(azomethine) derived from 4-pentadecylbenzene-1,3-diamine and terephthaldehyde is reproduced in **Figure 5b.1**. The band at 1630 cm^{-1} corresponds to azomethine or imine linkage (-HC=N-).
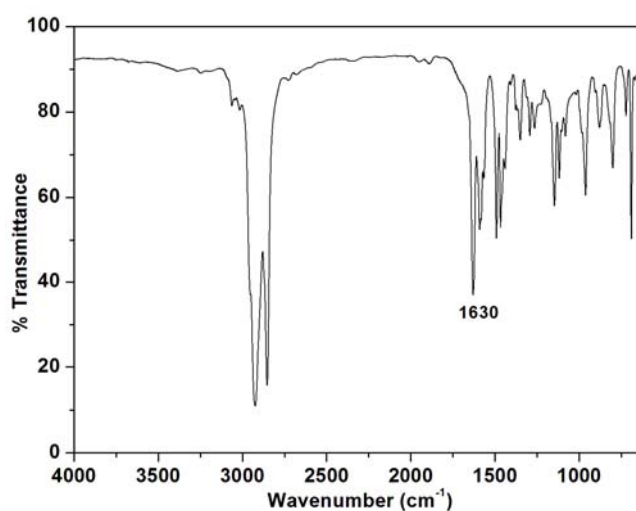
Figure 5b.1 FT-IR spectrum (Film) of poly(azomethine) derived from 4-pentadecylbenzene-1,3- diamine and terephthalaldehyde

A representative ^{1}H-NMR spectrum of poly(azomethine) (**PAZ-I**) in CDCl$_3$, derived from 4-pentadecylbenzene-1,3-diamine and terephthaldehyde along with assignments is reproduced in **Figure 5b.2**.
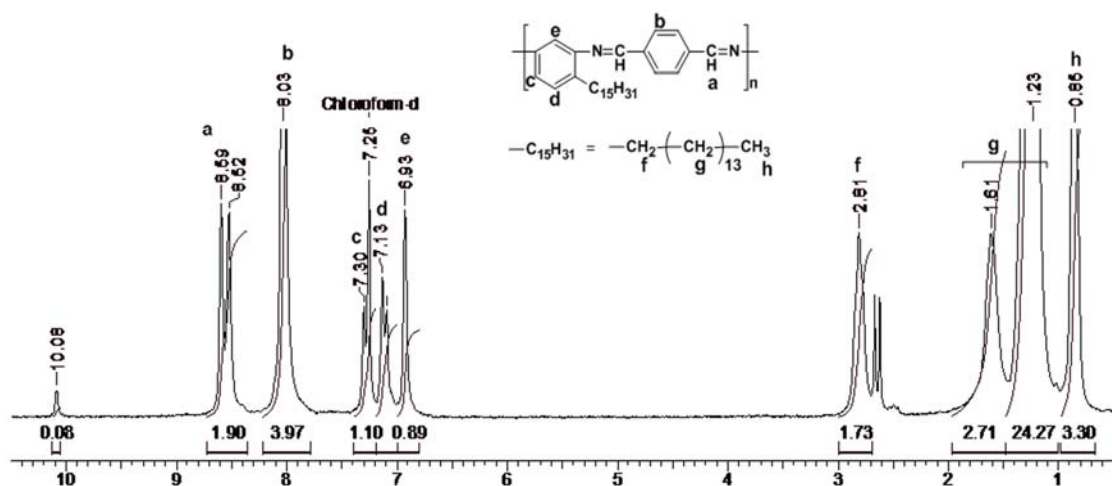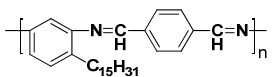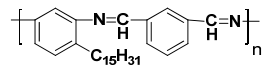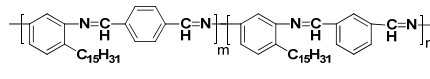
Figure 5b.2 ^{1}H-NMR spectrum of poly(azomethine) (CDCl₃) derived from 4-pentadecyl benzene-1,3-diamine and terephthalaldehyde

Two separate singlets of azomethine protons 'a' were observed at 8.59 and 8.52 δ, ppm, indicating the presence of constitutional isomerism. In the ^{1}H-NMR spectrum of **PAZ-I**, theoretically one would expect four signals corresponding to azomethine protons due to constitutional isomerism. However, 400 MHz NMR spectrum of **PAZ-I** displayed only two distinct singlets at 8.59 and 8.52 δ, ppm for imine proton. Similar observations have been reported previously in case of poly(azomethine)s containing pendent pentadecyl chains.[41] The four aromatic protons of aromatic dialdehyde moiety 'b' appeared as a broad singlet at 8.03 δ, ppm due to magnetic equivalence. The aromatic protons of diamine moiety 'c' and 'd' appeared as doublets at 7.30 and 7.13 δ, ppm, respectively. The aromatic proton 'e' exhibited a singlet at 6.93 δ, ppm. The low intensity signal positioned at 10.08 δ, ppm corresponds to the aldehydic proton (chain-end - CHO). The benzylic –CH₂ 'f' appeared as a triplet at 2.81 δ, ppm. The methylene protons 'g' appeared in the range 1.23 - 1.61 δ, ppm. Methyl group protons 'h' appeared as a triplet at 0.85 δ, ppm.

5b.4.3 Solubility measurements

Solubility of poly(azomethine)s was tested in various organic solvents at 3 wt % concentration and data is summarized in **Table 5b.2.**

Table 5b.2 Solubility data of poly(azomethine)s derived from 4-pentadecylbenzene- 1,3-diamine and aromatic dialdehydes

Poly(azomethine)		Solvent								
		NMP	DMF	DMSO	*m*-Cresol	CHCl$_3$	THF	Pyridine	Nitrobenzene	Acetone
PAZ-I		+	+-	+-	++	++	+-	+-	+-	--
PAZ-II		+	--	+-	++	++	++	++	--	--
PAZ-III		+	+-	+-	++	++	++	++	--	--

++ : soluble at room temperature; + : soluble on heating; +- : partially soluble on heating; -- : insoluble

Poly(azomethine)s containing pendent pentadecyl chains were soluble in CHCl$_3$ and *m*-cresol at room temperature whereas reference poly(azomethine)s derived from 1,3-phenylene diamine dissolved only sparingly in concentrated sulphuric acid or formic acid and are reported to be insoluble in common organic solvents.[52,53] Poly(azomethine) containing pendent pentadecyl chains derived from isophthalaldehyde and 50:50 mol % mixture of isophthaldehyde and terephthaldehyde were soluble in THF and pyridine at room temperature. The enhanced solubility of poly(azomethine)s containing pendent pentadecyl chains could be attributed to the long alkyl chain which disrupted the packing of polymer chains as well as provided additional 'handle' for interaction with solvents.

5b.4.4 X-Ray diffraction studies

X-Ray diffractograms of poly(azomethine)s derived from 4-pentadecylbenzene-1,3-diamine and aromatic dialdehydes are reproduced in **Figure 5b.3**.

X-Ray diffractograms of poly(azomethine)s exhibited a broad halo in the wide angle region at about 2θ ≈ 20° indicating that the polymers were amorphous. In addition to this, poly(azomethine)s exhibited reflections in the small-angle region at 2θ ≈ 3°. These peaks are characteristic of typical layered structures formed due to the incorporation of long pentadecyl chains along the polymer backbone.
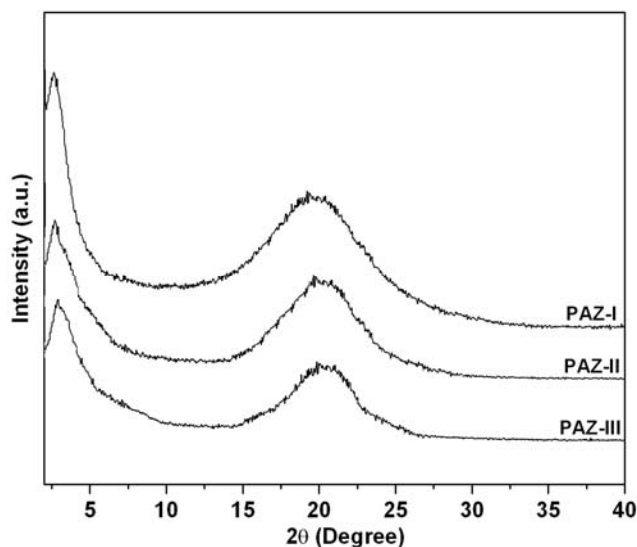
Figure 5b.3 X-Ray diffractograms of poly(azomethine)s derived from 4-pentadecylbenzene-1,3-diamine and aromatic dialdehydes

It is reported in the literature that rigid-rod polymers with flexible long side chains strongly tend to form layered crystalline structure in the solid state.[36,43,54,55]

5b.4.5 Thermal properties

Thermal stability of poly(azomethine)s was determined by thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. TG curves of poly(azomethine)s are shown in **Figure 5b.4**.
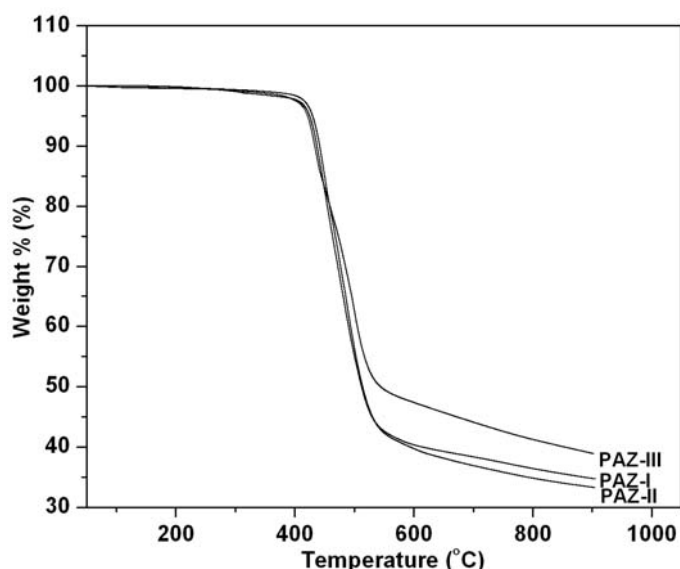
Figure 5b.4 TG curves of poly(azomethine)s derived from 4-pentadecylbenzene-1,3-diamine and aromatic dialdehydes

Initial decomposition temperature (IDT), temperature at 10 % weight loss (T_{10}) and the weight residues at 900 ^{o}C were determined from thermograms and the data is given in **Table 5b.3**.

Table 5b.3 Thermal properties of poly(azomethine)s derived from 4- pentadecylbenzene-1,3-diamine and aromatic dialdehydes

Poly(azomethine)		IDT[a] (^{o}C)	T_{10}[b] (^{o}C)	T_g (^{o}C)[c]	Weight residue at 900°C (%)
PAZ-I		430	440	55[d]	35
PAZ-II		420	440	16	35
PAZ-III		410	425	45	40

a : Initial decomposition temperature; *b* : temperature at which 10 % weight loss was observed; *c: g*lass transition temperature (T_g) measured on DSC at a heating rate of 20 ^{o}C/min in N_2; *d*: Corresponding reference poly(azomethine) had melting transition at 400 ^{o}C.[49]

T_{10} values obtained from TG curves for poly(azomethine)s were in the range 425-440 °C indicating their good thermal stability. The weight residue of poly(azomethine)s when heated to 900 °C in nitrogen was in the range 35-40 %.

Glass transition (T_g) temperature of the poly(azomethine)s was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of poly(azomethine) samples at a heating rate of 20 ^{o}C / minute. DSC curves are reproduced in **Figure 5b.5** and T_g values are given in **Table 5b.3**.
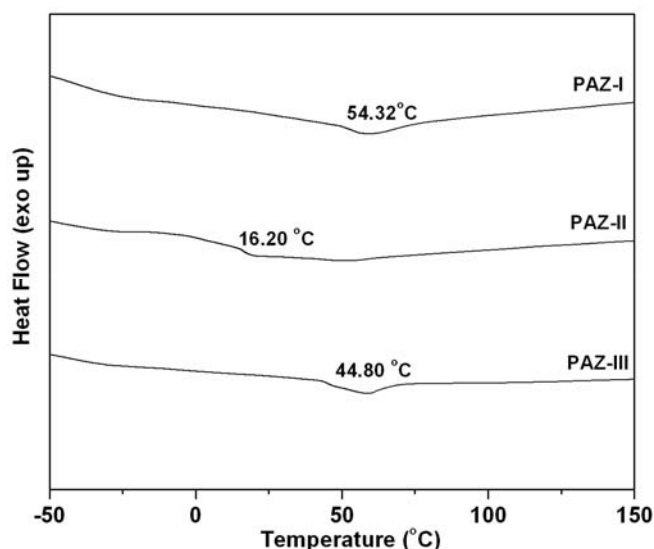
Figure 5b.5 DSC curves of poly(azomethine)s derived from 4-pentadecylbenzene-1,3-diamine and aromatic dialdehydes

It is interesting to note that in contrast with the fact that poly(azomethine)s are high T_g materials, the polymers synthesized in the present study exhibited glass transitions in the range 16-55 ^{o}C (**Table 5b.3**). Poly(azomethine) derived from 1,3-phenylene diamine and terephthaldehyde is reported to possess melting transition above 400 ^{o}C[49]. The large depression

in T_g values resulted from the presence of pendent pentadecyl chains. The flexible pentadecyl side-chains are acting as a bound solvent or 'internal plasticizer' for the polymer backbone. In 'internal plasticization', the plasticizer is chemically attached (grafting) to or incorporated in the polymer backbone (copolymerization) or by use of a monomer (with pentadecyl chain attached as in the present case) and it promotes segmental mobility by reducing interchain interactions. It is reported that the introduction of flexible side groups onto the polymer backbone brings about lowering of the glass transition temperature.[56] The presence of pendent pentadecyl chains along the polymer backbone is expected to disrupt intermolecular interactions which increases the segmental motion and allow the polymer backbone more freedom for flow during processing.

The increasing order of T_g corresponds to an increase in the rigidity of the dialdehyde monomer. **PAZ-I** had the highest T_g (55 $^{\circ}$C) among the series of poly(azomethine)s due to the rigid 1,4-phenylene linkages present in terephthaldehyde-based poly(azomethine)s.

5b.4.6 UV and photoluminescence study of poly(azomethine)s

The UV-Vis absorption and photoluminescence spectra of poly(azomethine)s were investigated in dilute solutions (10^{-5} mol/l) in $CHCl_3$. The UV-Vis absorption spectra of poly(azomethine)s were characterized by two bands (**Figure 5b.6**)
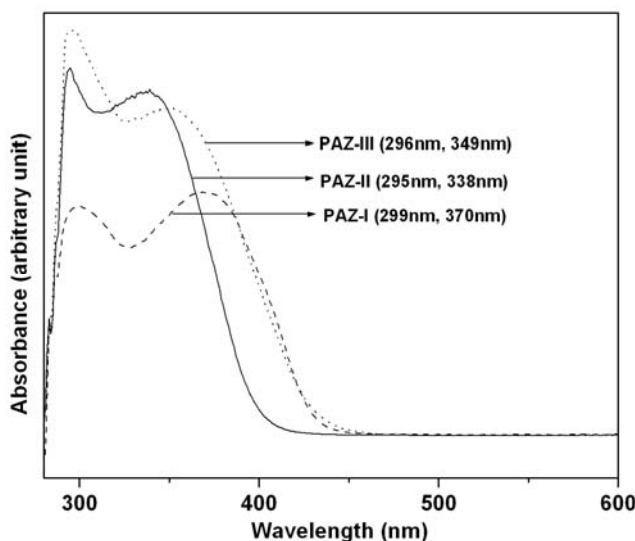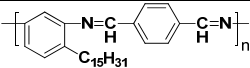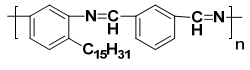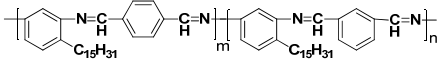
Figure 5b.6 UV absorption spectra of poly(azomethine)s containing pendent pentadecyl chains

For poly(azomethine)s, the absorption band in the range 295-299 nm was assigned to the π-π^* transition in the aromatic rings, while the absorption band in the range 338-370 nm was due to the π-π^* transition in the conjugated chain (**Table 5b.3**).

