EXPLOITATION OF CASHEW NUT SHELL LIQUID AS A STARTING MATERIAL FOR THE SYNTHESIS OF MONOMERS USEFUL IN THE PREPARATION OF THERMALLY STABLE POLYMERS

A thesis submitted to the

SAVITRIBAI PHULE PUNE UNIVERSITY

for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

BHAUSAHEB V. TAWADE

Research Guide
DR. PRAKASH P. WADGAONKAR

Polymers and Advanced Materials Laboratory,
Polymer Science and Engineering Division,
CSIR-National Chemical Laboratory,
PUNE 411 008
INDIA

June 2015

To,

Late

Aajee (Grandmother),

Bapu (Uncle)

and Kaku (Aunty)

सीएसआयआर–राष्ट्रीय रासायनिक प्रयोगशाला
(वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद)
डॉ. होमी भाभा मार्ग, पुणे – 411 008. भारत
CSIR-NATIONAL CHEMICAL LABORATORY
(Council of Scientific & Industrial Research)
Dr. Homi Bhabha Road, Pune - 411008. India

Certificate of the Guide

Certified that the work included in the thesis entitled: **"Exploitation of Cashew Nut Shell Liquid as a Starting Material for the Synthesis of Monomers Useful in the Preparation of Thermally Stable Polymers"**, submitted by **Mr. Bhausaheb V. Tawade** was carried out under my supervision/guidance. Such material as obtained from other sources has been duly acknowledged in the thesis.

PPWadgaonkar

June 2015
Pune

Dr. Prakash P. Wadgaonkar
Chief Scientist,
Polymers and Advanced Materials Laboratory
Polymer Science and Engineering Division
CSIR-National Chemical Laboratory
Pune-411 008, India.

DECLARATION

I hereby declare that all the experiments embodied in the thesis entitled "**Exploitation of Cashew Nut Shell Liquid as a Starting Material for the Synthesis of Monomers Useful in the Preparation of Thermally Stable Polymers**", submitted for the degree of Doctor of Philosophy in Chemistry, to the Savitribai Phule Pune University has been carried out by me at the Polymer Science and Engineering Division, CSIR-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.

June 2015
Pune

Bhausaheb V. Tawade
Senior Research Fellow
Polymers and Advanced Materials Laboratory
Polymer Science and Engineering Division
CSIR-National Chemical Laboratory
Pune-411 008, India.

Acknowledgement

My Ph.D. dissertation journey has been very special part of my life and it is about to fruition through support of some very special people. I would like to appreciate them for being so special to me.

*The first and foremost, I am deeply grateful to my research guide, **Dr. Prakash P. Wadgaonkar** for his constant support and able guidance during my Ph.D. tenure. My everlasting gratitude goes to him for the immense help, kindness, encouragement and believing in me and making things happen.*

I would like to thank CSIR, New Delhi for the award of Junior Research fellowship and The Director, CSIR-NCL for giving opportunity and facilities to execute research work in the nation's prestigious institution. I owe my sincere thanks to former Director Dr. S. Sivaram, for sparking inspiration towards polymer science through stimulating lectures and discussions. I would also like to thank Dr. Ashish K. Lele, HOD, Polymer Science and Engineering Division, Dr. A. J. Varma and Dr. M. G. Kulkarni (former HODs Polymer Science and Engineering Division), for providing access to the divisional facilities. I am thankful to the NCL staff from Student Academic Office, Library, Medical Centre, Stores and Purchase section, Glass blowing section, Bills and Accounts section, DIRC and Engineering sections for their co-operation.

I wish to record my sincere gratitude towards Dr. N. N. Joshi and group members Manmath, Ravi and Revannath who introduced me to basic lessons in chemistry research and supported in my initial days at NCL.

I would like to thank Dr. P. R. Rajamohanan and group members Amol, Shrikant, Sanoop for valuable discussions, suggestions and help in NMR analysis.

I extend my gratitude towards Dr. C.V. Avadhani, Dr. Ashootosh Ambade, Mr. Anandrao Patil, Mr. Shamal Menon, Dr. Nilakshi Sadavarte, Dr. B. D. Sarwade, Dr. M. V. Badiger, Mrs. Deepa Dhoble, Dr. U. K. Kharul, Dr. Samir Chikkali, Mr. K. J. Raut, Dr. K. Guruswamy, Dr. Suresh Bhat, Dr. C. Ramesh, Dr. S. K. Asha, Dr. K. Krishnamoorthy, Dr. J. Nithyanandhan, Dr. B. B. Idge, Dr. S. B. Idge, Dr. N. N. Chavan, Dr. Neelima Bulakh, Mr. Saroj Jha, Mrs. Poorvi Purohit, Mrs. Sangeeta Hambir for their valuable guidance and help.

I would like to express special thanks to Dr. U. P. Mulik, C-MET, Pune, Prof. S. V Lonikar, Solapur University, Solapur, and Dr. U. K. Kharul, for valuable guidance from time to time.

I would like to mention gratitude towards Ex-PPWians, Rahul, Anjana, Pandurang, Snehalata, Arun (curing kinetics teacher), Arvind, Prakash (secondary mentor), Savita, Kishor, Ankush, Vijay, Ramchandra, Sushilkumar, Parimal, Sharad, Shivakumar, Anil, Mahadeo, Nagendra, Mahesh, Jagdish for their valuable suggestions and sharing their experience as PPW group member. I express special thanks to present labmates Indravadan, Nagendra, Naganath, Sachin Patil, Sachin Kuhire, Samadhan, Nitin Basutkar, Deepak, Deepshikha, Kavita, Vikas, Sachin Basutkar, Shymbho, Murugesan, Ashwini, Uday, Shraddha, Sayali (for gas permeation *studies), Rupali, Amol, Bharat, Nitin, Abhijeet, Aarti, Durgaprasad and Satyawan for their kindness and cheerful environment in the Lab.*

I am thankful to Mohan Mani and Yogesh Marathe for help in XRD analysis, Ralph Antao and Prashant Patil for DMA measurements, Pravin, Chayanika and Chitravel for study of opto-electronic properties, Chinmay, Nagesh, Rekha, Nisha, Shekhar, Swapnil, Prajeeta, Saibal, Pradip, Digmbar, Sandip Yanchalwal, Megha, Yogesh, Ajay, Maithili, Arul, Manik, Satej, Rajeshwari, Vivek, Sameer, Amruta, Samrudhi, Ravi Ghorpade, Anumon, Shahaji, Satej, Vijay, Bhausaheb, Bhushan, Sachin Mane, Rupesh, Anita, Bishnu and Anand for their assistance. I would like to thank Amit, Vrushali, Niharika, Subrashish and Tamal (members at room A-113) for peaceful and friendly ambiance at the time of the thesis writing.

I can never forget the assistance and helpful suggestions from Abhijeet Purude, Ganesh Kokate, Devendra Bhange, Datta Mhamane, Anil Suryawanshi, Prasad Wakchaure, Sharad Suryawanshi, Abasaheb, Satish Biradar, Nagesh Khupse, Bharat, Gurale, Ankush Bhise, Kedar R., Deepak J., Abhijeet K., Dhanraj, Pankaj, Malvi, Mangesh, Sandeep G., Kiran Patil, Digamber Shinde, Asif Shaikh, Swaroop, Umesh Kumar, Sumantra Valmik Shinde, Satish Badhade, Majid, Atul, Arun, Pavin, Sumit, Anand, Santosh, Sagar, Govinda, Dnyaneshwar, Nalinee, Krishanu, Shyam, Zhumur, Rajesh T, Chakadola, Mandakini, Raju, Ajay B, Narshimha K, Shivakumar B, Sanjeev K, Eldo M, Lenin R, Balanagalu, Bhogesh, Manoj, Venu, Achintya, Animesh, Arpan, Anjan, D Pati, Shaikat H, Tamas, Arjit, Chandan, Sharath, Manoj, Brijesh, Mritunjay and all friends at GJH and NCL family.

I would like to thank 8th TLEP 2011 friends, facebook friends, friends those are unseen, untalked in previous several years or in the past but still inspiring me to be a better person.

I would like to thank all my teachers in my entire acadamic journey from Z. P. School Dhanagarwadi to Shivaji University, Kolhapur for imbibing good morals and knowledge in me.