Table 5b.4 Photophysical properties of poly(azomethine)s containing pendent pentadecyl chains

Poly(azomethine)		$\lambda_{abs'max}$ (nm)	Emission peaks (nm)	E_g^a
PAZ-I		370	410, 435, 475	2.82
PAZ-II		338	410, 435, 475	3.10
PAZ-III		349	410, 435, 475	2.86

[a] HOMO-LUMO gap measured according to the maximum of the UV absorption.

Figure 5b.7 depicts the fluorescence spectra of poly(azomethine)s containing pendent pentadecyl chains.
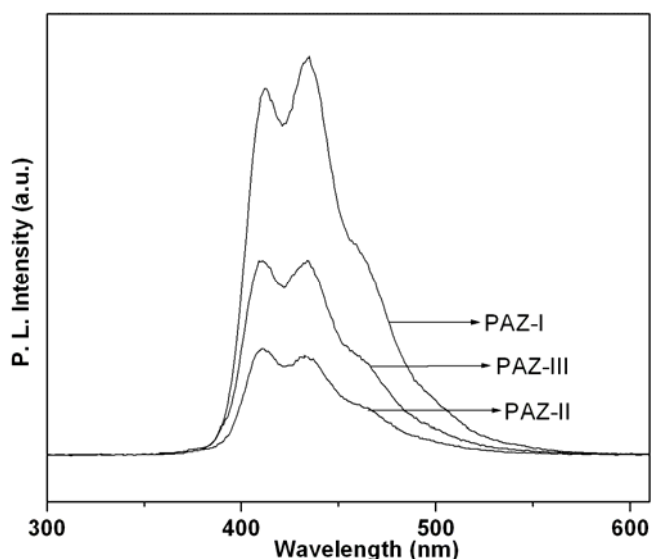
Figure 5b.7 Fluorescence spectra of poly(azomethine)s containing pendent pentadecyl chains

All poly(azomethine)s showed emission peaks at 410, 435 and 475 nm when they were excited at their λ_{max}. Optical band gap values (E_g) were calculated from the onset of UV-Vis absorption band and they were found to be in the range 2.82-3.10 eV (**Table 5b.3**). This result indicates their potential application in photovoltaic devices.

5b.5   Conclusions

1. Poly(azomethine)s containing pendent pentadecyl chains were synthesized by the polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic dialdehydes. Inherent viscosities of poly(azomethine)s were in the range 0.33-0.38 dL/g indicating formation of medium molecular weight polymers.

2. Poly(azomethine)s containing pendent pentadecyl chains were found to be soluble in $CHCl_3$, *m*-cresol, THF and pyridine at room temperature or upon heating. Transparent, flexible and stretchable films of the poly(azomethine)s could be cast from $CHCl_3$ solution.

3. Wide angle X-ray diffraction patterns indicated that poly(azomethine)s containing pendent 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 poly(azomethine)s were in the range 425-440 °C indicating good thermal stability.

5. T_g values of poly(azomethine)s were in the range 16-55 °C. A large difference in T_g and decomposition temperature of poly(azomethine)s offers a broad processing window.

6. Poly(azomethine)s were characterized by optical band gap values (E_g) and they were found to be in the range 2.82-3.10 eV, which indicates their potential application in photovoltaic devices.

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Chapter 6

Synthesis and Characterization of Poly(amideimide)s Containing Pendent Pentadecyl Chains

6.1   Introduction

Poly(amide-imide) (PAI) is one of the most successful classes of copolyimides which has the property advantages of both polyamides and polyimides and thus possesses thermal stability balanced with processability.[1-11] Poly(amideimide)s are generally synthesized by trimellitic anhydride (TMA) route, from an amide containing monomer or from an imide containing monomer.[12-17] To further improve the processability of poly(amideimide)s, several strategies have been adapted in the last few decades, such as incorporation of thermally stable but flexible[18-26] or asymmetric linkages in the backbone,[27-29] introduction of large polar / non-polar substituent or bulky pendent groups along the polymer backbone,[30-41] etc. All these modifications decrease the rigidity of the polymer backbone and inhibit packing, thus reducing the interchain interactions leading to improved processability. Isomeric structures also distort linearity of the chain and increase the interchain distance which lowers the energy necessary for rotation resulting into the lowering of glass transition temperature.[42,43] For example, going from the all *para*-structure of Kevalar to *meta*-linked Nomex, solubility improves along with decrease in the melting transition (from 530 °C to 435 °C).[44]

In view of the above, *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) **I** (*para*-linked) and *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-aminobenzamide) **II** (*meta*-linked), containing preformed amide linkages and pentadecyl chains were considered as useful monomers for the synthesis of processable poly(amideimide)s.

The objective of the present work was to synthesize poly(amideimide)s containing pendent pentadecyl chains based on **I** and **II** and aromatic dianhydrides, *viz.*, pyromellitic dianhydride, 4,4'-biphenyltetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride. As a reference, a series of aromatic poly(amideimide)s were synthesized by polycondensation of *N,N'*-(1,3-phenylene)bis(4-aminobenzamide) (**Ref I**) and *N,N'*-(1,3-phenylene)bis(3-aminobenzamide) (**Ref II**) with the same aromatic dianhydrides. The synthesized poly(amideimide)s were characterized by inherent viscosity measurements, solubility tests, IR and NMR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies. The thermal stability and solubility properties of poly(amideimide)s containing pendent pentadecyl chains were studied and compared with that of reference poly(amideimide)s.

6.2   Experimental

6.2.1   Materials

N,N'-(4-Pentadecyl-1,3-phenylene)bis(4-aminobenzamide) (PDP-4AB) (**I**) and *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-aminobenzamide)   (PDP-3AB) (**II**) were synthesized as described in **Chapter 3**. Two reference diamines, *viz.*, *N,N'*-(1,3-phenylene)bis(4-

aminobenzamide) (**Ref I**) and *N,N'*-(1,3-phenylene)bis(3-aminobenzamide) (**Ref II**) were synthesized as per the procedure reported in literature by condensing *m*-PDA with 4-nitro benzoyl chloride and 3-nitro benzoyl chloride, respectively, followed by reduction of the dinitro derivatives.[45,46] The dianhydrides, benzene-1,2,4,5-tetracarboxylic dianhydride or pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA), 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.[47]

6.2.2   Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in DMAc at 30 ± 0.1 °C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \dfrac{2.303}{C} x \log \dfrac{t}{t_0}$

where *t* and t_0 are flow times of polymer solution and solvent, respectively and *C* is the concentration of polymer solution.

FT-IR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer at a resonance frequency of 400 MHz in DMSO-d$_6$.

The solubility of poly(amideimide)s was determined at 3 wt % concentration in various solvents at room temperature or on heating.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 10 °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 20 °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 film or powder was used for X-ray measurements.

6.3   Synthesis of poly(amideimide)s

A representative procedure for the synthesis of poly(amideimide)s is given below:

Into a 25 mL three-necked round bottom flask equipped with a nitrogen gas inlet and a calcium chloride guard tube were added *N,N'*-(4-pentadecyl-1,3-phenylene)bis(4-

aminobenzamide) (0.40 g, 0.72 mmol) and dry DMAc (4 mL). After complete dissolution of diamine, pyromellitic dianhydride (0.212 g, 0.72 mmol) was added in portions to the stirred solution at room temperature under a stream of nitrogen. After the addition of dianhydride was complete, the reaction was allowed to proceed for 18 h at room temperature in nitrogen atmosphere. The intermediate poly(amide amic acid) solution thus obtained was spread onto a glass plate, dried at 80 $^{\circ}$C under dry nitrogen atmosphere and then thermally imidized by heating in vacuum at 150 $^{\circ}$C, 250 $^{\circ}$C, and 300 $^{\circ}$C for 1 h at each temperature.

A similar procedure was followed for the synthesis of other poly(amideimide)s.

6.4   Results and discussion

6.4.1   Synthesis of poly(amideimide)s

Scheme 5.1 illustrates synthesis of a new series of poly(amideimide)s (Ia-d and IIa-d) synthesized by polycondensation of aromatic diamines, PDP-4AB (**I**) and PDP-3AB (**II**) containing preformed amide linkages and pentadecyl chains, with aromatic dianhydrides at room temperature in DMAc. Poly(amideimide)s were synthesized by two-step method *via* poly(amide amic acid) intermediate, followed by thermal imidization.
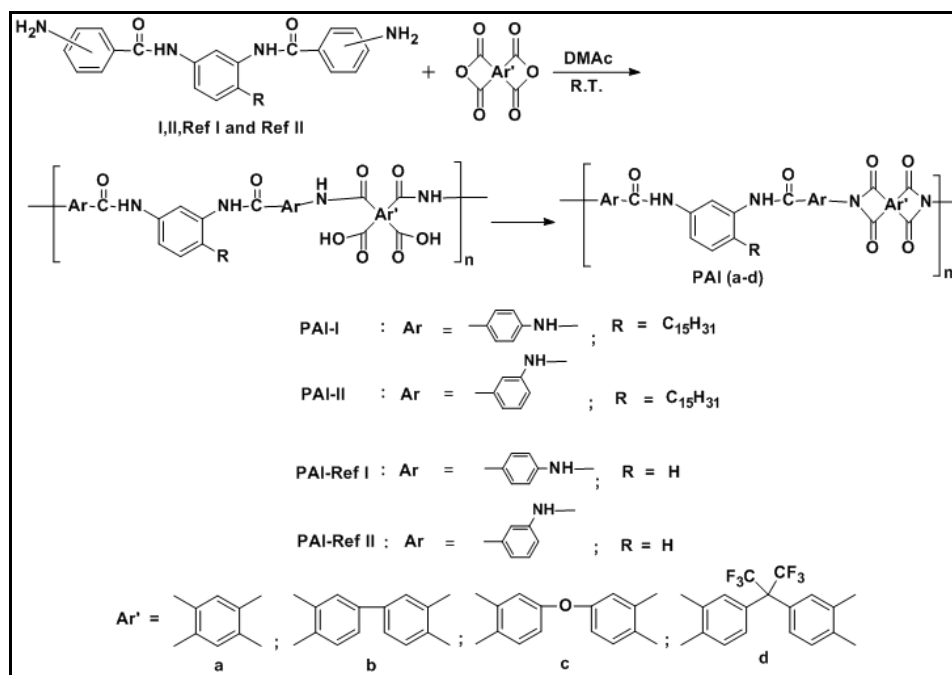
Scheme 6.1 Synthesis of poly(amideimide)s containing pendent pentadecyl chains and reference poly(amideimide)s

The reference poly(amideimide)s were prepared by polycondensation of reference diamines **Ref I** and **Ref II** with aromatic dianhydrides by the same method. All the reactions proceeded in a homogeneous fashion. The imidization of poly(amic acid)s can be achieved either chemically or thermally. In the present work, the imidization of poly(amic acid)s containing preformed amide linkages was carried out using thermal imidization. In the thermal imidization,

the solution of poly(amic acid) containing preformed amide linkages was spread onto a glass plate and the solvent was evaporated at 80 ^{o}C/ 2 h in a slow stream of nitrogen flow. Then, the semi-dried film was thermally cured at 150, 250 and 300 ^{o}C for 1h each in vacuum.

Transparent, flexible and tough films of poly(amideimide)s were obtained after thermal imidization of poly(amic acid) solution containing preformed amide linkages. Inherent viscosities of PAIs Ia-d and IIa-d were in the range 0.72-1.23 dL/g and 0.37-0.51 dL/g, respectively, indicating the formation of medium to high molecular weight polymers. Inherent viscosities of reference poly(amideimide)s were determined at poly(amide amic acid) stage due to insolubility of poly(amideimide)s in organic solvents and were in the range 0.34-0.70 dL/g. The results of polymerization are summarized in **Table 6.1**.

Table 6.1 Synthesis of poly(amideimide)s containing pendent pentadecyl chains and reference poly(amideimide)s

PAIs	Diamine	Dianhydride	Yield (%)	η_{inh} (dL/g)^a
Ia	**I**	PMDA	96	0.72
Ib	**I**	BPDA	95	1.04
Ic	**I**	ODPA	97	0.73
Id	**I**	6-FDA	98	1.23
IIa	**II**	PMDA	96	0.37
IIb	**II**	BPDA	96	0.51
IIc	**II**	ODPA	98	0.44
IId	**II**	6-FDA	98	0.42
Ref-Ia	**Ref-I**	PMDA	95	0.36*
Ref-Ib	**Ref-I**	BPDA	95	0.70*
Ref-Ic	**Ref-I**	ODPA	96	0.53*
Ref-Id	**Ref-I**	6-FDA	96	0.55*
Ref-IIa	**Ref-II**	PMDA	93	0.34*
Ref-IIb	**Ref-II**	BPDA	95	0.37*
Ref-IIc	**Ref-II**	ODPA	96	0.36*
Ref-IId	**Ref-II**	6-FDA	97	0.37*

a: η_{inh} was measured with 0.5 % (w/v) solution of poly(amideimide)s in DMAc at 30 ± 0.1 ^{o}C; *: η_{inh} was measured with 0.5 % (w/v) solution of poly(amic acid))s in DMAc at 30 ± 0.1 ^{o}C

6.4.1.1   Structural characterization

The formation of poly(amideimide)s was confirmed by FT-IR and ^{1}H-NMR spectroscopy. A representative FT-IR spectrum of poly(amideimide) derived from *N,N'*-(4-

pentadecyl-1,3-phenylene)bis(4-aminobenzamide) and pyromellitic dianhydride is reproduced in

Figure 6.1
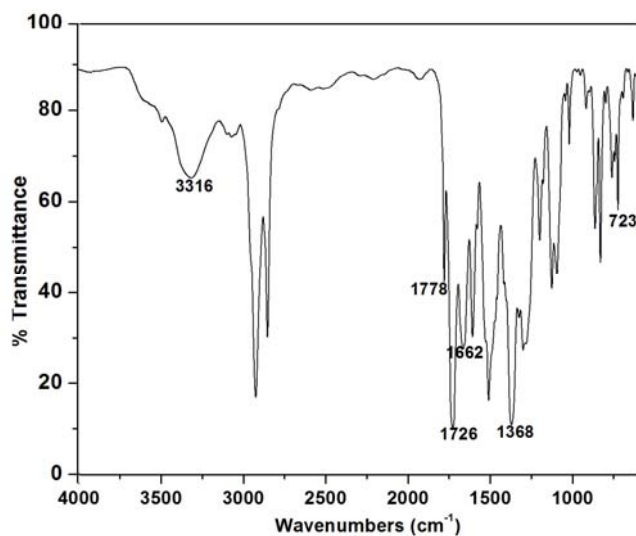
Figure 6.1 FT-IR spectrum of poly(amideimide) derived from *N,N'*-(4-pentadecyl-1,3-phenylene)bis(4-aminobenzamide) and pyromellitic dianhydride

The characteristic absorption bands at 1778 cm^{-1} (C=O symmetric stretching of imide I), and 1726 cm^{-1} (C=O asymmetric stretching), 1368 cm^{-1} (C-N stretching of imide II) and 737 cm^{-1} (imide ring deformation) indicated the formation of imide rings. The absorption band at 3316 cm^{-1} correspond to N-H stretching of amide linkage. The band at 1662 cm^{-1} was assigned to the C=O of the amide linkage which was overlapped with the asymmetrical C=O stretching vibration of the imide ring.

A representative ^{1}H-NMR spectrum of PAI-IId is depicted in **Figure 6.2.**
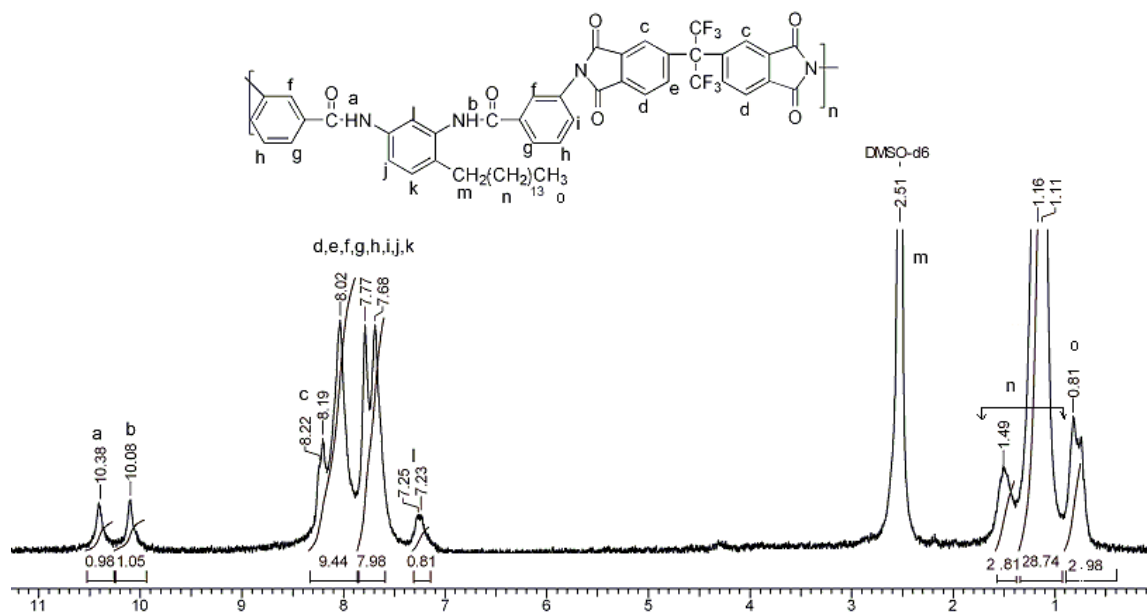
Figure 6.2 ^{1}H-NMR spectrum (DMSO-d$_6$) of poly(amideimide) derived from PDP-3AB (I) and 4,4'-(hexafluorisopropylidene) diphthalic anhydride

Interestingly, two separate peaks ('a, b') were observed in ^{1}H-NMR spectrum for -NH of the amide linkage at 10.38 and 10.08 δ, ppm. This magnetic non-equivalence of protons 'a' and 'b' is due to asymmetry introduced by the presence of pentadecyl chain. The aromatic protons of the dianhydride unit ('c, d and e') and the diamine moiety ('f, g, h, i, j, k and l') appeared in the region 7.68–8.22 δ, ppm. The aromatic proton 'l' appeared as a doublet at 7.23 δ, ppm. The peaks corresponding to the benzylic methylene protons 'm' was overlapped with solvent peak (DMSO-d$_6$) at at 2.51 δ, ppm. The other methylene protons 'n' appeared in the range 1.11–1.49 δ, ppm. Methyl group protons 'o' appeared as a triplet at 0.81 δ, ppm.

6.4.1.2   Solubility measurements

Solubility of poly(amideimide)s was tested in various organic solvents at a 3 wt % concentration and data is summarized in **Table 6.2.**

Table 6.2 Solubility data of poly(amideimide)s containing pendent pentadecyl chains and reference poly(amideimide)s

PAIs	Solvent									
	DMAC	NMP	DMF	DMSO	m-Cresol	CHCl$_3$	THF	Pyridine	Nitroben zene	Acetone
Ia	++	++	+	+	--	--	--	+	+	--
Ib	++	++	+	+-	+	--	--	++	+-	--
Ic	++	++	++	+-	++	--	+-	++	+	--
Id	++	++	++	+	++	--	++	++	+	+-
IIa	++	++	+	+	++	--	--	++	+	--
IIb	++	++	++	+-	++	--	--	++	+-	--
IIc	++	++	++	+	++	--	+-	++	+	--
IId	++	++	++	++	++	--	++	++	++	++
Ref-Ia	--	--	--	--	--	--	--	--	--	--
Ref-Ib	--	--	--	--	--	--	--	--	--	--
Ref-Ic	+	+	+	+	+	--	--	--	--	--
Ref-Id	+	+	++	+	+	--	--	+	+-	--
Ref-IIa	--	++	++	+	--	--	--	--	--	--
Ref-IIb	--	++	+-	+	--	--	--	--	--	--
Ref-IIc	++	++	++	+	+	--	+-	--	--	--
Ref-IId	++	++	++	++	++	--	+-	++	+-	+-

^{a} --, Insoluble; +- partially soluble or swollen; + soluble on heating; ++, soluble at room temperature.

Poly(amideimide)s containing pendent pentadecyl chains (Ia-d and IIa-d) were soluble in aprotic polar solvents such as DMAc, NMP, DMF and DMSO, and in even moderately polar solvents such as *m*-cresol, pyridine and tetrahydrofuran. Poly(amideimide)s containing pendent pentadecyl chains and derived from rigid dianhydrides like PMDA, BPDA (Ia, Ib, IIa, IIb) were soluble in DMAc, NMP, DMF, DMSO, *m*-cresol, pyridine and nitrobenzene at room temperature or upon heating whereas reference poly(amideimide)s, Ref-Ia and Ref-Ib were insoluble in the above solvents and Ref-IIa and Ref-IIb were soluble only in NMP at room temperature. The enhanced solubility of poly(amideimide)s containing pendent pentadecyl chains can be attributed to the presence of pentadecyl chains which weakens intermolecular interactions and thus facilitate the diffusion of solvent molecules in the polymer chains.

In addition to this, all *meta*-linked polymers (PAIs IIa-d) showed enhanced solubility compared to *para*-linked polymers (PAIs Ia-d). For example, PAI-Ia derived from **I** and PMDA was insoluble in *m*-cresol whereas the corresponding *meta*-linked polymer PAI-IIa was readily soluble in *m*-cresol at room temperature. Also PAI-Ia was soluble in pyridine only upon heating whereas PAI-IIa was soluble in pyridine at room temperature. The better solubility of all *meta*-linked polymers indicates that "kinks" introduced by *meta*-linkages in the polymer backbone result in higher entropy state of the polymer chains which decreases the rigidity of the polymer backbone, thus further reducing the interchain interactions and H-bonding.

6.4.1.3 X-Ray diffraction studies

X-Ray diffractograms of poly(amideimide)s derived from aromatic diamines **I**, **II**, **Ref-I** and **Ref-II** containing preformed amide linkages and aromatic dianhydrides are depicted in **Figure 6.3**.
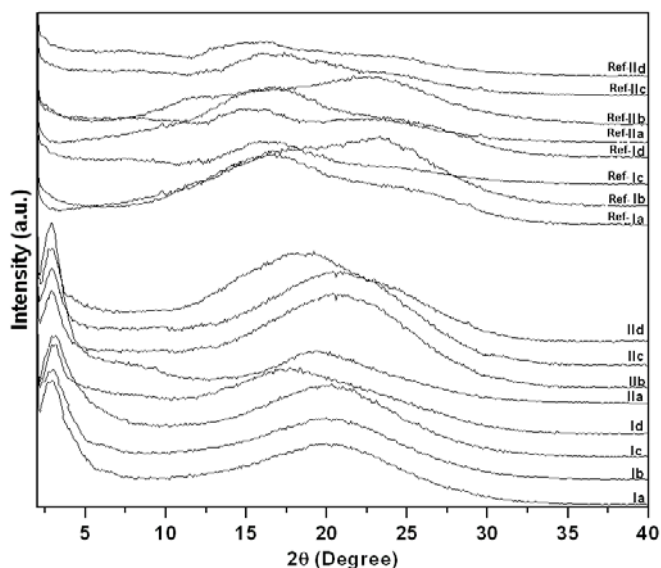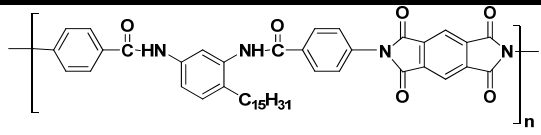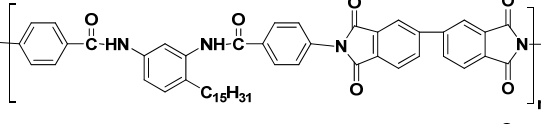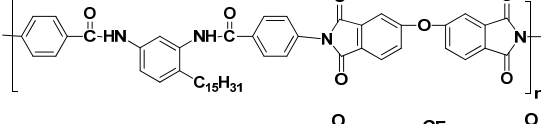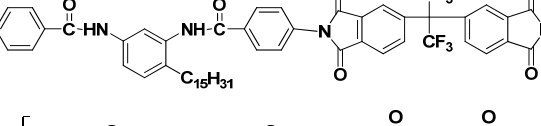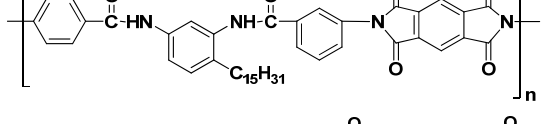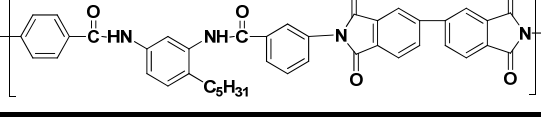
Figure 6.3 X-Ray diffractograms of poly(amideimide)s containing pendent pentadecyl chains and reference poly(amideimide)s

X-Ray diffractograms of poly(amideimide)s containing pendent pentadecyl chains and reference poly(amideimide)s exhibited a broad halo at about $2\theta \approx 20\text{-}25^{o}$ in the wide angle region indicating that poly(amideimide)s were amorphous in nature. In addition to this, poly(amideimide)s containing pendent pentadecyl chains (Ia-d and IIa-d) showed reflections in the small angle region at about $2\theta \approx 3^{\ o}$. These peaks are characteristic of typical layered structures. It is reported in the literature that polymers with pendent long chains strongly tend to form layered crystalline structure in the solid state.[48-51]

6.4.1.4 Thermal properties

Thermal stability of poly(amideimide)s was determined by thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C/min under nitrogen atmosphere and thermograms are shown in **Fig. 6.4**. Initial decomposition temperature (IDT), temperature at 10 % wt loss (T_{10}) and the weight residues at 900 ^{o}C were determined from thermograms and the data is given in **Table 6.3**.

Table 6.3 Thermal properties of poly(amideimide)s containing pendent pentadecyl chains and reference poly(amideimide)s

Poly(amideimide)	IDT^a (^{o}C)	T_{10}^{b} (^{o}C)	Weight residue at 900 ^{o}C (%)	T_g^{c} (^{o}C)
Ia	455	470	40	286
Ib	460	480	44	244
Ic	455	470	41	206
Id	460	475	42	223
IIa	450	460	41	233
IIb	460	480	44	208

Label	Structure	a	b	c	
IIc		455	470	43	162
IId		455	475	40	164
Ref-Ia		480	490	50	N.D.
Ref-Ib		490	515	52	316
Ref-Ic		470	500	46	306
Ref-Id		480	510	50	330
Ref-IIa		470	490	45	331
Ref-IIb		470	490	43	301
Ref-IIc		460	470	45	275
Ref-IId		465	485	45	287

a: Initial decomposition temperature, *b*: temperature at which 10 % weight loss is observed, *c*: Glass transition temperature (T_g) measured on DSC at a heating rate of 20 ^{o}C/min in N_2.

The initial decomposition temperatures of reference poly(amideimide)s were in the range 460-490 ^{o}C and that of poly(amideimide)s containing pendent pentadecyl chains were in the range 450-460 ^{o}C which indicates that due to the presence of thermally labile pentadecyl chains, PAIs Ia-d and IIa-d were slightly inferior in thermal stability compared to the reference polymers. Such reduction in thermal stability is commonly observed in many aromatic polymers with flexible aliphatic side chains.[52-55]
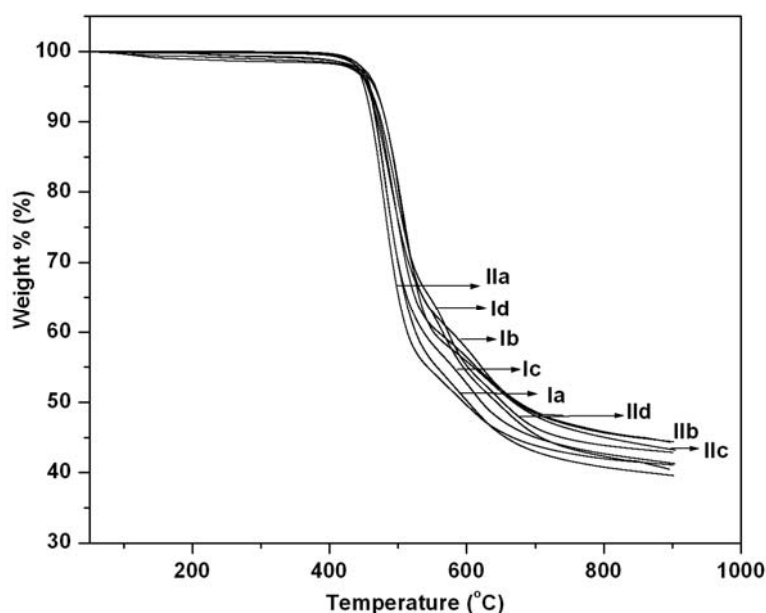
Figure 6.4 TG curves of poly(amideimide)s containing pendent pentadecyl chains

A representative differential thermogravimetric analysis (DTG) curve of PAI IIc is shown in **Fig. 6.5.** Poly(amideimide)s containing pendent pentadecyl chains showed two stage weight loss: the first stage was presumably due to the concurrent decomposition of pendent pentadecyl chains and amide linkages while the second stage decomposition was due to degradation of imide linkages. The char yield of PAIs was in the range 40-52 %.
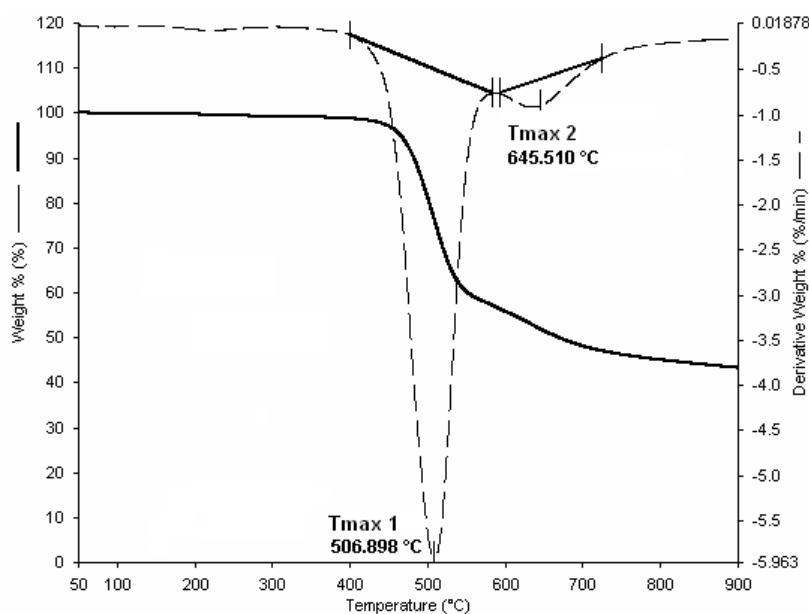
Figure 6.5 DTG curve of poly(amideimide) derived from N,N'-(4-pentadecyl-1,3-phenylene)
bis(3-aminobenzamide) and 4,4'-oxydiphthalic anhydride

Glass transition temperature (T_g) of poly(amideimide)s was evaluated by differential scanning calorimetry (DSC). T_g values were obtained from second heating scans of

poly(amideimide) samples at a heating rate of 20 ^{o}C/minute. DSC curves are reproduced in **Figure 6.6** and T$_g$ values are given in **Table 6.3**.
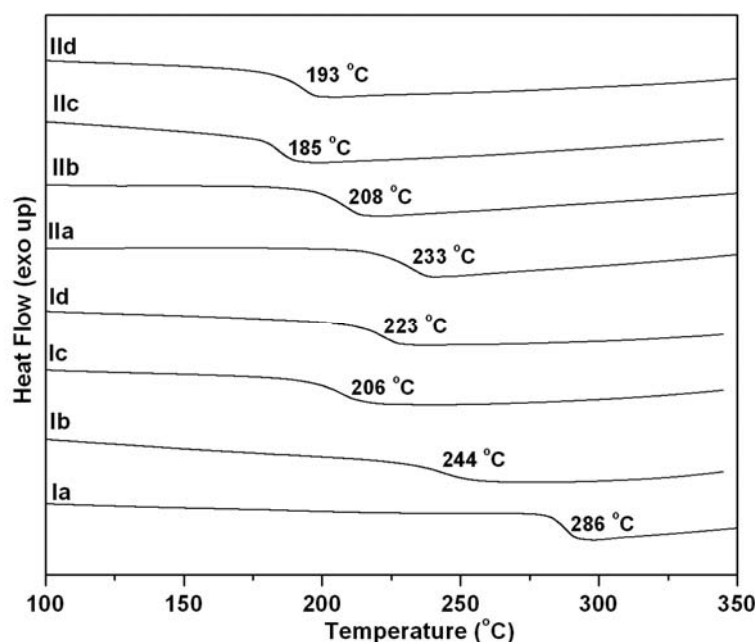
Figure 6.6 DSC curves of poly(amideimide)s containing pendent pentadecyl chains

        T$_g$ values of reference PAIs were in the range 275-331 ^{o}C while T$_g$ values of PAIs Ia-d and IIa-d were in the range 185-286 ^{o}C which indicates a large drop in T$_g$ due to the presence of pendent pentadecyl chains. The depression in T$_g$ of PAIs Ia-d and IIa-d demonstrated the "plasticization" effect of pentadecyl chains. Furthermore, T$_g$ values of PAIs IIa-d were lower than the corresponding PAIs Ia-d, this was attributed to "kinks" in the polymer backbone introduced by *meta-meta* catenation of aromatic rings. T$_g$ values of PAI series were found to be in the increasing order of PAI IIa-d < PAI Ia-d < PAI Ref-IIa-d < PAI Ref-Ia-d. Thus T$_g$ values of PAIs IIa-d were lowest among the series due to the combined effect of presence of pendent pentadecyl chains and *meta-meta* catenation of aromatic rings in the polymer backbone. T$_g$ values of poly(amideimide)s were found to be in the increasing order of ODPA < FDA < BPDA < PMDA which corresponds with the rigidity of aromatic dianhydrides. A large difference between T$_g$ (185-286 ^{o}C) and IDT (450-460 ^{o}C) was observed which offers poly(amideimide)s containing pendent pentadecyl chains a wide processing window.