I would like to take this opportunuty to express gratefulness towards The Wadgonakars. Shubhangi Madam, Shivani, Ganesh Dada, Vibha Vahini, and Yash for love and support and welcoming me at anytime without hesitation.

I would like to thank my family. My mother-Aai (Suman), who taught me importance of hard work and politeness; my father-Aba (Vilas), who instilled ethics and spirituality in my heart; my elder brother Bhupal-Dada, who has always been an Ideal to me. Mandakini (Sister in law), Harsh and Shivam (nephews) for cheerful atmosphere at home, especially Harsh and Vahini who have been fulfilling my absence at the home from last five years. Further I would like to thank my Uncles, Aunties and Cousins. I am blessed with such a big and wonderful joint family and without their love and encouragements this dissertation would not have been completed.

Above all, I owe it all to Almighty God for granting me the wisdom, health and strength to undertake the dissertation task and enabling me to its completion.

Bhausaheb Vilas Tawade

Table of Contents

Chapter 1 Introduction and Literature Survey

Chapter 3 Synthesis and Characterization of Condensation Monomers Starting from CNSL

Chapter 4 Synthesis and Characterization of Polyesters Containing Ether Linkages and Pendent Pentadecyl Chains

Chapter 5 Synthesis and Characterization of Polyimides Containing Multiple Ether Linkages and Pendent Pentadecyl Chains

Chapter 6 Synthesis and Characterization of Polyhydrazides and Poly(1,3,4-oxadiazole)s Containing Multiple Ether Linkages and Pendent Pentadecyl Chains

Chapter 7 Synthesis and Characterization of Poly(arylene ether)s based on 3-Pentadecyl 4,4' Biphenol

Chapter 8 **Synthesis and Characterization of Thermosetting Resins Containing Pentadecyl Chains**

Chapter 8a **Synthesis and Characterization of Cyanate Ester Based on 4-(4-Hydroxyphenoxy)-3-pentadecylphenol**

Chapter 8b **Synthesis and Characterization of Bismaleimide Based on 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline**

Chapter 8c Synthesis and Characterization of Epoxy Resin Based on 4-(4-Hydroxyphenoxy)-3-pentadecylphenol

Chapter 9 Summary and Conclusions

Abstract

The replacement of petroleum-based materials by renewable bio-based materials is an interesting topic of research for academic and industrial scientists. The approaches concerning development of biobased-polymers include utilization of sugars, polysaccharides, vegetable oils, lignin, furans and so on.[1, 2] These renewable resources can be turned into viable macromolecular materials *via* a series of chemical transformations and thus could be potentially useful candidates for the replacement of both thermoplastics and thermosetting materials.

The overall objective of the present thesis was to design and synthesize a series of difunctional monomers using cashew nut shell liquid (CNSL)- an agricultural waste product-as a starting material and utilization of these monomers for synthesis of high performance/ thermally stable polymers. Towards this end, a series of difunctional monomers, *viz,* aromatic diamine, diacid, diphenol and dinitrile containing pendent flexible pentadecyl chain was synthesized starting from CNSL. These difunctional monomers were utilized for the synthesis of high performance polymers such as aromatic polyesters, polyimides, polyhydrazides, poly(1,3,4-oxadiazole)s and poly(arylene ether)s. Additionally, cyanate ester, bismaleimide and epoxy resin containing pendent pentadecyl chains were synthesized using selected difunctional monomers derived from CNSL. The effect of pendent pentadecyl chains on properties of polymers was investigated.

Chapter 1 describes a literature review on recent advances in the field of polymers from renewable resource materials with particular emphasis on aromatic difunctional monomers and polymers derived from hemicellulose, lignin and CNSL. A comprehensive review of the literature on high performance polymers, viz., polyesters, polyimides, poly(1,3,4-oxadiazole)s and poly(arylene ether)s covering the aspects such as methods of synthesis, structure property relationship, etc., are also included.

Chapter 2 describes scope and objectives of the thesis

Chapter 3 describes synthesis of new difunctional monomers containing pendent pentadecyl chain using 3-pentadecyl phenol as a starting material which in turn is obtained from CNSL. The following difunctional monomers were synthesized:

1. 4-(4-Formylphenoxy)-2-pentadecylbenzaldehyde
2. 4-(4-Hydroxyphenoxy)-3-pentadecylphenol
3. 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline

4. 4-(4-(4-(4-Carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid
5. 4-(4-(4-(4-(Hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide
6. 3-Pentadecyl 4,4' biphenol
7. 2, 2-Pentadecyl-[1,1'-biphenyl]-4,4'-diol
8. 4,4'-Dibromo 3-pentadecyl biphenyl
9. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid, and
10. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

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

Chapter 4 deals with synthesis and characterization of a series of aromatic (co)polyesters based on 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP) and aromatic diacid chlorides. A series of copolyesters was synthesized from a mixture of HPPDP and bisphenol-A (BPA) with terephthalic acid chloride using phase-transfer catalysed interfacial polycondensation. Inherent viscosities of (co)polyesters were in the range 0.70-1.21 dL/g and number average molecular weights, measured by GPC in chloroform with polystyrene as a standard, were in the range 16,000-48,300. **(**Co)polyesters were soluble in chloroform, dichloromethane, pyridine and *m*-cresol at room temperature and could be cast into tough, transparent and flexible films from chloroform solutions. Polyesters containing pendent pentadecyl chains showed broad halo in the wide angle region ($2\theta = \sim 20°$) which revealed their amorphous nature. T_{10} values for (co)polyesters were in the range 425-455 °C indicating their good thermal stability. A drop in Tg values (27-202 °C) and storage modulus (E') of (co)polyesters was observed due to the presence of flexible pentadecyl chains which act as packing disruptive groups.

Chapter 5 describes synthesis and characterization of polyetherimides containing pendent pentadecyl chains and multiple ether linkages based on 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy)aniline and commercially available aromatic dianhydrides namely 3,3',4,4'-oxydiphthalic anhydride (ODPA), 4,4'-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA) and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) using one-step solution polycondensation in *m*-cresol. Inherent viscosity of polyetherimides was in the range 0.66-0.70 dL/g, indicating formation of reasonably high molecular weight polymers. Polyetherimides were soluble in organic solvents such as chloroform, dichloromethane,

tetrahydrofuran, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, pyridine, *m*-cresol and dimethyl sulfoxide. Polyetherimides could be cast into tough, transparent and flexible films from chloroform solution. The non-symmetrical structure of multiring diamine resulted into constitutional isomerism in polyetherimdes as evidenced from ^{1}H NMR studies. X-Ray diffraction analysis showed that polyetherimides were amorphous in nature and a reflection in small angle region indicated layered packing of pentadecyl chains. T_g values of polyetherimides containing pendent pentadecyl chains were in the range 113-131 °C. Thus a significant drop in T_g was observed compared to analogous polyetherimides without pentadecyl chains. T_{10} values of polyetherimides were in the range 460-470 °C indicating their good thermal stability. The incorporation of pendent pentadecyl chains and flexible ether linkages increased gap between T_g and T_{10} values of polyetherimides and thus offered a wider processing window.