6.5   Conclusions

1. A series of new aromatic poly(amideimide)s (Ia-d and IIa-d) was prepared by two-step polycondensation of two diamines *N,N'*-(4-pentadecyl-1,3-phenylene)bis(4-aminobenzamide), and *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-aminobenzamide) and aromatic dianhydrides in DMAc *via* poly(amic acid) intermediate followed by thermal imidization.

2. Inherent viscosities of poly(amideimide)s were in the range 0.37-1.23 dL/g indicating formation of medium to high molecular weight polymers.

3. Poly(amideimide)s containing pendent pentadecyl chains (Ia-d and IIa-d) exhibited improved solubility not only in highly polar solvents such as DMAc, NMP, DMF and DMSO, but also in moderately polar solvents such as pyridine and tetrahydrofuran. Poly(amideimide)s derived from rigid dianhydrides such as PMDA and BPDA (Ia, Ib, IIa, IIb) were also soluble in DMAc, NMP, DMF, DMSO, *m*-cresol, pyridine and nitrobenzene at room temperature or upon heating This indicates that the incorporation of pendent 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 pendent 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 containing pentadecyl chains were in the range 460-480 ^{o}C indicating their good thermal stability.

7. T_g values of PAI Ia-Id and PAI IIa-IId were in the range 206-286 ^{o}C and 162-233 ^{o}C, respectively, indicating a large drop in T_g due to presence of pendent pentadecyl chains.

8. Overall, polymer processability/solubility was improved by the combined effect of incorporation of pendent pentadecyl chains *via* "internal plasticization" and "kinks" in the polymer backbone due to *meta*-catenation.

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Chapter 7

Synthesis and Characterization of Poly(esterimide)s and Polyesters Containing Pendent Pentadecyl Chains

Chapter 7a

Synthesis and Characterization of Poly(esterimide)s Based on 2,2'-(4-Pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid)

7a.1   Introduction

Aromatic poly(esterimide)s (PEIs) are an important class of thermally stable polymers, with a combination of two different functionalities (ester and imide.[1] PEIs have found various commercial applications such as coatings for enameled wires, high strength fibers, etc.[2,3] The general methods for synthesis of PEIs are: direct polycondensation of trimellitic anhydride with a mixture of a diamine and a diol,[4] reaction of a dicarboxylic acid containing a preformed imide group with a diol,[5,6] polycondensation of a diphenol containing an imide ring with a diacid chloride,[7] reaction between a dianhydride containing an ester group and a diamine,[8] and direct polycondensation of a diisocyanate containing an ester linkage with a dianhydride.[9]

Aromatic PEIs are generally infusible and insoluble in common organic solvents and pose processing difficulties, limiting their widespread utility.[10] Much efforts have been made to develop poly(esterimide)s[11-19] with improved solubility.

The objective of the present work was to synthesize a series of poly(esterimide)s containing pendent pentadecyl chains along the backbone and to examine the effect of their incorporation on the polymer properties such as solubility and thermal behavior. Thus, a series of new aromatic poly(esterimide)s containing pendent pentadecyl chains was synthesized by diphenylchlorophosphate (DPCP)-activated direct polycondensation of new diimide-dicarboxylic acid, *viz.*, 2,2'-(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid), containing preformed imide rings and pentadecyl chain, with five commercially available bisphenols, *viz.*, 4,4'-isopropylidenediphenol, 4,4'-(hexafluoroisopropylidene) diphenol, 4,4'-oxydiphenol, 4,4'-biphenol and 4,4'-(9-fluorenylidene)diphenol in a medium consisting of pyridine and lithium chloride. The synthesized poly(esterimide)s were characterized by inherent viscosity measurements, gel permeation chromatography (GPC), solubility tests, IR, ^{1}H-NMR spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies.

7a.2   Experimental

7a.2.1   Materials

2,2'-(4-Pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid) (PDPDA) was synthesized as described in **Chapter 3.** 4,4'-Isopropylidenediphenol, 4,4'-(hexafluoroisopropylidene) diphenol, 4,4'-oxydiphenol, 4,4'-biphenol and 4,4'-(9-fluorenylidene) diphenol (Sigma-Aldrich) were purified by sublimation under reduced pressure. Anhydrous lithium chloride (Sigma-Aldrich) was dried at 180 $^{\circ}$C for 8 h under reduced pressure. Pyridine was purified by distillation over KOH and stored over 4Å molecular sieves. Diphenylchlorophosphate (DPCP; from AVRA Chemicals) was used without further purification. All other chemicals were of CP grade and were used without further purification.

7a.2.2   Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in CHCl$_3$ at 30 ± 0.1 ^{o}C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \dfrac{2.303}{C} x \log \dfrac{t}{t_0}$

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(esterimide)s 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.

FT-IR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

^{1}H-NMR spectra were recorded on a Bruker NMR spectrophotometer (200 or 400 MHz) in CDCl$_3$ solution at room temperature.

The solubility of poly(esterimide)s was determined at 3 wt % concentration in various solvents at room temperature or on heating.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 10 °C/minute under nitrogen atmosphere. Sample weight taken was ~5-7 mg.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 20 °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 were used for X-ray measurements.

7a.3   Synthesis of poly(esterimide)s

A representative procedure for the synthesis of poly(esterimide)s is described below:

Into a 25 mL three-necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and an addition funnel, were added 2,2'-(4-pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid) (0.5 g, 0.75 mmol), 4,4'-(9-fluorenylidene) diphenol (0.263 g, 0.75 mmol) and pyridine (2 mL) and the mixture was heated to 120 ^{o}C. Into a separate 10 mL round bottom flask, diphenylchlorophosphate (0.40 mL, 1.95 mmol), LiCl (0.064 g, 1.5 mmol) and pyridine (4 mL) were added and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. and then added drop-wise to the above reaction mixture over a period of 20 min. After completion of addition, the reaction mixture was heated at 120 ^{o}C for 12 h under

stirring. The reaction mixture was cooled to room temperature and poured into methanol (100 mL). The fibrous polymer obtained was filtered, washed with hot water, methanol and dried at 80 °C under vacuum overnight.

Yield: 0.69 g (96 %).

7a.4   Results and discussion

7a.4.1 Synthesis of poly(esterimide)s

Scheme 7a.1 illustrates synthesis of poly(esterimide)s from 2,2'-(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid) and commercially available bisphenols (I-V).
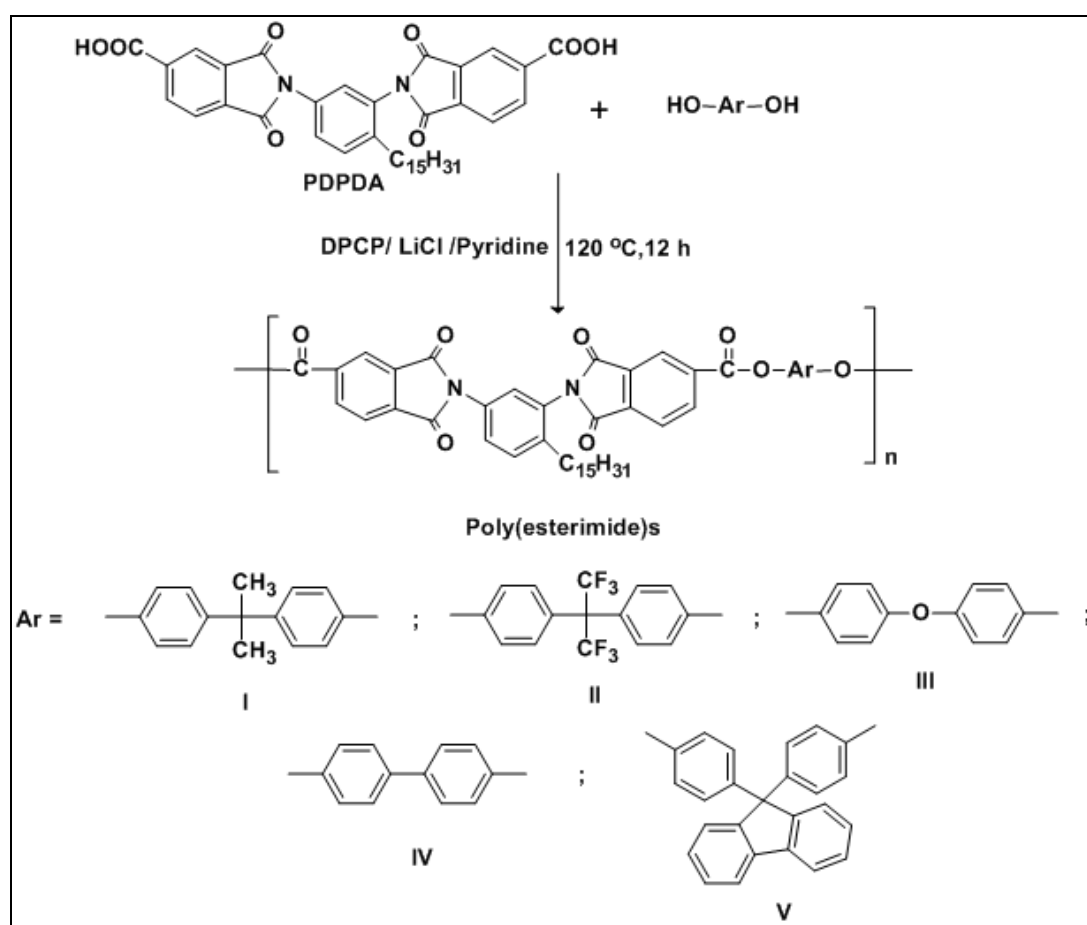
Scheme 7a.1 Synthesis of poly(esterimide)s containing pendent pentadecyl chains

The results of polymerizations are summarized in **Table 7a.1**.

Table 7a.1 Synthesis of poly(esterimide)s containing pendent pentadecyl chains

PEI	Bisphenol	Yield (%)	η_{inh} (dL/g)^a	GPC^b		
				M_w	M_n	M_w/M_n
PEI-I	I	95	0.66	74,400	31,000	2.4
PEI-II	II	96	0.58	61,700	29,400	2.1
PEI-III	III	95	0.54	58,100	26,400	2.2
PEI-IV	IV	95	0.72	86,600	41,000	2.1
PEI-V	V	96	0.83	1,13,000	51,000	2.2

a: η_{inh} was measured with 0.5% (w/v) solution of poly(esterimide)s in CHCl$_3$ at 30 ± 0.1^oC, *b*: determined from gel permeation chromatography (mobile phase: chloroform; calibration: polystyrene standards).

The polymerizations were carried out *via* solution polycondensation using diphenylchlorophosphate in the presence of pyridine and lithium chloride, according to the procedure reported in the literature.[20, 21] All the reaction mixtures were homogeneous throughout the course of polymerization.

Inherent viscosities of poly(esterimide)s containing pendent pentadecyl chains were in the range 0.54-0.83 dL/g indicating formation of medium to reasonably high molecular weight polymers. This was further supported by GPC measurements which gave M_n and polydispersities (M_w/M_n) in the range 26,400 – 51,000 and 2.1 - 2.4, respectively. However, molecular weights measured by GPC should not be taken as absolute as the measurements were carried out using polystyrene standards. Tough, transparent, and flexible films of poly(esterimide)s could be cast from their chloroform solutions.

7a.4.2   Structural characterization

The formation of poly(esterimide)s was confirmed by FT-IR and ^{1}H-NMR spectroscopy.

A representative FT-IR spectrum of PEI-II based on PDPDA and 4,4'-(hexafloroisopropylidene) diphenol is reproduced in **Figure 7a.1.** The spectrum exhibited characteristic absorption bands at 1784 cm^{-1} (C=O symmetric stretching of imide I) and 1725 cm^{-1} (C=O asymmetric stretching). Absorption bands at 1370 (imide-II) and 730 cm^{-1} (imide-IV) correspond to the C–N–C stretching and bending vibrations of the imide, respectively. Absorption band at 1100 cm^{-1} (imide-III) corresponds to imide ring deformation. The characteristic C=O absorption band of ester functional groups appeared at 1725 cm^{-1}, which was overlapped with the asymmetrical C=O stretching vibration of the imide ring.
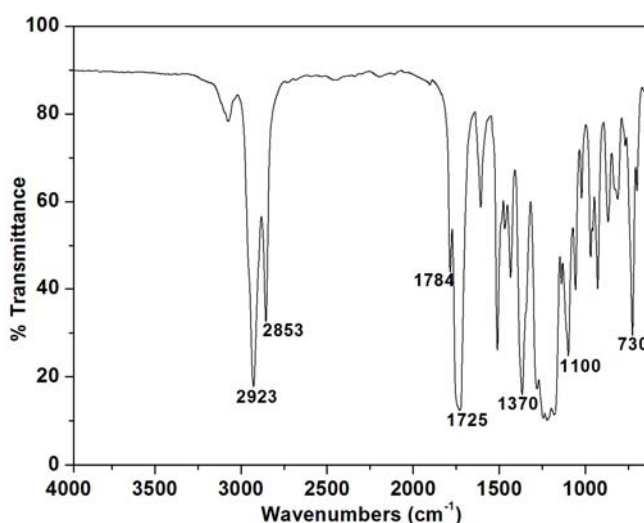
Figure 7a.1 FT-IR spectrum (Film) of poly(ester-imide) (PEI-II) based on PDPDA and 4,4'

hexafluoroisopropylidene) diphenol

A representative ^{1}H-NMR spectrum of PEI-II derived from PDPDA and 4,4'-(hexafluoroisopropylidene)diphenol is depicted in **Figure 7a.2**.
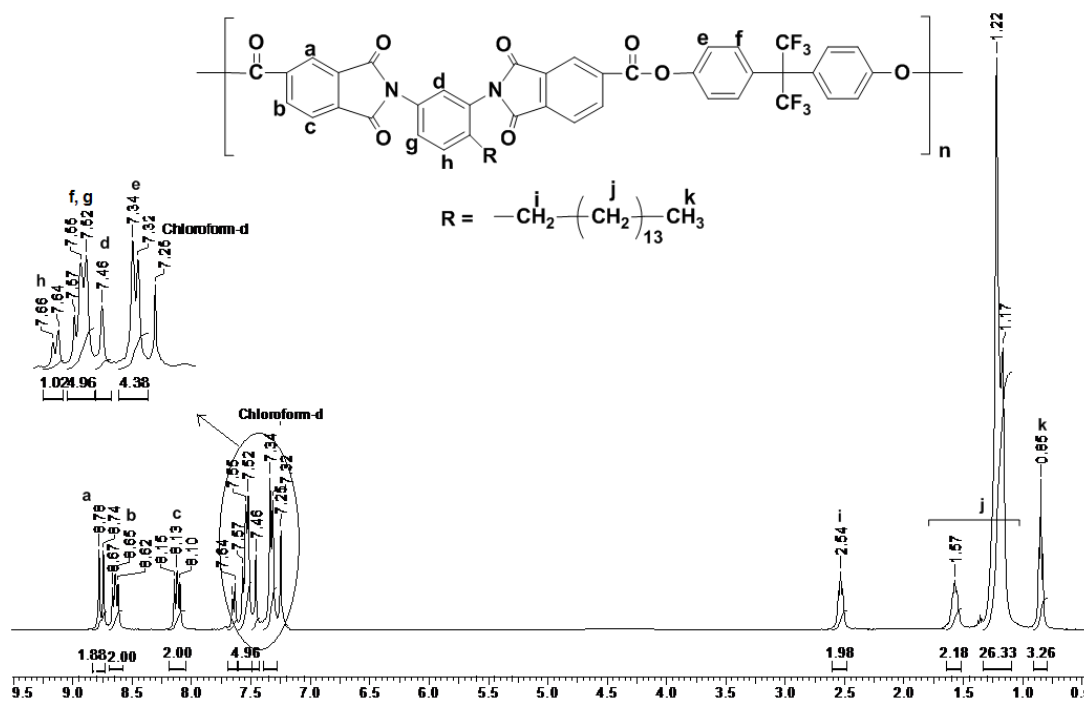
Figure 7a.2 ^{1}H-NMR spectrum (CDCl$_3$) of PEI-II based on PDPDA and 4,4'-hexafluoro

isopropylidene) diphenol

The aromatic protons of the diimide-dicarboxylic acid unit appeared in the range 7.55-8.78 δ, ppm while the atomatic protons of bisphenol moiety displayed peaks in the region 7.32-7.52 δ, ppm. The benzylic methylene protons exhibited a triplet at 2.54 δ, ppm while the other methylene protons appeared in the range 1.22-1.57 δ, ppm. Methyl group protons appeared as a triplet at 0.85 δ, ppm.

7a.4.3 Solubility measurements

The solubility of poly(esterimide)s was tested at 3 % (w/v) concentration in various organic solvents and the data is summarized in **Table 7a.2**.

Table 7a.2 Solubility data of poly(esterimide)s containing pendent pentadecyl chains[a]

PEI	Solvent									
	DMAc	NMP	DMF	DMSO	*m*-Cresol	CHCl₃	THF	Pyridine	Nitrobenzene	Acetone
PEI-I	++	++	+	--	++	++	++	++	++	+-
PEI-II	++	++	+	--	++	++	++	++	++	+-
PEI-III	++	++	+	--	++	++	++	++	++	+-
PEI-IV	++	++	+	--	++	++	++	++	++	--
PEI-V	++	++	+	--	++	++	++	++	++	--

[a] --, Insoluble; +- partially soluble or swollen; + soluble on heating; ++, soluble at room temperature.

Poly(esterimide)s containing pendent pentadecyl chains dissolved readily in common organic solvents such as chloroform, tetrahydrofuran, *m*-cresol and pyridine and are also found to be readily soluble in aprotic polar solvents such as *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP) and nitrobenzene. The good solubility of these poly(esterimide)s results from the presence of pendent pentadecyl chains which inhibits tight chain packing and leads to reduced intermolecular interactions.

7a.4.4 X-Ray diffraction studies

X-Ray diffractograms of poly(esterimide)s containing pendent pentadecyl chains are reproduced in **Figure 7a.3**. X-Ray diffractograms of poly(esterimide)s containing pendent pentadecyl chains exhibited a broad halo at about $2\theta = \sim 20^{o}$ in the wide angle region indicating that the polymers are amorphous in nature.
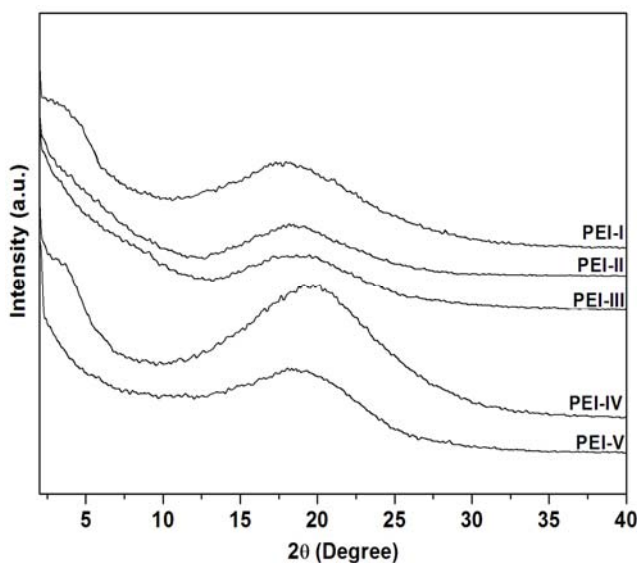
Figure 7a.3 X-Ray diffractograms of poly(esterimide)s containing pendent pentadecyl chains

In addition to this, poly(esterimide)s exhibited diffuse reflections in the small-angle region at $2\theta \approx 3^{\circ}$ which can be attributed to the formation of loosely developed layered structure due to the packing of pentadecyl chains. Similar observations have been reported for other polymers having long flexible side chains.[22-25]

7a.4.5   Thermal properties

Thermal stability of poly(esterimide)s was determined by TGA at a heating rate of 10 $^{\circ}$C/min under nitrogen atmosphere. TG curves of poly(esterimide)s are reproduced in **Figure 7a.4**.
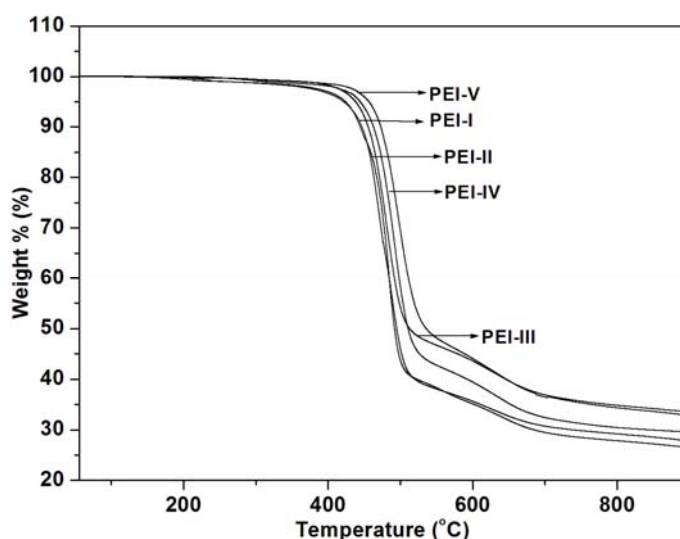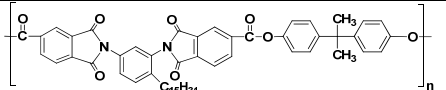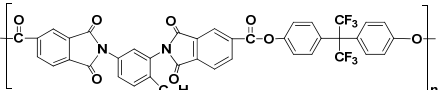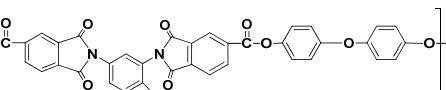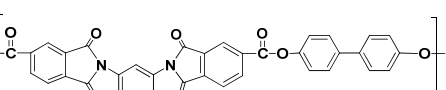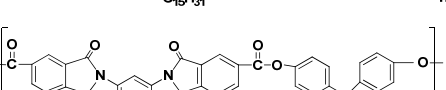
Figure 7a.4 TG curves of poly(esterimide)s containing pendent pentadecyl chains

Initial decomposition temperature (IDT), temperature at 10 % weight loss (T_{10}) and the weight residues at 900 $^{\circ}$C were determined from thermograms and the data is given in **Table**

7a.3. T_{10} values obtained from TG curves for poly(esterimide)s containing pendent pentadecyl chains were in the range 450-470 ^{o}C, in nitrogen atmosphere indicating good thermal stability.

Table 7a.3 Thermal properties of poly(esterimide)s containing pendent pentadecyl chains

Poly(esterimide)		IDT^a (^{o}C)	$T_{10}{}^b$ (^{o}C)	T_g (^{o}C)	Weight residue at 900°C (%)
PEI-I		440	455	151	28
PEI-II		440	455	153	27
PEI-III		435	450	145	34
PEI-IV		445	460	183	30
PEI-V		460	470	198	33

a: Glass transition temperature (T_g) measured on DSC at a heating rate of 20 ^{o}C/min in N_2, b: Initial decomposition temperature, c: Temperature at which 10 % weight loss is observed

A representative differential thermogravimetric (DTG) analysis curve of PEI-III derived from PDPDA and 4,4'-oxydiphenol is reproduced in **Figure 7a.5.**
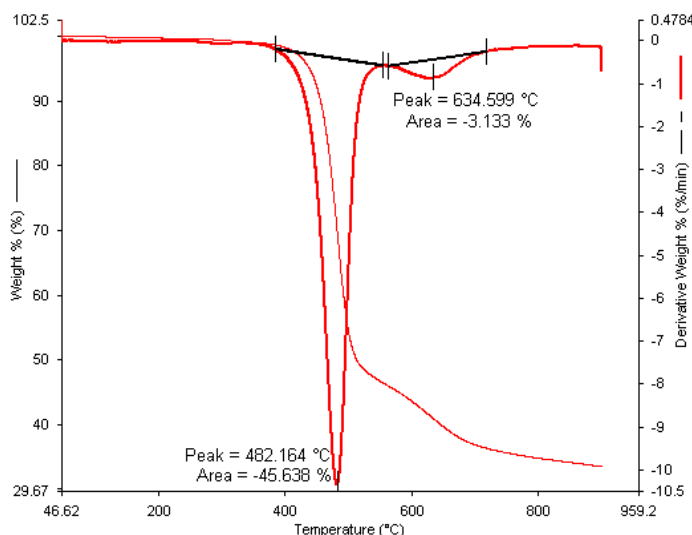
Figure 7a.5 TG and DTG curves of PEI-III based on 2'-(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid) and 4,4'-oxydiphenol

Poly(esterimide)s containing pendent pentadecyl chains showed two stage weight loss: the first stage was presumably due to the concurrent decomposition of pendent alkyl groups and

ester linkages while the second stage decomposition was due to degradation of imide linkages. The weight residues of poly(esterimide)s when heated to 900 ^{o}C, in nitrogen were in the range 27-34 %.

DSC curves of PEIs containing pendent pentadecyl chains are reproduced in **Figure 7a.6** and T$_g$ values obtained from second heating scans at a heating rate of 20 ^{o}C/min are listed in **Table 7a.3**.
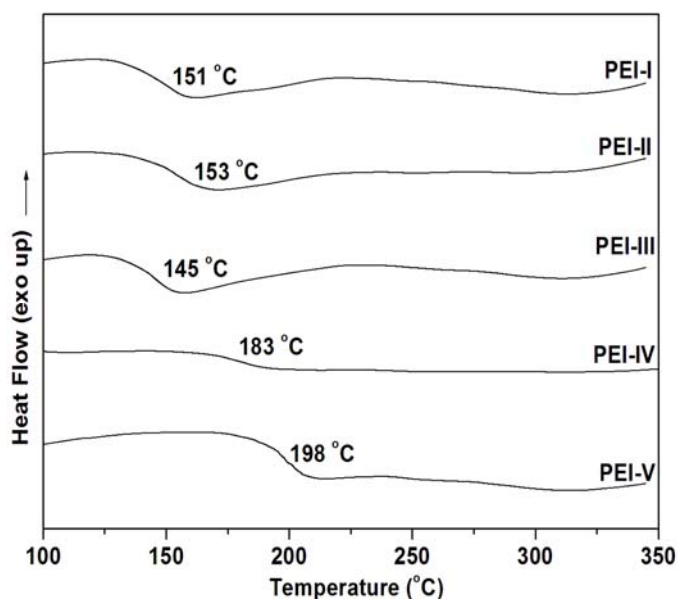
Figure 7a.6 DSC curves of poly(esterimide)s containing pendent pentadecyl chains

T$_g$ values of PEIs containing pendent pentadecyl chains were in the range 145-198 ^{o}C and were found to be in the increasing order of PEI-III < PEI-II ≈ PEI-I < PEI-IV < PEI-V. This result is attributed to increasing rigidity of bisphenols, thus, PEI-III, derived from PDPDA and 4,4'-oxydiphenol showed the lowest T$_g$ value of 145 ^{o}C and PEI-V, derived from 4,4'-(9-fluorenylidene)diphenol exhibited the highest T$_g$ value of 198 ^{o}C. PEI-I based on bisphenol A showed a T$_g$ of 151 ^{o}C whereas the corresponding reference polymer is reported to possess a T$_g$ value of 270 ^{o}C.[26] This result is reasonable and can be attributed to the presence of pendent pentadecyl chains along the polymer backbone which is acting as an 'internal plasticizer' It is reported that the introduction of flexible side groups onto the polymer backbone brings about lowering of the glass transition temperature.[27] The presence of pendent pentadecyl chains along the polymer backbone is expected to disrupt intermolecular interactions which increases the segmental motion and allow the polymer backbone more freedom for flow during processing. A large difference in T$_g$ and decomposition temperature of poly(esterimide)s offers a broad processing window. This gives an opportunity for these poly(esterimide)s to be melt processed or compression molded.

7a.5   Conclusions

1. A new series of poly(esterimide)s containing pendent pentadecyl chains was synthesized from 2,2'-(4-pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid), containing preformed imide rings and pentadecyl chain by the diphenylchlorophosphate-activated direct polycondensation with five commercially available bisphenols.

2. Inherent viscosities of poly(esterimide)s were in the range 0.54-0.83 dL/g indicating formation of medium to reasonably high molecular weight polymers.

3. Poly(esterimide)s containing pendent pentadecyl chains were soluble in organic solvents such as chloroform, *m*-cresol, *N,N*-dimethylacetamide, 1-methyl-2-pyrrolidinone, pyridine and nitrobenzene.

4. Tough, transparent and flexible films of poly(esterimide)s could be cast from their chloroform solutions.

5. WAXD patterns showed that poly(esterimide)s containing pendent pentadecyl chains were amorphous in nature. A loosely developed layered structure formation was observed due to the packing of pentadecyl chains.

6. T_{10} values for poly(esterimide)s were in the range 450-470 °C indicating their good thermal stability.

7. The glass transition temperature of poly(esterimide)s containing pentadecyl chains was in the range 145-198 °C. The depression in Tg values of poly(esterimide)s could be attributed to the presence of pendent pentadecyl chains along the polymer backbone.

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Chapter 7b

Synthesis and Characterization of Polyesters Based on 2-Pentadecylbenzene-1,4-diol

7b.1   Introduction

Aromatic polyesters or polyarylates are an important class of high performance polymers which possess high thermal stability, chemical resistance and excellent mechanical properties.[1] They find wide applications in electronic industry, automobile parts production, industrial construction, laminates, insulation, coatings, adhesives and molding compounds.[2,3] Polyesters derived from isophthalic/ terephthalic acid with bisphenol A have been commercialized.[4] However, most aromatic polyesters are difficult to process due to their high glass transition or melting temperature coupled with their insolubility in organic solvents. For example, poly(1,4-phenylene-terephthalate) and poly-(4-hydroxybenzoate) have extremely high melting points, on the order of 600 ^{o}C and cannot be processed without decomposition by conventional methods.[5] However, a number of structural variations can lower the melting temperatures and improve the solubility of aromatic polyesters based on the principle of reducing chain symmetry and regularity. These structural variations include: copolymerization,[6] molecular asymmetry,[7] introduction of kinks or flexible units in the main chain,[8-10] replacement of conventional aromatic monomers with monomers containing bulky pendent groups or heterocyclic units,[11-21] introduction of alicyclic units to polymer backbone,[22] etc.