Chapter 6 embodies the synthesis and characterization of polyhydrazides and poly(1,3,4-oxadizole)s containing multiple ether linkages and pendent pentadecyl chains. The polyhydrazides were synthesized by polycondensation of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide (HPPPB) with aromatic diacid chlorides and were subsequently cyclized using $POCl_3$ to the corresponding poly(1,3,4-oxadiazole)s. Inherent viscosities of polyhydrazides and poly(1,3,4-oxadiazole)s were in the range 0.65-0.72 dL/g and 0.54-0.62 dL/g, respectively. Polyhydrazides were soluble in polar aprotic solvents viz., N,N-dimethylformamide, N,N-dimethylacetamide, pyridine, dimethyl sulfoxide and *m*-cresol whereas poly(1,3,4-oxadiazole)s were soluble in common organic solvents, such as chloroform, dichloromethane, and tetrahydrofuran. X-Ray diffractograms of both polyhydrazides and poly(1,3,4-oxadiazole)s exhibited a broad halo at $2\theta = 20°$ indicating amorphous nature and a reflection in small angle region ($2\theta = 2$-$3°$), characteristic of layered packing of pentadecyl chains. The T_{10} values for poly(1,3,4-oxadiazole)s were in the range 425-440 °C indicating their good thermal stability. The T_g values of polyhydrazides and poly(1,3,4-oxadiazole)s were in the range 92-103 °C and 175-192 °C, respectively. The lowering of T_g in polyhydrazides and poly(1,3,4-oxadiazole)s could be attributed to the presence of packing disruptive pendent flexible pentadecyl chains and flexiblizing ether linkages in the backbone. Poly(1,3,4-oxadiazole)s exhibited maximum UV-Vis absorption in the range 304-337 nm whereas maximum of fluorescence emission was in the range 380-394 nm in

chloroform solution. The optical band (E_g) values for poly(1,3,4-oxadiazole)s were found to be in the range 3.33-3.65 eV indicating their potential application in opto-electronic devices

Chapter 7 provides study on synthesis and characterization of poly(arylene ether)s containing biphenylene linkages in the backbone and pendent pentadecyl chains obtained by polycondensation of 3-pentadecyl biphenol with commercially available aromatic dihalides by nucleophilic aromatic substitution reaction. Poly(arylene ether)s exhibited inherent viscosities in the range 0.50-0.81 dL/g indicating formation of reasonably high molecular weight polymers. The number average molecular weights (M_n) measured by GPC were in the range 2.2 x 10^4 - 8.3 x 10^4 with polydispersity of 2.2. ^{1}H NMR studies of poly(arylene ether)s indicated the presence of constitutional isomerism which existed due to the non-symmetrical structure of 3-pentadecyl biphenol. Poly(arylene ether)s were soluble in common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. Tough, transparent and flexible films of poly(arylene ether)s could be cast from their chloroform solutions. X-Ray diffraction patterns showed halos over the range 2θ =15-25° and broad reflections in the small-angle region at about $2\theta \approx 3°$ indicating amorphous nature and layered pentadecyl chain packing, respectively. Poly(arylene ether)s exhibited T_g in the range 35-60 °C which are lower than that of analogous poly(arylene ether)s without pentadecyl chains. The lowering of T_g could be attributed to packing disruptive effect of flexible pendent pentadecyl chains. The 10% decomposition temperatures (T_{10}) of poly(arylene ether)s were in the range 410-455 °C, indicating their good thermal stability. The gas permeation study of poly(ether sulfone) containing pendent pentadecyl chains revealed moderate increase in permeability for helium, hydrogen and oxygen with lower permselectivity. However, there was large increase in permeability for carbon dioxide due to internal plasticizing effect of pentadecyl chains.

Chapter 8 is divided into three sections

Chapter 8a deals with synthesis, characterization and curing study of 4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene (HPPDPCN), containing ether linkage and pendent pentadecyl chain. HPPDPCN was synthesized from 4-(4-hydroxyphenoxy)-3-pentadecylphenol by Grigat and Putter method and was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The melting point of

HPPDPCN was found to be 31 °C, which is lower than that of bisphenol-A based cyanate ester (BPACN, MP = 84 °C). The non-isothermal curing kinetics of HPPDPCN was studied by DSC and the activation energy of uncatalyzed curing was found to be 108.06 KJ/mol.

Chapter 8b deals with synthesis, characterization, curing kinetics and thermal properties of 4, 4’-bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether (C15BMI). C15BMI was synthesized by the ring-opening addition reaction of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline with maleic anhydride followed by cyclodehydration of N,N-bismaleamic acid using acetic anhydride and sodium acetate. The structure of C15BMI was confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The melting point of C15BMI was found to be 90 °C, which is lower than that of 4,4’-bis(maleimido)diphenylether (ODABMI, M.P., 183 °C). 4, 4’-Bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether exhibited excellent solubility in common organic solvents such as chloroform, dichloromethane and tetrahydrofuran. Activation energy for curing of C15BMI was determined in non-isothermal curing mode using Coats-Redfern method and was found to be 75.32 KJ/mol. The T_{10} value of cured C15BMI resin was 430 °C indicating its good thermal stability.

Chapter 8c presents synthesis and characterization of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol. 4-(4-Hydroxyphenoxy)-3-pentadecylphenol was reacted with epichlorohydrin in the presence of NaOH to obtain diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol which was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Chapter 9 summarizes the results and outlines salient conclusions and future perspectives of research work carried out in the present thesis.

Glossary

CNSL	Cashew nut shell liquid
T_g	Glass transition temperature
T_{10}	10% Decomposition temperature
T_m	Melting transition
P_2O_5	Phosphorus pentoxide
$POCl_3$	Phosphorus oxychloride
HF	Hydrogen fluoride
BF_3	Boron trifluoride
HBr	Hydrobromic acid
n-BuLi	n-Butyl lithium
$NaHCO_3$	Sodium bicarbonate
$MgSO_4$	Magnesium sulfate
HPPDP	4-(4-hydroxyphenoxy)-3-pentadecylphenol
TLC	Thin layer chromatography
Br_2	Bromine
CuCN	Copper cyanide
$CuSO_4$	Copper sulfate
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
PTC	Phase transfer catalyst
TPC	Terephthalic acid chloride
IPC	Isophthalic acid chloride
BPA	2,2-Bis(4-hydroxyphenyl)propane or bisphenol-A
PE	Polyester
PEI	Polyetherimide
PHA	Polyhydrazide
POD	Poly(1,3,4-oxadiazole)
PES	Poly(ether sulfone)
BIPSF	Biphenol polysulfone
PEK	Poly(ether ketone)
ODA	4,4’-Oxydianiline
BPDA	3,3’,4,4’-Biphenyl tetracarboxylic dianhydride
ODPA	4,4’-Oxydiphthalic anhydride
6-FDA	4,4’-(Hexafluoro isopropylidene)diphthalic anhydride

APDPPA	4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline
HPPDPB	4-(4-(4-(4-(Hydrazinocarbonyl) phenoxy)-2-pentadecylphenoxy) phenoxy) benzohydrazide
PDBP	3-Pentadecyl 4,4’-biphenol
DFB	4,4’-Difluorobenzophenone
BFB	1,3-Bis(4–fluorobenzoyl)benzene
FPS	Bis(4-fluorophenyl)sulfone
NMP	1-Methyl-2-pyrrolidinone
DMAc	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
THF	Tetrahydrofuran
DCM	Dichloromethane
η_{inh}	Inherent viscosity
GPC	Gel permeation chromatography
Mn	Number average molecular weight
Mw	Weight average molecular weight
PDI	Polydispersity index
WAXD	Wide angle X-ray diffraction
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
COSY	Correlation spectroscopy
HMBC	Heteronuclear multiple-bond correlation spectroscopy
HSQC	Heteronuclear single-quantum correlation spectroscopy
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
HPPDPCN	4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene
BPACN	Bisphenol A dicyanate
ΔH	Enthalpy
ΔE	Activation energy
A	Arrhenius frequency factor
BMI	Bismaleimide
ODABMI	4,4’-Bis(maleimido)diphenylether
C15BMI	4, 4’-Bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether
DGEBA	Diglycidyl ether of bisphenol A

List of Tables

List of Schemes

List of Figures

Chapter 1

Introduction and Literature Survey

1.1 Introduction

Synthetic polymers have important role in modernization of the world and their development is eventually a triumph of human inventions. The exploitation of synthetic polymers fulfills many basic human needs such as food, clothing, shelter, health, transportation, etc.