The substitution of aromatic rings in aromatic polyesters is one of the possible ways to achieve improvement in the solubility / processability along with a reduction of transition temperature. It is generally recognized that the use of asymmetrically substituted monomers and introduction of flexible alkyl chains along the polymer backbone improves the solubility / processability of aromatic polyesters.[23-29]   In this context, asymmetrically substituted hydroquinone monomer, *viz.,* 2-pentadecylbenzene-1,4-diol containing pentadecyl chain was considered as a useful monomer for synthesis of aromatic polyesters with improved processability characteristics.

The objective of the present work was to synthesize a series of aromatic polyesters containing pendent pentadecyl chains along the backbone and to examine the effect of incorporation of pentadecyl chains on the polymer properties such as solubility and thermal behavior. Thus, a series of new polyesters was synthesized by diphenylchlorophosphate (DPCP)-activated direct polycondensation of 2-pentadecylbenzene-1,4-diol, with commercially available diacids, *viz.,* isophthalic acid, a 50:50 mol % mixture of isophthalic acid and terephthalic acid, and terephthalic acid in a medium consisting of pyridine and lithium chloride. The synthesized polyesters were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetric (DSC).

7b.2   Experimental

7b.2.1 Materials

2-Pentadecylbenzene-1,4-diol was synthesized as described in **Chapter 3.** Terephthalic acid (TPA) and isophthalic acid (IPA) received from Sigma-Aldrich, USA, were sublimed before use. Anhydrous lithium chloride (Sigma-Aldrich) was dried at 180 ^{o}C for 8 h under reduced pressure. Pyridine was purified by distillation over KOH and stored over 4Å molecular sieves. Diphenylchlorophosphate (DPCP; from AVRA) was used without further purification.

7b.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in CHCl$_3$ at 30±0.1 ^{o}C using an Ubbelhode suspended level viscometer.

Inherent viscosity was calculated using the equation: $n_{inh} = \dfrac{2.303}{C} x \log \dfrac{t}{t_0}$

where t and t_0 are flow times of polymer solution and solvent, respectively and C is the concentration of polymer solution.

FT-IR spectra were recorded using polymer films on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker 400 MHz spectrophotometer at resonance frequency of 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR using CDCl$_3$ as a solvent.

The solubility of polyesters was determined at 3 wt % concentration in various solvents at room temperature or on heating.

Thermogravimetric analysis was performed on Perkin-Elmer TGA-7 system at a heating rate of 10 °C/minute under nitrogen atmosphere. Sample weight taken was ~5-7 mg. DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 20 °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.

7b.3   Synthesis of polyesters

A representative procedure for the synthesis of polyesters is described below:

Into a 25 mL three-necked round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and an addition funnel, were added 2-pentadecylbenzene-1,4-diol (0.3 g, 0.94 mmol), isophthalic diacid (0.16 g, 0.94 mmol) and pyridine (2 mL) and the mixture was heated to 120 ^{o}C. Into a separate 10 mL round bottom flask, a solution of diphenylchlorophosphate (0.50 mL, 2.43 mmol), LiCl (0.08 g, 1.9 mmol) and pyridine (4 mL) was stirred under nitrogen

atmosphere at room temperature for 30 min. and then added drop-wise to the above reaction mixture over a period of 20 min. After completion of addition, the reaction mixture was further heated at 120 °C for 12 h under stirring. The reaction mixture was cooled to room temperature and poured into methanol (100 mL). The fibrous polymer obtained was filtered, washed with hot water, methanol and dried at 80 °C under vacuum overnight.

Yield: 0.42 g (95 %).

7b.4   Results and discussion

7b.4.1 Synthesis of polyesters

Aromatic polyesters are generally prepared by acid chloride route, by interfacial polycondensation of the dialkali metal salt of a diphenol (aqueous phase) with diacid chlorides (organic phase). In the present case, polyesters were synthesized by direct esterification of diacid and diphenol in the presence of an activating / condensing agent such as diphenylchlorophosphate (DPCP).[30] The advantage of this method is that it avoids the use of moisture-sensitive diacid chlorides and is a useful method for the laboratory scale preparation of polyesters.[31,32]

Scheme 7b.1 illustrates synthesis of polyesters containing pendent pentadecyl chains, prepared by direct polycondensation of 2-pentadecylbenzene-1,4-diol and aromatic diacids, in the presence of DPCP.
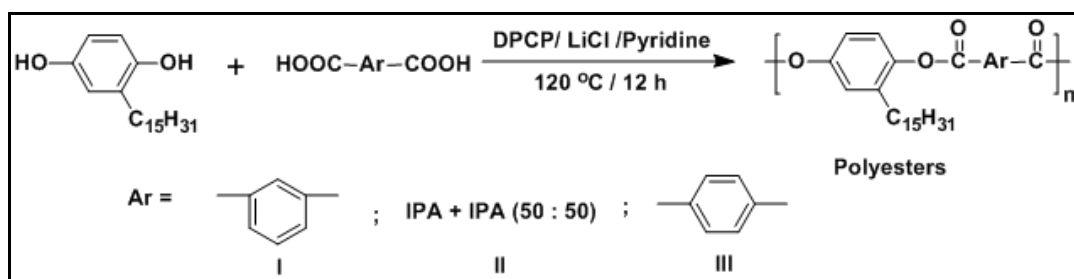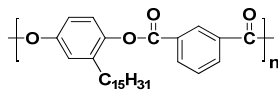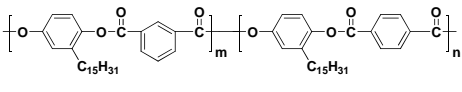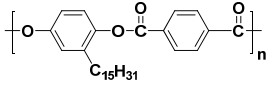
Scheme 7b.1 Synthesis of polyesters form 2-pentadecylbenzene-1,4-diol and aromatic diacids

Polyesterification of an aromatic dicarboxylic acid and an aromatic diol is very sluggish even at high temperature because of low reactivity of monomers. DPCP acts an activating agent for diacid and the activated diacid intermediate formed condenses with bisphenol to form polyesters. The polycondensation reactions were carried out at 120 °C for 12 h.

The results of polymerization are summarized in **Table 7b.1**. During the polymerization, reaction mixtures were homogeneous, except for **PES-III** which showed phase separation from the reaction medium due to insolubility of the polymer in reaction medium. Inherent viscosities of polyesters were in the range 0.47- 0.53 dL/g, indicating the formation of medium molecular weight polymers **(Table 7b.1)**.

Table 7b.1 Synthesis of polyesters from 2-pentadecylbenzene-1,4-diol and aromatic diacids

Polyester		Yield (%)	η_{inh} (dL/g)[a]
PES-I		95	0.53
PES-II		94	0.51
PES-III		92	0.47[b]

a: η_{inh} was measured with 0.5% (w/v) solution of polyesters in CHCl$_3$ at $30 \pm 0.1^{\circ}$C, *b*: η_{inh} was measured with 0.5% (w/v) solution of polyester in *m*-cresol at $30 \pm 0.1^{\circ}$C

Tough, transparent, and flexible films of polyesters (**PES-I and PES-II**) could be cast from their chloroform solutions.

7b.4.2   Structural characterization

The formation of polyesters was confirmed by FT-IR and ^{1}H-NMR spectroscopy.

A representative FT-IR spectrum of polyester based on 2-pentadecylbenzene-1,4-diol and isophthalic acid is reproduced in **Figure 7b.1** which exhibited characteristic band of ester carbonyl at 1750 cm^{-1}.
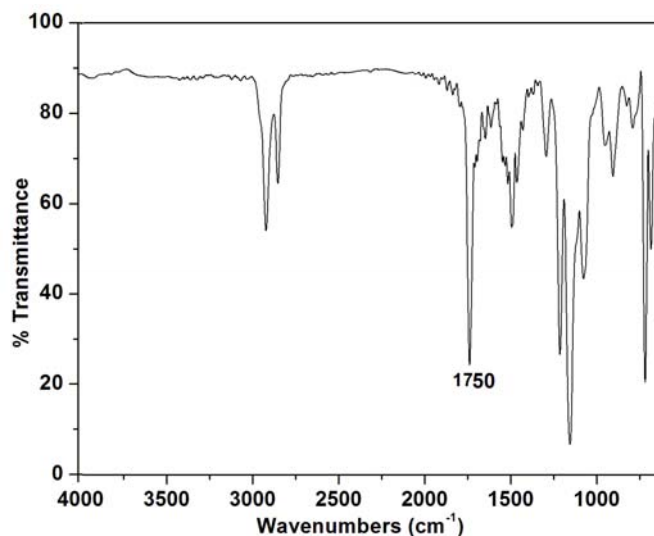
Figure 7b.1 FT-IR spectrum (film) of polyester (PES-I) based on 2-pentadecylbenzene-1,4-diol and isophthalic acid

^{1}H-NMR spectrum of polyester derived from 2-pentadecylbenzene-1,4-diol and isophthalic acid along with assignment is depicted in **Figure 7b.2.**
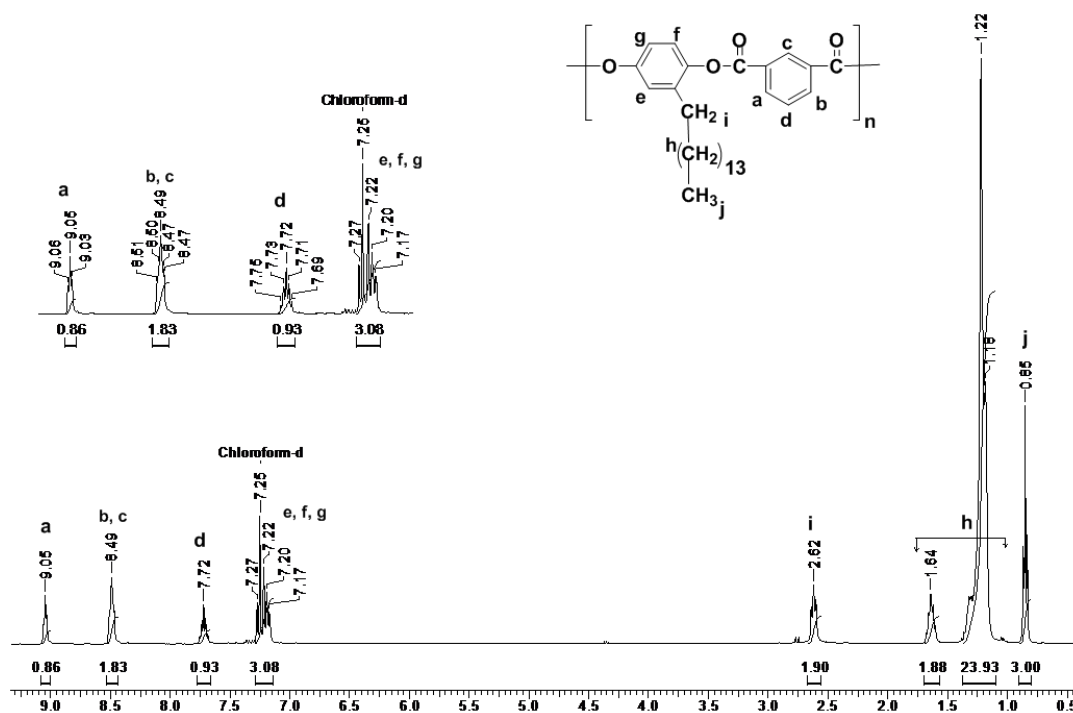
Figure 7b.2 ^{1}H-NMR spectrum (CDCl$_3$) of polyester derived from 2-pentadecylbenzene-1,4-diol and isophthalic acid

^{1}H-NMR spectrum of polyester derived from 2-pentadecylbenzene-1,4-diol and isophthalic acid showed the presence of a triplet at 9.05 δ, ppm for aromatic proton 'a' of isophthalic acid while aromatic protons 'b and c' displayed multiplet in the range 8.47- 8.51 δ, ppm. The aromatic proton 'd' appeared as multiplet in the range 7.69-7.75 δ, ppm. The aromatic protons of 2-pentadecylbenzene-1,4-diol appeared in the range 7.17- 7.27 δ, ppm. The benzylic methylene protons 'i' exhibited a triplet at 2.62 δ, ppm while the other methylene protons 'h' appeared in the range 1.18 - 1.64 δ, ppm. Methyl group protons 'j' appeared as a triplet at 0.85 δ, ppm.

^{13}C-NMR spectrum of polyester derived from 2-pentadecylbenzene-1,4-diol and isophthalic acid along with assignment is presented in **Figure 7b.3.** The assignment of carbon atoms was confirmed by the corresponding DEPT spectrum.
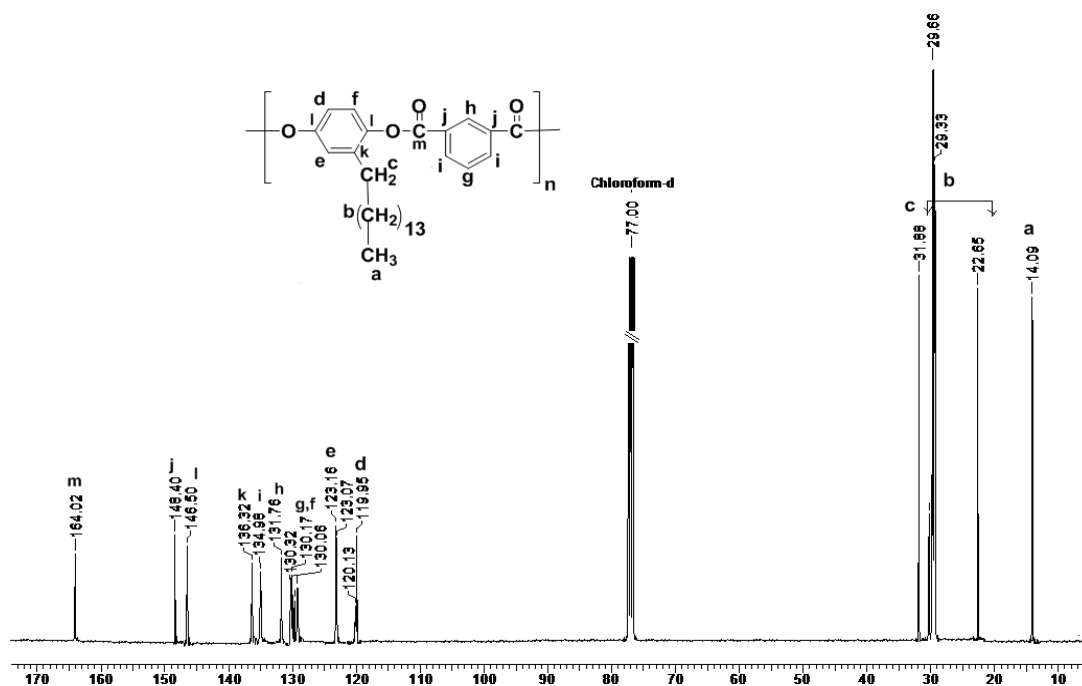
Figure 7b.3 **¹³C-NMR spectrum (CDCl₃) of polyester derived from 2-pentadecylbenzene-1,4-diol and isophthalic acid**

The carbonyl carbons 'm' exhibited a signal at 164.02δ, ppm and quaternary carbons appeared in the range 136.32- 148.40 δ, ppm.

7b.4.3   Solubility measurements

The solubility of polyesters was tested at 3 % (w/v) concentration in various organic solvents and the data is summarized in **Table 7b.2.**

Table 7b.2 Solubility data of polyesters derived from 2-pentadecylbenzene-1,4-diol and aromatic diacids[a]

Polyester		DMAC	NMP	DMF	DMSO	m-Cresol	CHCl₃	THF	Pyridine	Nitrobenzene	Acetone
PES-I		+-	+	--	+-	++	++	++	++	++	--
PES-II		+-	+	--	+-	+	++	++	++	++	--
PES-III		--	+-	--	--	+	--	+-	+	+	--

[a] --, Insoluble; +- partially soluble or swollen; + soluble on heating; ++, soluble at room temperature.