Today, it is difficult to imagine human life without the use of polymers. Synthetic polymers gain their characteristics as elastomers, fibers or thermosets because of their particular macromolecular structures. Similarly, bio-polymers are present in the forms such as natural fibers, skin, hair, shellac, wood, etc. The first completely synthetic polymer, *Bakelite* (invented by Leo Baekeland in 1909) was derived from fossil resources.[1] For synthetic polymers, essentially monomers are required and currently these are mostly derived from fossil resources. On the other hand, extreme utilization of fossil fuels for automobile, industrial and domestic applications has resulted into rapid depletion of their stocks and there is a fear that they would be completely vanished in the near future. The expert study revealed that accessibility of fossil resources, *viz.*, coal, petrol and natural gas would be in a useful time scale for future one to three generations only.[2, 3] Consequently, there is a serious concern about depletion of fossil resources.[4-6]

The energy concerns are vigorously discussed and number of alternative renewable energy sources such as solar energy, nuclear power, biomass combustion, wind energy, hydropower, geothermal, biofuel and hydrogen derived from renewables and others are being implemented. On the other hand, renewable non-food biomass of vegetable and animal origin is the only viable source for organic chemicals, monomers and polymers.[7] Therefore, research programs are being ubiquitously administered for escalating need in the form of the increased funds for production of biomass derived chemicals and polymers by the concerned Organizations and Institutions (e.g. EU, UNIDO, INCU, etc.) and the private industries.[8-13] This is also reflected in amazingly growing the number of scientific journals, papers, patents as well as International conferences[14] on the topic of utilization of biomass for the production of biobased polymers.(**Figure 1.1)**

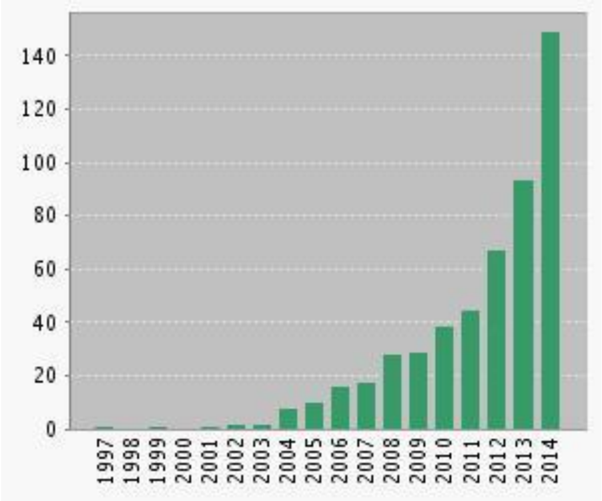


Figure 1.1 The number of publications in each year on keyword 'biobased polymers' (Source: Web of Science)

The process of extraction of valuable chemicals from biomass is termed as 'bio-refinery or biomass-refinery'[10] which is analogous to 'petroleum-refinery'. The different components of a biomass are isolated by means of chemical or biochemical processes. Therefore, value added chemicals and monomers for polymer industry, biologically active compounds for pharmaceutical industry, natural fibers, resins and oils (as such or modified) and bio-plastics produced by bacteria have potential to replace petrol-based products.[15] For instance, different components of wood could be extracted and valorized into: (a) cellulose for papermaking and reinforced composite materials; (b) lignin as useful macromonomer for preparation of novel plastics and for valuable chemicals like vanillin, eugenol, ferulic acid, etc; (c) bark tanning used for leather treatment and (c) some rare chemicals for medical applications such as neutraceticals. In fact, utilization of biomass resources for production of chemicals and monomers for polymer industry could replace fossils and decrease the burden of fossil dependence. Biomass is available so ubiquitously that any country in the globe would be profited from their valorization. However, several difficulties should be overcome prior to production of chemicals and monomers from the biomass, particularly extraction or isolation of such chemicals from biomass. Therefore, the concept of bio-refinery is very crucial for exploitation of biomass into monomers and polymers, in particular for separation of its constituents and their conversion into value added chemicals using suitable chemical transformations.[16-18]

The efforts towards utilizing renewable resource materials for polymer synthesis deal with two strategies: i) synthesis of polymers composed of entirely renewable materials and ii) synthesis of partially renewable polymers in combination with petroleum-based components. The industrial transition from fossil-based chemicals towards renewable resource-based chemicals is quite challenging and could not be possible without interdisciplinary approach. For instance, biocatalytic transformations using enzymes or micro-organisms can be the first-step which then is followed by catalytic transformations using solid acid catalysts. Further step may be transition metal-based catalytic transformation to a) reproduce existing petroleum-based monomers (‘drop-in’ substitute or bioreplacement) and b) obtain new monomers providing new polymers which could mimic commodity polymers. Moreover, new biobased monomers and polymers could be designed with the intention to achieve polymers with improved processibility i.e. bioadvantaged polymers.[19-22]

The objective of this dissertation is to study the utilization of renewable resources as a starting material for synthesis monomers and polymers therefrom. The present chapter includes the general introduction on exploitation of renewable resources for synthesis of aromatic difunctional monomers and high performance polymers. Therefore, it consists of brief review on the monomers and polymers derived from lignin and cashew nut shell liquid (CNSL). The aliphatic monomers derived from renewable resources are out the scope of the thesis and these have been reviewed elsewhere.[7, 23-38]

1.2 Bio-based aromatic difunctional monomers

The most important renewable resources which provide aromatic chemicals are namely; a) furan derivatives obtained from biomass, b) Lignin- by-product of papermaking industry c) cashew nut shell liquid (CNSL) and d) polyphenols obtained from tannis.[7 39-41]

1.2.1 Furan-based difunctional monomers

The hemicellulose is a major constituent of lignocellulosic structures present in the annual plants as well as in some of their products *viz.*, xylan which a polysaccharide based on C-5 glycosidic units. The acid-catalysed depolymerization and dehydration of residual agricultural species such as sugarcane, bagasse, corn cobs, rice hull, etc into furfural has been a versatile industrial process for a century with worldwide production of approx. 300,000 tons. Around 85% of furfural (market price approx. \$1/kg)[42] is utilized for production of furfural alcohol which is an important starting material for various resins and polymeric materials. Secondly, furfural is utilized for fine chemicals and intermediates required for pharmaceuticals and other chemicals.[43] Further, hydroxymethylfurfural is also produced from C-6 sugars and polysaccharides using similar process for furfural synthesis and its industrial production will be started very soon.[44, 45] Thus, two furan derivatives namely; furfural and hydroxymethylfurfural can be obtained directly from biomass (**Figure 1.2)** and act as motivation for the approaches such as, (i) converting them into monomers for chain and step polymerization (ii) studying these polymerizations and establishing comparison with standard systems, and (iii) characterizing furan polymers to develop structure property relationship to prove their viability with respect to other polymeric materials.[46, 47]