PES-I and **PES-II** derived from isophthalic acid and a 50:50 mol % mixture of isophthalic acid and terephthalic acid were soluble at room temperature in organic solvents such as CHCl$_3$, THF, *m*-cresol, pyridine and nitrobenzene. **PES-III** derived from terephthalic acid was soluble in *m*-cresol, pyridine and nitrobenzene upon heating. The reference polyesters derived from hydroquinone and terephthalic acid or isophthalic acid have been reported to be insoluble in the above mentioned solvents.[32] The improved solubility **PES-I** and **PES-II** could be attributed to the co-operative effect of weakening of the intermolecular interactions and entropy effect due to pentadecyl chains, and lowering the regularity and molecular ordering due to *meta*-linkages of isophthalic acid moiety.

7b.4.4 X-Ray diffraction studies

X-Ray diffractograms of polyesters derived from 2-pentadecylbenzene-1,4-diol and aromatic diacids are reproduced in **Figure 7b.4**.
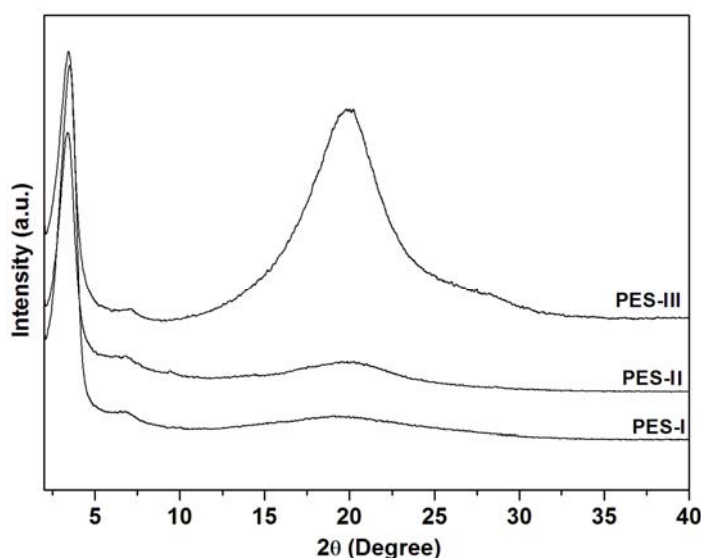
Figure 7b.4 X-Ray diffractograms of polyesters derived from 2-Pentadecylbenzene-1,4-diol and aromatic diacids

X-Ray diffractograms of polyesters exhibited a broad halo at about $2\theta \approx 20^o$ in the wide angle region indicating that the polymers are amorphous in nature. In addition to this, polyesters exhibited sharp reflections in the small-angle region at $2\theta \approx 3^o$. These peaks are characteristic of typical layered structures resulting from ordered packing of the pentadecyl chains.[33,34] Berger and Ballauff[35] reported such low angle peaks for a series of polyesters containing 2-alkyl-1,4-phenylene terephthalate repeat units in which long alkyl chain contains carbon atoms from 6 to 12.

7b.4.5   Thermal properties

Thermal stability of polyesters was determined by TGA at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. TG curves of polyesters are reproduced in **Figure 7b.5**.
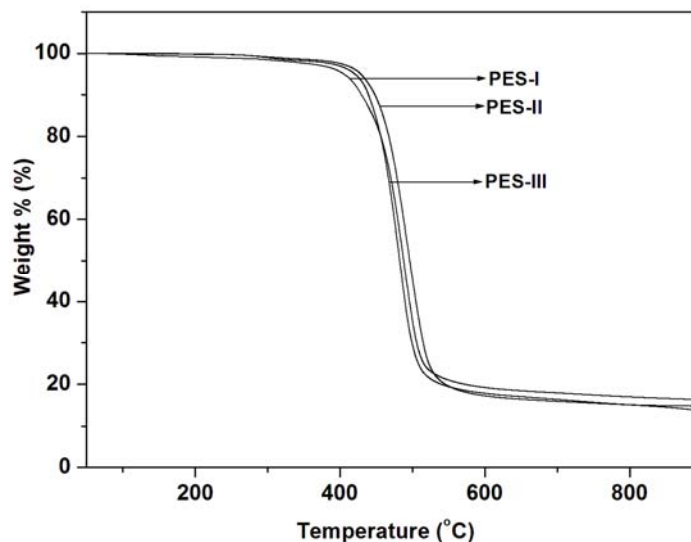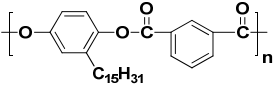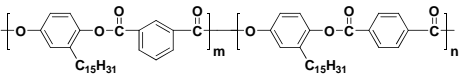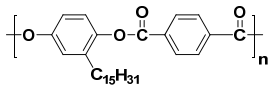
Figure 7b.5 TG curves of polyesters derived from 2-pentadecylbenzene-1,4-diol and aromatic diacids

Initial decomposition temperature (IDT), temperature at 10 % weight loss (T_{10}) and the weight residues at 900 ^{o}C were determined from thermograms and the data is given in **Table 7b.3**.

Table 7b.3 Thermal properties of polyesters derived from 2-pentadecylbenzene-1,4-diol and aromatic diacids

Polyester		IDT^{a} (^{o}C)	T_{10}^{b} (^{o}C)	T_g (^{o}C)	Weight residue at 900°C (%)
PES-I		430	440	88	13
PES-II		420	430	91	15
PES-III		440	450	95	16

a : Initial decomposition temperature, *b* : temperature at which 10% weight loss is observed.

T_{10} values obtained from TG curves were in the range of 430-450 ^{o}C for polyesters indicating their good thermal stability. The weight residues of polyesters when heated to 900 ^{o}C, in nitrogen were in the range 13-16 %.

DSC curves of polyesters are reproduced in **Figure 7b.6** and T_g values obtained from the second heating scans of polyester samples at a heating rate of 20 ^{o}C/minute are listed in **Table 7b.3**.
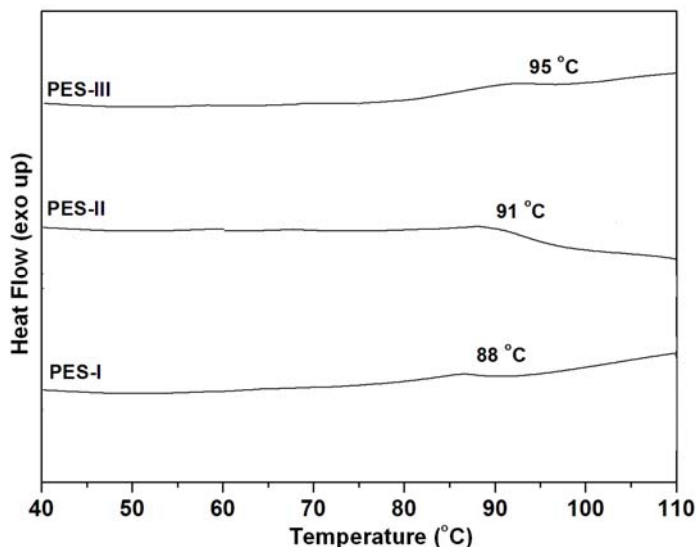
Figure 7b.6 DSC curves of polyesters derived from 2-pentadecylbenzene-1,4-diol and aromatic diacids

T_g values of polyesters containing pendent pentadecyl chains were in the range 88-95 ^{o}C. Poly(1,4-phenylene terephthalate) derived from hydroquinone and terephthalic acid is reported to possess a T_g value of 267 ^{o}C whereas poly(1,4-phenylene isophthalate) derived from hydroquinone and isophthalic acid exhibited a melting transition at 392 ^{o}C. [36, 37] This result indicated that the introduction of flexible pentadecyl chains along the polymer backbone decreases the rigidity of the polymer by increasing the number of degrees of freedom available. Thus, pendent pentadecyl chains along the backbone of polymers are thought to act as an "internal plasticizer". A large window between glass transition temperature and polymer degradation temperature was observed which gives an opportunity for these polyesters to be melt-processed or compression molded.

It is reported in the literature that, polyesters derived from monosubstituted hydroquinones exhibited a multiphase behavior. For example, Majunsz et al[38, 39] demonstrated that poly(2-*n*-alkyl-1,4-phenylene terephthalate)s were liquid crystalline and had melting temperature in the range 217- 300 ^{o}C when the alkyl substituent attached to the hydroquinone moiety ranged from hexyl to dodecyl. Also, it was reported that, poly(*p*-phenylene isophthalate) melts directly to the isotropic liquid phase.[40] The study of phase behavior depends upon several factors including the thermal history, the molecular weight and the size of alkyl substituent in the polymer. Polyesters containing pendent pentadecyl chains could be perspective candidates for the phase behavior study; however, such study is beyond the scope of this thesis.

7b.5   Conclusions

1. A series of new aromatic polyesters containing pendent pentadecyl chains was synthesized by diphenylchlorophosphate-activated direct polycondensation of 2-pentadecylbenzene-1,4-diol and aromatic diacids.

2. Inherent viscosities of polyesters were in the range 0.47-0.53 dL/g indicating formation of medium molecular weight polymers.

3. Polyesters **PES-I** and **PES-II** were soluble at room temperature in organic solvents such as $CHCl_3$, THF, *m*-cresol, pyridine and nitrobenzene. **PES-III** derived from rigid diacid was soluble in *m*-cresol, pyridine and nitrobenzene upon heating. This indicates that the incorporation of pendent flexible pentadecyl chains leads to improvement in solubility of polyesters.

4. Tough, transparent and flexible films of **PES-I** and **PES-II** could be cast from their solution in $CHCl_3$.

5. WAXD patterns showed that polyesters containing pendent 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 polyesters were in the range 430-450 °C indicating the good thermal stability of polymers.

7. DSC analysis showed that the attached pentadecyl side chain induced the depression of T_g (88-95 ^{o}C).

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Chapter 8

Summary and Conclusions

8.1   Summary and Conclusions

Irreversible consumption of carbon sources by humankind resulted in diminishing reserves of fossil fuels and global warming by CO_2 emission. This issue has prompted a shift of economy to replace fossil-based resources with renewable and sustainable ones. In this context, cashew nut shell liquid (CNSL) has received significant attention as a renewable resource material.

The aim of the present thesis was to utilize CNSL as a starting material to design and synthesize various difunctional condensation monomers. Another objective was to synthesize high performance polymers *viz.,* polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and polyesters containing pendent flexible pentadecyl chains and to investigate the effect of incorporation of pentadecyl chains on the solubility and thermal properties of the polymers.

Nine new difunctional monomers containing pendent pentadecyl chain were synthesized utilizing CNSL as starting material *viz*;

     a.   4-Pentadecylbenzene-1,3-diamine,

     b.   *N,N'*-(4-Pentadecyl-1,3-phenylene)bis(4-aminobenzamide)

     c.   *N,N'*-(4-Pentadecyl-1,3-phenylene)bis(3-aminobenzamide)

     d.   2,4-Diisocyanato-1-pentadecylbenzene

     e.   3,5-Diamino-4'-pentadecyl benzophenone,

     f.   3,5-Diamino-*N*-(4-pentadecylphenyl)benzamide,

     g.   2,2'(4-Pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid),

     h.   2-Pentadecylbenzene-1,4-diol, and

     i.   4-Methoxy-6-pentadecylisophthalonitrile

The most important aspect in designing of monomers was the presence of flexible linear pentadecyl chain. The incorporation of pentadecyl chain along the polymer backbone aids in improvement in the polymer processability/ solubility.

All the monomers and intermediates involved in their synthesis were characterized by spectroscopic techniques such as FT-IR and NMR spectroscopy and elemental analyses. These difunctional monomers were utilized for the synthesis of a variety of high performance polymers such as polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and polyesters. The effects of incorporation of pendent pentadecyl chains on solubility and thermal properties of the polymers were evaluated.

4-Pentadecylbenzene-1,3-diamine was polycondensed with commercially available aromatic dianhydrides by a one-step solution polycondensation in *m*-cresol, to obtain a series of polyimides containing pendent pentadecyl chains. Inherent viscosities of polyimides were in the range 0.33-0.67 dL/g indicating formation of medium to reasonably high molecular weight

polymers. This was further supported by GPC measurements which gave M_n and polydispersities (M_w/M_n) in the range 14,700 – 52,200 and 1.9 - 2.2, respectively. Polyimides were soluble at room temperature in polar solvents such as DMAc, NMP, *m*-cresol as well as in common organic solvent such as CHCl$_3$. The presence of C$_{15}$ alkyl chain disrupted the packing of polymer chains, as well as provided the additional 'handle' for interaction with solvents. Tough, transparent and flexible films could be cast from the solution of polyimides in CHCl$_3$. Wide angle X-ray diffraction patterns showed that polyimides containing pendent pentadecyl chains were amorphous in nature. Layered structure formation was observed due to the packing of pentadecyl chains in the polymer backbone. T_{10} values for polyimides were in the range 470-480 °C indicating the good thermal stability of polymers. DSC analysis showed that the attached pentadecyl side chain induced the depression of T_g (158-206 ^{o}C). A large window between glass transition temperature (158-206 ^{o}C) and initial decomposition temperature (470-480 °C) was observed which gives an opportunity for these polyimides to be melt-processed or compression molded. Overall, internal plasticization effect of the pentadecyl chain was shown to be effective in achieving processable polyimides.

New polyamides containing pendent pentadecyl chains were synthesized by the direct polycondensation of 4-pentadecylbenzene-1,3-diamine with various aromatic diacids *viz.,* biphenyl-4,4'dicarboxylic acid, 4,4'-oxybisbenzoic acid, terephthalic acid and isophthalic acid by Yamazaki-Higashi reaction (phosphorylation reaction). Inherent viscosities of polyamides were in the range 0.35-0.56 dL/g and polyamides could be cast into tough, transparent and flexible films from DMAc solution. Most of the polyamides were found to be soluble in DMAc, DMF, NMP, pyridine and *m*-cresol at room temperature or upon heating. This indicates that the incorporation of pendent flexible pentadecyl chains leads to a significant improvement in solubility of polyamides. Wide angle X-ray diffraction patterns indicated that polyamides containing pendent pentadecyl chains were amorphous in nature. X-Ray diffractograms of polyamides showed sharp reflections in the small-angle region ($2\theta \approx 3^o$) characteristics of formation of layered structure arising from packing of pentadecyl chains. T_{10} values for polyamides were in the range 430-460 °C indicating good thermal stability of polyamides. Polyamides showed glass transition temperatures in the range 169-215 ^{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 and also increases the free volume, thereby increasing segmental mobility, thus resulting in a reduction in the T_g. A large difference between glass transition (169-215 ^{o}C) and initial decomposition temperature (410-445 ^{o}C) was observed which offers these polyamides a broad processing window.

A series of new poly(azomethine)s containing pendent pentadecyl chains was synthesized by solution polycondensation of 4-pentadecylbenzene-1,3-diamine with aromatic

dialdehydes *viz.*, terephthaldehyde, isophthaldehyde and a 50:50 mol % mixture of terephthaldehyde and isophthaldehyde. Inherent viscosities of poly(azomethine)s were in the range 0.33-0.38 dL/g indicating formation of medium molecular weight polymers. Poly(azomethine)s containing pendent pentadecyl chains were found to be soluble in $CHCl_3$, THF, *m*-cresol and pyridine at room temperature or upon heating. Transparent, flexible and stretchable films of the poly(azomethine)s could be cast from $CHCl_3$ solution. Wide angle X-ray diffraction patterns indicated that poly(azomethine)s containing pendent pentadecyl chains were amorphous in nature. The formation of layered structure was observed due to the packing of pentadecyl chains. T_{10} values for poly(azomethine)s were in the range 425-440 °C indicating good thermal stability. T_g values of poly(azomethine)s were in the range 16-55 °C. A large difference in T_g and decomposition temperature of poly(azomethine)s offers a large processing window. Poly(azomethine)s were characterized by optical band gap values (E_g) and they were found to be in the range 2.82-3.10 eV, which indicates their potential application in photovoltaic devices.