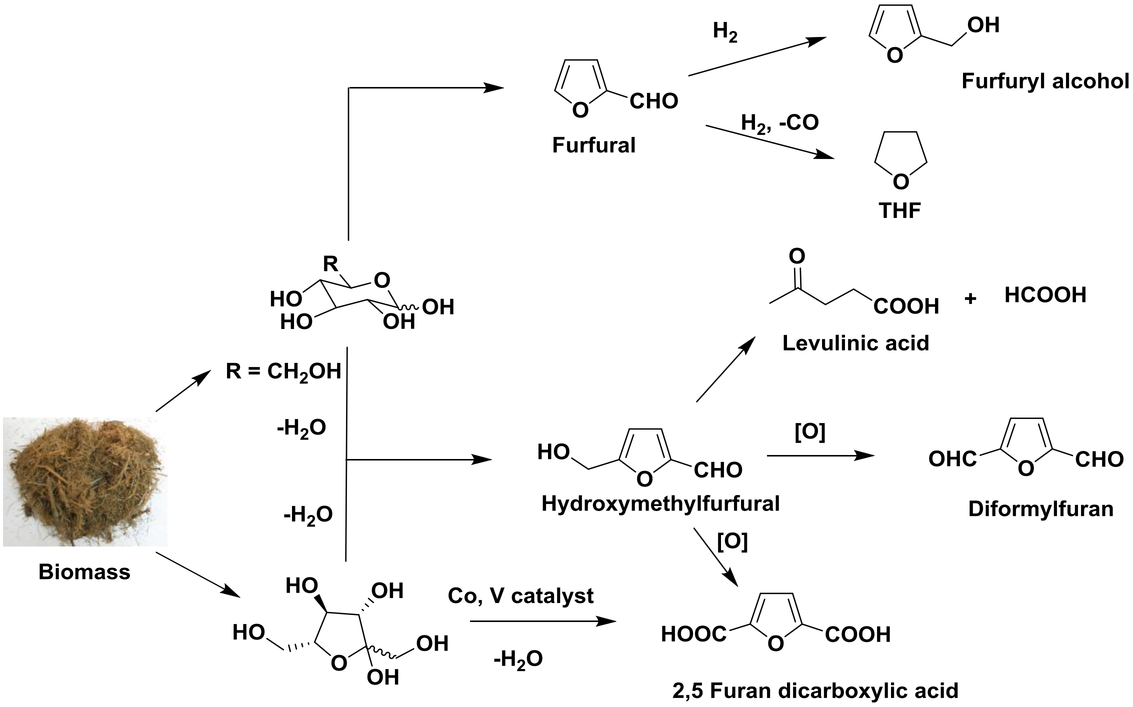


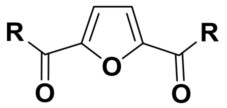
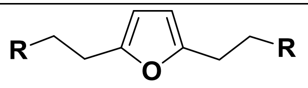
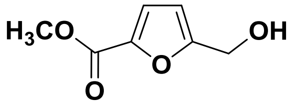
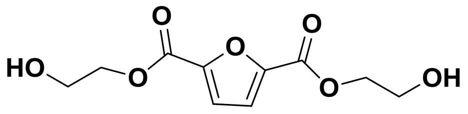
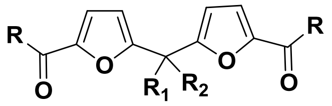
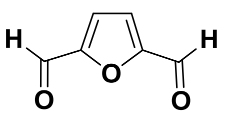
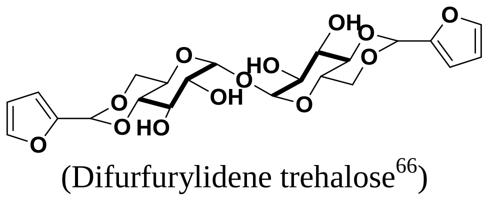
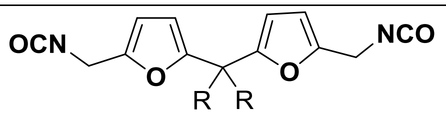
Figure 1.2 Synthesis and transformation of furans

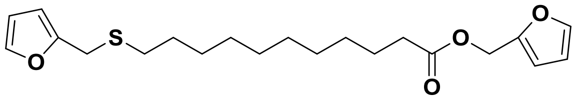
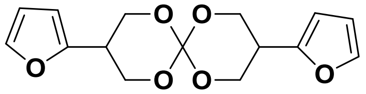
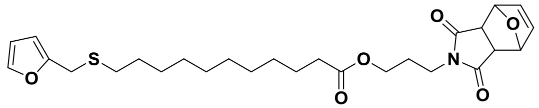
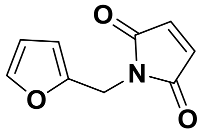
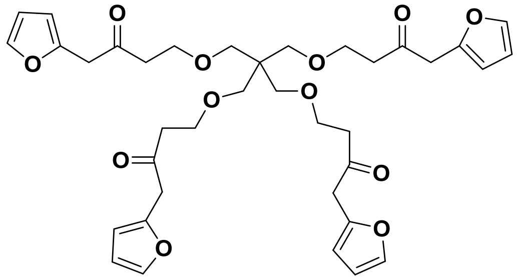
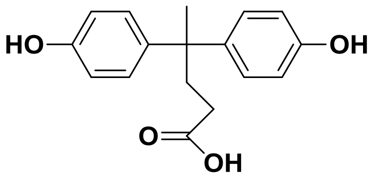
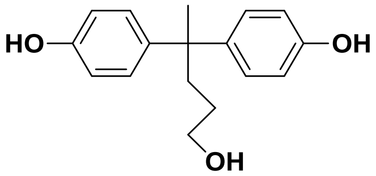
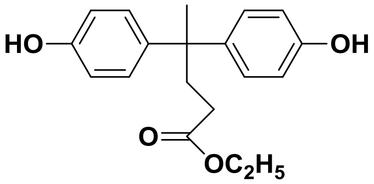
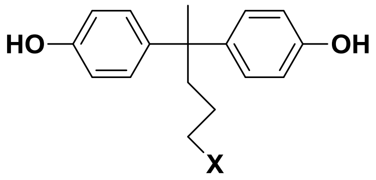
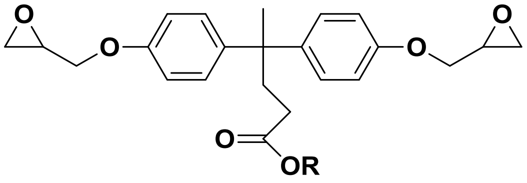
Some of the furan-based polymers are found to be promising and better options to fossil-based polymers e.g., (i) mixed furanic polyamide has properties comparable to that of Kevlar,[48] (ii) furan-based polyurethanes have thermoplastic elastomeric properties along with ability to form high graphinic residue on pyrolysis,[49, 50] and (iii) furan-based conjugated polymers and oligomers have good electronic conductivity on doping, photo- and electroluminescence and photo-cross-linking ability.[51, 52] Another area of polymer chemistry where furans can afford a considerable contribution is associated to the chemical properties of furan ring. For example, 2-substituted furan has tendency to undergo electrophilic substitution selectively at C5 position, it was utilized to obtain end functionalized poly(isobutene) and block copolymers by cationic ring opening polymerization in the presence of a suitable furan derivatives. The click reactions such as thiol-ene reaction, Diels-Alder reaction, etc have opened new approaches for different macromolecular architectures required for various applications by combination of furan and vegetable oils.[46, 53]

Levulinic acid-one of the top-ten platform chemicals[54] is obtained from hemicellulosic waste and it can be transformed into diphenolic acid and different bisphenols.

The list of selected monomers derived from hemicellulosic biomass is presented in **Table 1.1**

Table 1.1 List of selected hemicellulose-based monomers

Structure of monomer (Polymer prepared)	**Structure of monomer (Polymer prepared)**
 **R = OH, OCH_3, Cl** (Polyesters,[55] Polyamides[48])	 **R = OH, NH_2** (Polyesters,[56-58] Polyamides,[58] Polyurethanes[49, 59])
 (Polyesters[60])	 (Poly(ethylene 2,5-furandicarboxylate)[47])
 **R = OH, OCH_3, Cl, OC_2H_5, $NHNH_2$** **R_1 = H, CH_3, C_2H_5, C_6H_5** **R_2 = H, CH_3, C_2H_5, C_6H_5** (Polyamides,[61, 62] Polyesters, Polyhydrazides,[63] Poly(1,3,4-oxadiazole)s[63])	 (Polyazomthines[64, 65])
 (Difurfurylidene trehalose[66])	 **R = H, CH_3** (Polyurethanes[49, 59])

Structure of monomer (Polymer prepared)	**Structure of monomer (Polymer prepared)**
 (AA monomer for DA polymerization by combination of furan and vegetable oil[67])	 (Diels-Alder polycondensation to form polyadducts[68])
 (AB monomer for DA polymerization[67])	 (Diels-Alder polycondensation[69])
 (Self healing cross-linked polymeric material[70])	 (Polycarbonates[71], Polyesters[72-74])
 (Dendrons[75])	 (Polycarbonates[76], Polyesters[72])
 **X = N_3, Br** (Polyesters[77])	 **R = methyl, ethyl, n-butyl and n-pentyl** (Bio-based epoxy[78])

1.2.2 Aromatic difunctional monomers based on lignin

Lignin is a highly cross-linked amorphous aromatic polymer which acts as a surrounding matrix for the hemicellulose and cellulose present in plants and trees. It is the second largest abundant natural polymer after cellulose.[79, 80] The lignin content in the plants varies from plant to plant and with extraction methods also. The general trend is: lignin content in softwood (28 %) > hardwood (20 %) > grasses (< 20 %).

Although the structure of lignin varies for different plants, its basic building blocks could be simplified as C-9 unit which consists of phenolic moiety with three aliphatic carbons. The aromatic rings are usually substituted with methoxy groups while the aliphatic segment is present as variable C=C unsaturations. **Figure 1.3** represents hypothetical structure of lignin indicating how it differs in irregularity and cross-linking than other natural polymers such as cellulose and chitin in which the glycosidic units present are linear and cross-linked, respectively.

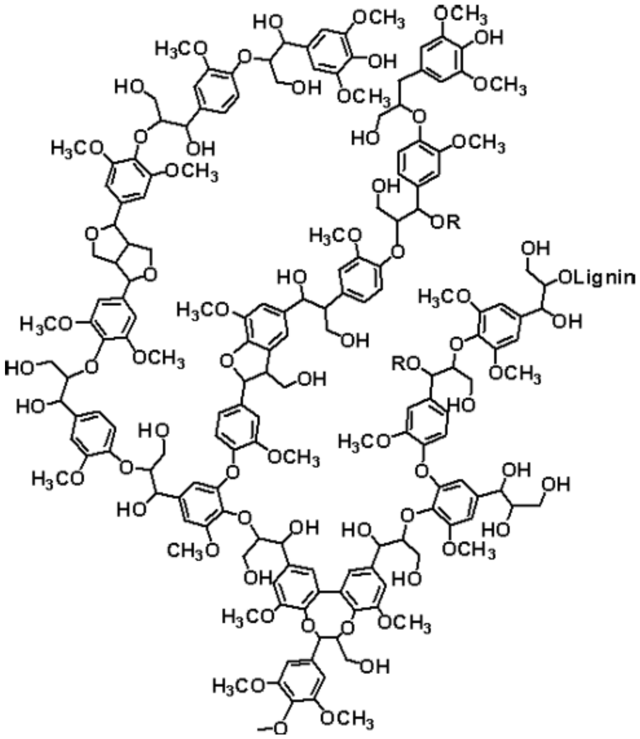


Figure 1.3 A hypothetical native structure of lignin

It is not an interesting approach to isolate and valorize lignin for macromolecular architectures because of its complex structure. Interestingly, many chemical processes such as pulp production for paper making and bioethanol production from lignocellulose produce large amount of lignin as a waste. So it is widely available and cheap material presently used for generating heat by burning it, lignosulfonates preparation and land filling also. On the other hand, lignin could be utilized as a source of aromatic monomers, value-added chemicals and fuels by depolymerising it. Therefore, many researchers across globe have been utilizing lignin as a potential renewable resource material for the synthesis of aromatic monomers, biofuels and value added chemicals. There are several articles and monographs which have reviewed the opportunities of converting lignin into value-added chemicals.[7, 81-

[84] The various important building-blocks derived from lignin are vanillin,[85] eugenol, ferulic acid, vanillic acid, etc. (**Figure 1.4**) The selected aromatic difunctional monomers derived from lignin are presented in **Table 1.2.**

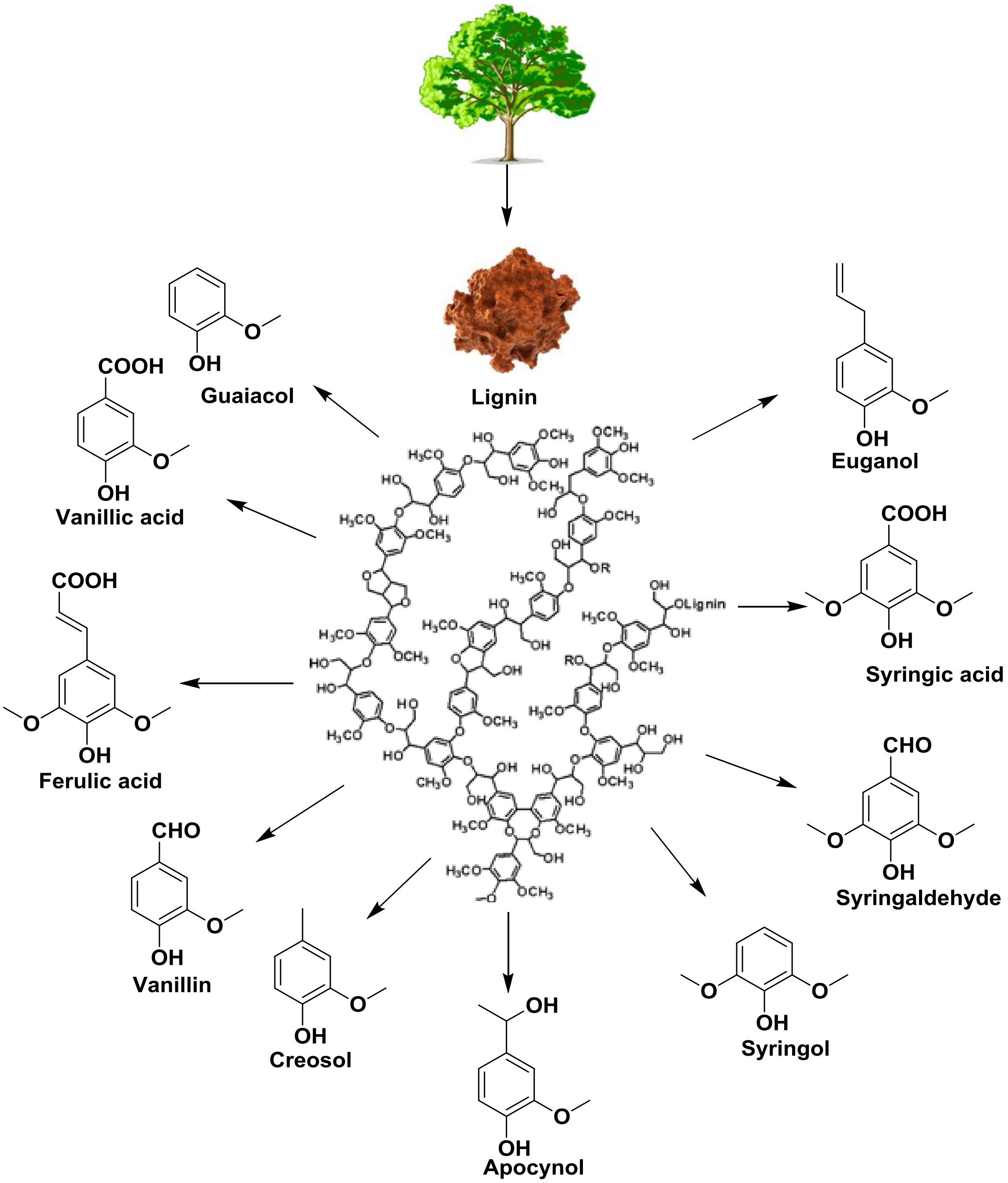
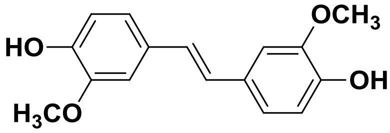
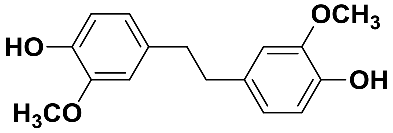
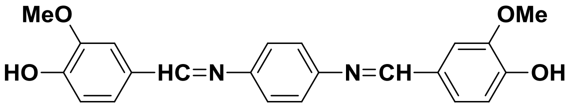
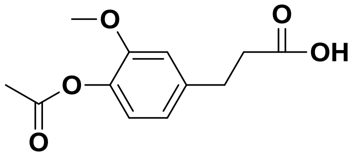
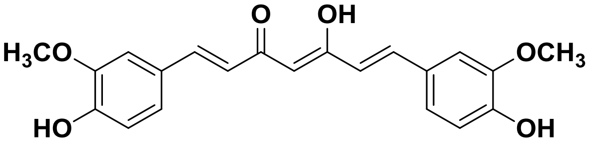
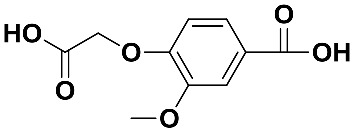
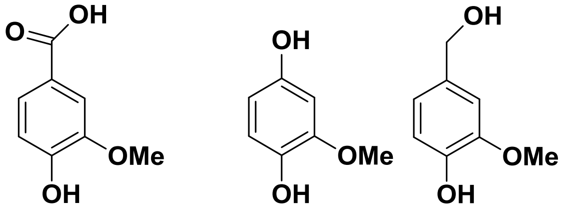
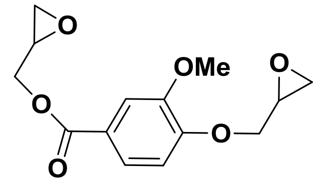
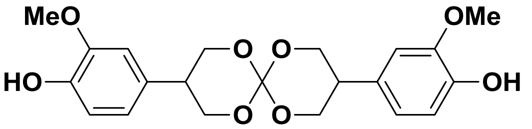
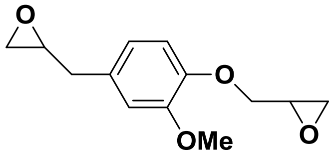
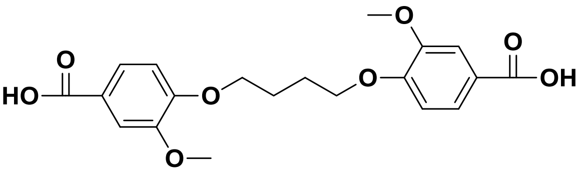
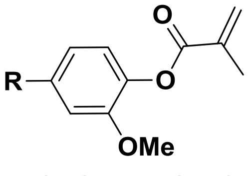
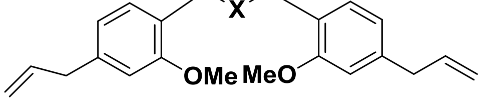
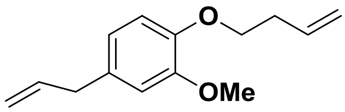
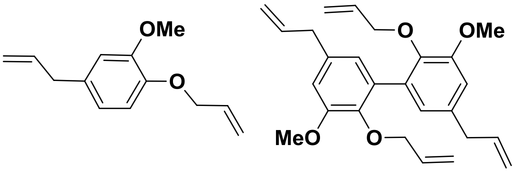
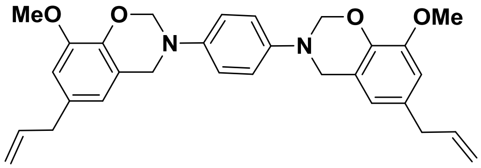