A series of new poly(amideimide)s was synthesized by polycondensation of *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) and *N,N'*-(4-pentadecyl-1,3-phenylene)bis(3-aminobenzamide) with four commercially available aromatic dianhydrides, *viz.*, pyromellitic dianhydride, 4,4'-biphenyltetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride in DMAc employing conventional two-step method *via* poly(amic acid) intermediate followed by thermal imidization. Reference poly(amideimide)s were synthesized by polycondensation of *N,N'*-(1,3-phenylene)bis(4-aminobenzamide) and *N,N'*-(1,3-phenylene)bis(3-aminobenzamide) with the same aromatic dianhydrides. Inherent viscosities of poly(amideimide)s containing pendent pentadecyl chains were in the range 0.37-1.23 dL/g in DMAc at 30 ± 0.1 °C indicating the formation of medium to high molecular weight polymers. Poly(amideimide)s containing pendent pentadecyl chains were found to be soluble in DMAc, NMP, DMF, pyridine and could be cast into transparent, flexible and tough films from their DMAc solution. Wide angle X-ray diffraction patterns exhibited broad halo indicating that the polymers were essentially amorphous in nature. X-Ray diffractograms also displayed sharp reflection in the small angle region ($2\theta \approx 3°$) for poly(amideimide)s containing pentadecyl chains indicating the formation of layered structure arising from packing of flexible pentadecyl chains. T_g values observed for reference poly(amideimide)s were in the range 331-275 °C and those for poly(amideimide)s containing pendent pentadecyl chains were in the range 185-286 °C indicating a large drop in T_g owing to the "internal plasticization" effect of pentadecyl chains. The temperature at 10 % weight loss (T_{10}), determined by TGA in nitrogen atmosphere, were in the range 460-480 °C indicating their good thermal stability.

New poly(esterimide)s containing pendent pentadecyl chains were synthesized from 2,2'-(4-pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid), containing preformed imide rings and pentadecyl chain by the diphenylchlorophosphate-activated direct polycondensation with five commercially available bisphenols, *viz.*, 4,4'-isopropylidenediphenol, 4,4'-(hexafluoroisopropylidene) diphenol, 4,4'-oxydiphenol, 4,4'-biphenol and 4,4'-(9-fluorenylidene) diphenol. Inherent viscosities of poly(esterimide)s were in the range 0.54-0.83 dL/g indicating formation of medium to reasonably high molecular weight polymers. Poly(esterimide)s containing pendent pentadecyl chains were soluble in polar solvents such as NMP, DMAc, *m*-cresol as well as in common organic solvent such as $CHCl_3$. Tough, transparent and flexible films of poly(esterimide)s could be cast from their $CHCl_3$ solutions. Wide angle X-ray diffraction patterns showed that poly(esterimide)s containing pendent pentadecyl chains were amorphous in nature. A loosely developed layered structure formation was observed due to the packing of pentadecyl chains. T_{10} values for poly(esterimide)s were in the range 450-470 °C indicating their good thermal stability. T_g values of poly(esterimide)s containing pentadecyl chains was in the range 145-198 °C.

A series of new aromatic polyesters was synthesized from 2-pentadecylbenzene-1,4-diol and aromatic diacids, *viz.*, isophthalic acid, a 50:50 mol % mixture of isophthalic acid terephthalic acid and terephthalic acid by diphenylchlorophosphate-activated direct polycondensation. Inherent viscosities of polyesters derived from isophthalic acid and a 50:50 mol % mixture of isophthalic acid terephthalic acid were 0.53 and 0.51 dL/g, respectively and were soluble at room temperature in organic solvents such as $CHCl_3$, THF, *m*-cresol, pyridine and nitrobenzene. Polyester derived from terephthalic acid was soluble in *m*-cresol, pyridine and nitrobenzene upon heating. Wide angle X-ray diffraction patterns showed that polyesters containing pendent pentadecyl chains were amorphous in nature. X-Ray diffractograms also displayed sharp reflection in the small angle region ($2\theta \approx 3°$) indicating the formation of layered structure arising from packing of flexible pentadecyl chains. T_{10} values for polyesters were in the range 430-450 °C indicating their good thermal stability. The glass transition temperature of polyesters containing pentadecyl chains was in the range 88-95 °C. A large difference between glass transition (88-95 °C) and initial decomposition temperature (420-440 °C) was observed which offers these polyesters a broad 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 was 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 pendent 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.

8.2   Perspectives

The present work on design and synthesis of difunctional monomers starting from CNSL and processable high performance 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.

- 1,5-Dibromo-2-methoxy-4-pentadecylbenzene 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. The dibromo compound could easily be converted into corresponding diphenol and diladehyde, which by themselves represent valuable monomers for synthesis of a host of high performance polymers.

- 4-Methoxy-6-pentadecylisophthalonitrile could be easily converted into corresponding diacid or diladehyde, which by themselves represent valuable monomers for synthesis of a host of high performance polymers such as polybenzimidazoles, polybenzoxazoles, polyamides, poly(1,3,4-oxadiazole)s, etc.

- 2,4-Diisocyanato-1-pentadecylbenzene is a potentially useful monomer for the synthesis of polyurethanes and polyureas.

- 3,5-Diamino-4'-pentadecylbenzophenone and 3,5-diamino-*N*-(4-pentadecyl phenyl) benzamide are useful monomers for the synthesis of a host of high performance polymers. It would be interesting to study the structure-property relationship of the derived polymers since the polymers would be differing only in the linkages (carbonyl and amide).

- The primary focus of the present work was to illustrate the influence of pendent pentadecyl chains on the solubility behavior and thermal properties of polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s and polyesters. 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 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.

- The synthesized polyimides containing pendent pentadecyl chains could be interesting candidates as alignment layers for Liquid Crystal Display (LCD) applications.

- The synthesized poly(azomethine)s containing pendent pentadecyl chains could be useful for photovoltaic application.

- Polyesters containing pendent pentadecyl chains could be interesting candidates for studying liquid crystallinity behavior.

Synopsis

Synopsis of the Thesis Entitled

"Difunctional Monomers Starting from Cashew Nut Shell Liquid (CNSL) and High Performance Polymers Therefrom "

Introduction:

The manufacture of edible goods from vegetable sources quite often causes the production of a large amount of waste. The disposal of waste is a serious environmental problem but, at the same time, these materials can be precious resources of organic renewable substrates, which, regrettably, are frequently lost. The recovering of such compounds by transformation into valuable chemicals represents a 'double green' action since recycling a waste goes along with the elimination of an expensive disposal. In this respect, cashew nut shell liquid (CNSL)- a renewable resource material- obtained as a by-product of cashew processing industry, holds considerable promise as a source of unsaturated hydrocarbon phenol, an excellent monomer for polymer production.[1] The extraction, chemistry, and composition of CNSL (*Anacardium occidentale* L.) has been well documented.[2] Considerable attention from polymer scientists throughout the world is devoted to utilize it's potential attributes as a substitute for petrochemical derivatives.[3,4] CNSL has already found use in phenolic resins in break lining, surface coatings and other miscellaneous applications.[2-9] Of late, it has been used in the preparation of many speciality materials such as liquid crystalline polyesters,[6,7] cross-linkable polyphenols,[8] polyurethanes[10-12] and a range of other speciality polymers and additives.[2]

The most attractive aspect of CNSL as a starting material is it's low cost and abundant availability. The materials / products based on CNSL exhibit flexibility due to the presence of long hydrocarbon / alkenyl 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[10-16] 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.

High performance / high temperature polymers such as polyimides, polyamides, poly(amideimide)s, poly(azomethine)s, etc exhibit unique combination of properties such as high thermal stability, high mechanical properties and excellent chemical resistance. These polymers find applications in aerospace, automobile and electronic industries. The high regularity and high rigidity of backbones of the high performance polymers results in strong interchain interactions, high melting points, high crystallinity and low solubility, thus their processing becomes difficult. Several approaches have been utilized[17] to improve the processability of high performance polymers such as introduction of kinks or flexible units in the main chain,[18-21] use of asymmetric

monomers,[22-25] introduction of bulky and cardo groups[26,27] and replacing the conventional monomers with ones containing pendent groups.[28,29] 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.[30] 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.[31,32]

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- a renewable resource material. The monomers were designed with a view to incorporate structural features such as: i) the presence of *meta*-catenation in the polymer backbone, and ii) the incorporation of pendent pentadecyl chains along the polymer backbone for improving processability *via* "internal plasticization" effect. Another objective of the present work was to synthesize high performance polymers containing pendent 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 diamines, diisocyanate, diacid, diphenol and dinitrile containing pendent flexible pentadecyl chain starting from CNSL.

➢ Synthesis of aromatic polyimides, polyamides, poly(amideimide)s, poly(azomethine)s, poly(esterimide)s and polyesters containing pendent pentadecyl chains.

➢ To study the effect of incorporation of pendent pentadecyl chains on polymer properties such as solubility and thermal behavior.

The thesis has been divided into the following eight chapters.

Chapter 1:   Introduction and Literature Survey

This chapter deals with brief overview on CNSL- a renewable resource material, with emphasis on monomers derived from CNSL and polymers therefrom. A comprehensive review of literature on polymers, *viz*., polyimides, polyamides, poly(amideimide)s, poly(azomethine)s, poly(esterimide)s and polyesters covering methods of synthesis, structure-property relationship, etc., is also presented.

Chapter 2:   Scope and Objectives

This chapter discusses scope and objectives of the thesis

Chapter 3:   Synthesis and Characterization of Condensation Monomers Starting from Cashew Nut Shell Liquid (CNSL)

This chapter describes synthesis of difunctional monomers containing pendent pentadecyl chain, *viz.,*

a.   4-Pentadecylbenzene-1,3-diamine,

b.   *N,N'*-(4-Pentadecyl-1,3-phenylene)bis(4-aminobenzamide)

c.   *N,N'*-(4-Pentadecyl-1,3-phenylene)bis(3-aminobenzamide)

d.   2,4-Diisocyanato-1-pentadecylbenzene

e.   3,5-Diamino-4'-pentadecyl benzophenone,

f.   3,5-Diamino-*N*-(4-pentadecylphenyl)benzamide,

g.   2,2'(4-Pentadecyl-1,3-phenylene)bis(1,3-dioxoisoindoline-5-carboxylic acid),

h.   2-Pentadecylbenzene-1,4-diol, and

i.   4-Methoxy-6-pentadecylisophthalonitrile

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

Chapter 4:   Synthesis and Characterization of Polyimides Based on 4-Pentadecylbenzene-1,3-diamine

This chapter describes:

i.   Synthesis of polyimides containing pendent pentadecyl chains based on 4-pentadecylbenzene-1,3-diamine and commercially available aromatic dianhydrides, *viz.*, 4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA), and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6-FDA), by one-step polycondensation in *m*-cresol.

ii.   Polyimides were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis, DSC and UV-Visible spectroscopy.

Chapter 5: Synthesis and Characterization of Polyamides and Poly(azomethine)s Containing Pendent Pentadecyl Chains

This chapter is sub-divided into two sections:

Chapter 5a: **Synthesis and Characterization of Polyamides Based on 4-Pentadecyl benzene-1,3-diamine**

This chapter deals with:

i. Synthesis of polyamides containing pendent pentadecyl chains by polycondensation of 4-pentadecylbenzene-1,3-diamine with commercially available aromatic diacids, *viz*., biphenyl-4,4'dicarboxylic acid, 4,4'-oxybisbenzoic acid, terephthalic acid and isophthalic acid.

ii. Polyamides were characterized by inherent viscosity measurements, solubility tests, IR and ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC.

Chapter 5b: **Synthesis and Characterization of Poly(azomethine)s Based on 4-Pentadecyl benzene-1,3-diamine**

This chapter describes:

i. Synthesis of poly(azomethine)s containing pendent pentadecyl chains by polycondensation of 4-pentadecylbenze-1,3-diamine with commercially available aromatic dialdehydes, *viz.,* terephthaldehyde, isophthaldehyde and 50:50 mol% mixture of terephthaldehyde and isophthaldehyde.

ii. Poly(azomethine)s were characterized by inherent viscosity measurements, solubility tests, IR and ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis, DSC, UV-Visible and photoluminescence spectroscopy.

Chapter 6: **Synthesis and Characterization of Poly(amideimide)s Containing Pendent Pentadecyl Chains**

This chapter describes:

i. Synthesis of poly(amideimide)s containing pendent pentadecyl chains by polycondensation *N,N'*-(4-pentadecyl-1,3-phenylene) bis(4-aminobenzamide) and *N,N'*-(4-pentadecyl-1,3-phenylene) bis(3-aminobenzamide) with commercially available aromatic dianhydrides, *viz.*, PMDA, BPDA, ODPA, and 6-FDA in *N,N*-dimethylacetamide employing conventional two step method *via* poly(amic acid) intermediate followed by thermal imidization. Reference poly(amideimide)s were synthesized by polycondensation of *N,N'*-(1,3-phenylene) bis(4-

aminobenzamide) and *N,N'*-(1,3-phenylene) bis(3-aminobenzamide) with the same aromatic dianhydrides.

ii. Poly(amideimide)s were characterized by inherent viscosity measurements, solubility tests, IR and ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC.

Chapter 7:   Synthesis and Characterization of Poly(esterimide)s and Polyesters Containing Pendent Pentadecyl Chains

This chapter is sub-divided into two sections:

Chapter 7a: Synthesis and Characterization of Poly(esterimide)s Based on 2,2'(4-Pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid)

This chapter describes:

i. Synthesis of poly(esterimide)s containing pendent pentadecyl chains by diphenylchlorophosphate-activated direct polycondensation of 2,2'(4-pentadecyl-1,3-phenylene) bis(1,3-dioxoisoindoline-5-carboxylic acid) with commercially available bisphenols, *viz.*, 4,4'-isopropylidenediphenol, 4,4'-(hexafluroisopropylidene) diphenol, 4,4'-oxydiphenol, 4,4'-biphenol and 4,4'-(9-fluorenylidene) diphenol.

ii. Poly(esterimide)s were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC.

Chapter 7b: Synthesis and Characterization of Polyesters Based on 2-Pentadecylbenzene-1,4-diol

This chapter describes:

i. Synthesis of aromatic polyesters based on 2-pentadecylbenzene-1,4-diol and commercially available aromatic diacids, *viz.*, isophthalic acid, terephthalic acid and 50:50 mol % mixture of isophthalic acid and terephthalic acid, by diphenylchlorophosphate-activated direct polycondensation.

ii. Polyesters were characterized by inherent viscosity measurements, solubility tests, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC.

Chapter 8:   Summary and Conclusions

This chapter summarizes the results and describes salient conclusions of the investigations reported in this thesis.

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List of Publications

1. Synthesis and characterization of new polyimides containing pendent pentadecyl chains.
    Nilakshi V. Sadavarte, Mahadeo Halhalli, C.V. Avadhani, , Prakash P. Wadgaonkar.
    Eur. Polym. J. **2009**, 45, 582.

2. Regularly alternating poly(amideimide)s containing pendent pentadecyl chains: Synthesis and characterization.
    Nilakshi V. Sadavarte, C.V. Avadhani, Parimal V. Naik, Prakash P. Wadgaonkar.
    Eur. Polym. J. **2010**, 46, 1307.

3. Synthesis and characterization of new organosoluble polyamides and polyazomethines containing pendent pentadecyl chains.
    Nilakshi V. Sadavarte, C.V. Avadhani, Prakash P. Wadgaonkar.
    High Perform. Polym. **2011**, 23(7), 494.

4. New organosoluble aromatic poly(esterimide)s containing pendent pentadecyl chains: Synthesis and characterization.
    Nilakshi V. Sadavarte, C.V. Avadhani, Prakash P. Wadgaonkar.
    (C*ommunicated*)

5. Synthesis and Characterization of new aromatic polyesters containing pendent pentadecyl chains.
    Nilakshi V. Sadavarte, Sachin S. Patil, C.V. Avadhani, Prakash P. Wadgaonkar.
    (To be C*ommunicated*)