Figure 1.4 Building-blocks obtained from depolymerization of lignin

Table 1.2 List of selected lignin based monomers

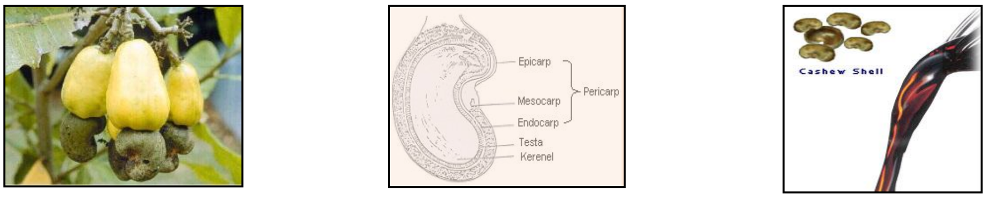
Structure of monomer (Polymer prepared)	**Structure of monomer (Polymer prepared)**
 (Cyanate esters[86-88])	 (Cyanate esters[86])
 (Epoxy[89])	 (Polyesters[90])
 (Polyesters[91])	 (Poly(ether-ester)s[92])
 (Polyester, ,[93] epoxy, polyurethanes, non-isocyanate polyurethanes[85])	 (Epoxy[85])
 (Epoxy[85])	 (Eugenol based epoxy[94])
 (Poly(ether-ester)s[92])	 R = -CHO, -H, - $CH_2CH=CH_2$ (Methacrylated vanillin, guaiacol, eugenol[95])
 X = C=O, $-(CH_2)_{10}-$,$-(CH_2)_2O(CH_2)_2-$ Dienes used for ADMET-polymerization to form unsaturated polyethers and polycarbonates[96]	 (Unsaturated polyethers [96])

Structure of monomer (Polymer prepared)	Structure of monomer (Polymer prepared)
 (Biobased polymer networks with Bismaleimides[97])	 (Eugenol based benzoxazine[98])

1.2.3 CNSL-based step-growth monomers

Cashew nut shell liquid (CNSL) is a by-product of cashew processing industry and is abundantly available in India, Brazil, Bangladesh, Kenya, Tanzania, Mozambique, South-East and Far-East Asia, and tropical regions of Africa. As CNSL is a non-edible oil, its utilization as an industrial raw material does not necessarily affect on the food supply chain. CNSL is one of important the renewable resource materials due to its unique structural features, abundant availability (450,000 metric tons per year) and low cost. A variety of chemicals and value added-products have been prepared using its three reactive sites *viz.*, phenolic hydroxyl, aromatic ring and unsaturation(s) in the alkenyl side chain. Literature reports number of reviews summarizing reactions and applications of CNSL.[99-112] Here, we would like to give short general information on CNSL covering its composition, purification and separation methods, reactivity and its utilization for synthesis of monomers for high performance polymers.

The liquid enclosed in the shell of cashew nut is known as 'CNSL' and it is a greenish-yellow colored viscous liquid placed in the soft honeycomb of the shell (**Figure 1.5**). Cashew is a fruit of the cashew tree (*Anacardium occidentale*), [113-115] which is an evergreen tree (10-12 m tall) and grows in the tropical region. In some countries, the cashew is produced as an agricultural crop, whereas some countries are importing cashew nuts for processing. The cashew tree provides cashew nuts as a main cash crop along with cashew apple, wood and gum. The cashew apple juice is rich in nutrients and vitamin C and is mostly used in beverages, fermented to vinegar and also have antimicrobial and antitumor properties.[116] The preserves, jams, jellies and chutneys are prepared from the cashew apple. The cashew nut appears greenish-grey in color while ripen cashew apple has either bright yellow or red color. The pericarp of the nut consists of a coriaceous epicarp, spongy mesocarp and a stony endocarp. 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.[116]



(a) (b) (c)

Figure 1.5 (a) Cashew fruit, (b) Cross section of cashew nut, (c) Cashew nut shell liquid

1.2.3.1 Extraction of CNSL

Conventionally, a variety of methods are used for extraction of CNSL from the nuts of cashew. Two processes are popular for the CNSL extraction: 1) hot oil process and 2) roasting process in which CNSL oozes out from the shell cashew nut.[117, 118] The other techniques including extraction of CNSL by various solvents viz, benzene, toluene, petroleum hydrocarbons and alcohols[119] as well as supercritical extraction of CNSL using a mixture of carbon dioxide and isopropyl alcohol are reported for extraction of CNSL.[120]

1.2.3.2 Composition and purification of CNSL

According to previous literature[103, 121, 122] regarding composition of CNSL, CNSL present in cashew nut is composed of four major compounds viz, anacardic acid, cardanol, cardol, and 2-methyl cardol. These are monohydric or dihydric phenols or phenolic acids with *meta*-substituted C-15 hydrocarbon side-chain with varying unsaturations (**Figure 1.6**)

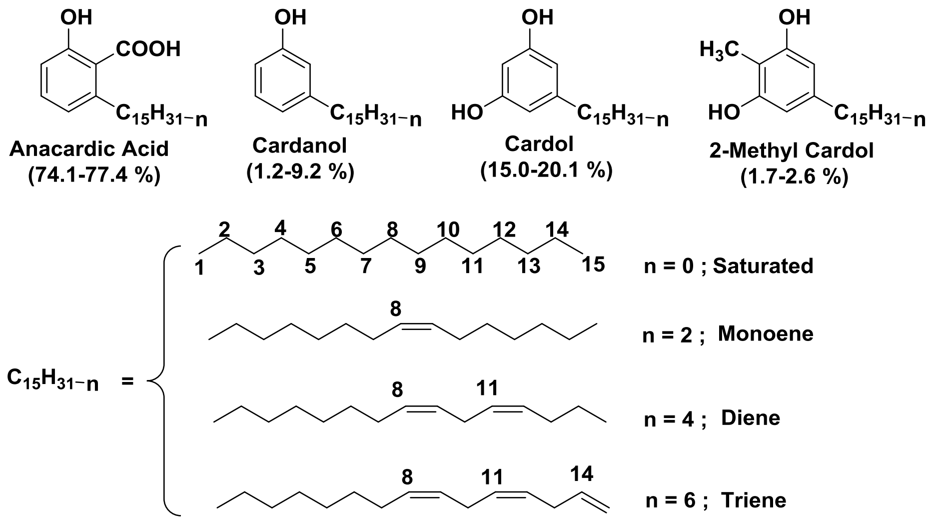
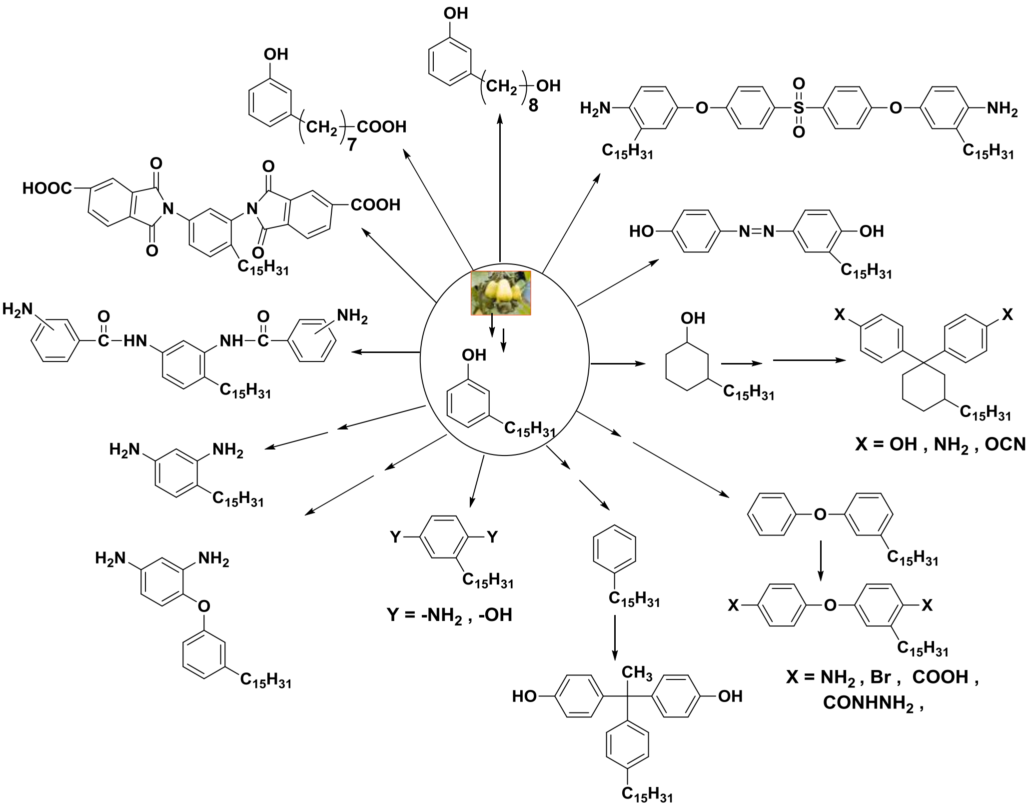


Figure 1.6 Components of CNSL

Industrial CNSL has no content of anacardic acid as it gets decarboxylated into cardanol during the roasting process.[123] Depending upon side chain unsaturation, the components of CNSL are again classified as saturated (~5-8 %), monoene (~48-49 %), diene (16-17 %) and triene (29-30 %) [124](**Figure 1.6**). The composition of natural and industrial CNSL was estimated by number of researchers using mainly chromatographic methods.[125-130] The presence of significant amounts of oligomeric and polymeric materials in both natural and technical CNSL has been reported by Tyman and co-workers.[123, 131, 132] The different purifications techniques such as distillation,[111, 133], solvent extraction,[134] paper chromatography, thin layer chromatography and column chromatography using various eluents and stationary phases were used for purification and separation of components of CNSL.[135-137 138]

1.2.3.3 Applications of CNSL in high performance polymers

Cardanol has been found to be an interesting renewable resource due to its three reactive sites (phenolic –OH, aromatic ring and unsaturation in side chain) for aromatic difunctional monomers for high performance polymers. Its utilization for the synthesis of various difunctional monomers such as diamines, diacids, diols, diacylhydrazide, dialdehydes, bisylides, etc. was successfully demonstrated (**Scheme 1.1**).[99, 139-158]



Scheme 1.1 CNSL-based difunctional monomers

A series of high performance polymers *viz.*, polyimides, polyamides, poly(azomethine)s, poly(amideimide)s, poly(esterimide)s, polyesters, polyhydrazides, poly(1,3,4-oxadiazole)s, etc. have been synthesized by polymerization of these CNSL-based monomers. The high performance polymers derived from CNSL are bestowed with pendent pentadecyl chain which is responsible for packing disruption of polymer chains and acts as an additional handle for interacting with solvent to enhance solubility. The polymers with pendent pentadecyl chains showed lower T_g than their analogous without pentadecyl chains because pendent pentadecyl chains hinder interchain interactions as well as increase the segmental motion in the polymer backbone. A large difference between glass transition temperatures (T_g) and temperatures for 10 % weight loss (T_{10}) of the CNSL-based polymers offers these polymers opportunities for melt-processability.

1.3 High performance polymers

High performance polymers is one of the speciality and well recognized areas of polymer science for more than 60 years. They have received tremendous demand for space programs in the ablative systems, high temperature adhesives and coatings and heat- and flame-resistant fibers. High performance polymers can broadly be defined as polymeric materials which exhibit thermal stability above 200 °C and also possess excellent mechanical strength, modulus and chemical stability.[159, 160]

Unfortunately, high performance polymers such as aromatic polyesters, polyimides, polyhydrazides, poly(1,3,4-oxadiazole)s, poly(arylene ether)s, etc. have high melting transitions and poor solubility because of high regularity and high rigidity of the backbone which results in strong interchain interactions. The higher melting transitions and insolubility in common organic solvents pose the serious problem of processability which limits their widespread applications in various advanced technologies. The various approaches have been demonstrated to improve processability of high performance polymers (**Figure 1.7**): (i) the introduction of flexible spacers between the rigid units; (ii) the introduction of bent or 'crank shaft' units along the aromatic backbone; and (iii) the introduction of bulky side groups or flexible side chains into the polymer backbone.[161]

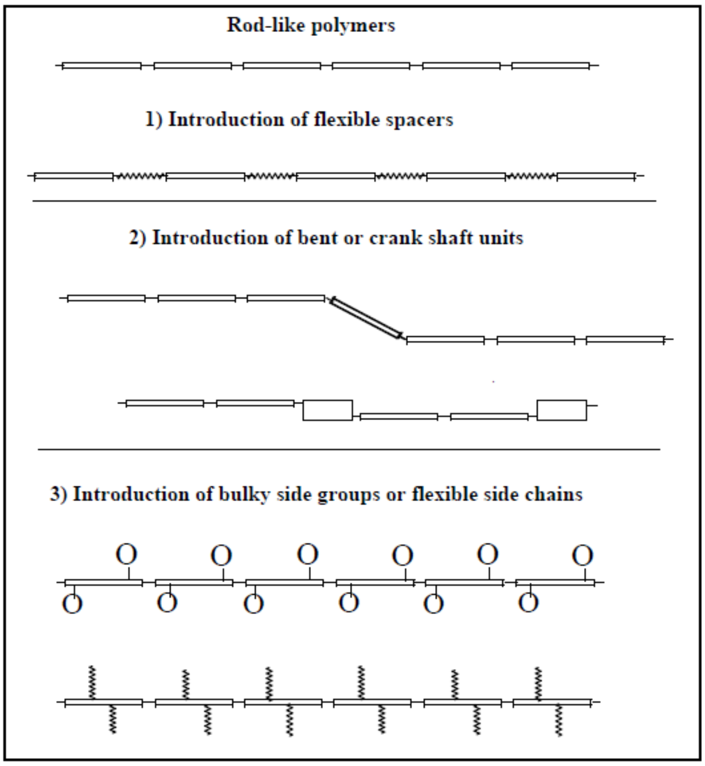


Figure 1.7 Macromolecular approaches for improving processability of high performance polymers

These structural features offer molecular dissymmetry; hinder close interchain packing and increase free volume resulting into improved solubility and processability of the polymer. Further, the improvement in processability should be carried out without sacrifying the thermal stability.[22]

The consequent sections discuss the advances in the chemistry of high performance polymers that resulted into improvements in their processability. The main focus of the discussion is on aromatic polyesters, polyimides, polyhydrazides, poly(1,3,4-oxadiazole)s and poly(arylene ether)s. The chemistry and structure-property relationship in cyanate esters, bismaleimides, and epoxy resins has been discussed in **Chapter 8.**

1.3.1 Aromatic polyesters

Aromatic polyesters or polyarylates are polymers containing repeating ester groups (-CO-O-) as a part of the polymer backbone. In 1957, Conix et al[162] have firstly reported reaction between aromatic dicarboxylic acids and bisphenols. Thereafter, a large number of reports on polyesters based on aromatic dicarboxylic acids are available in the literature.[163] Prior to the production of the first commercial polyarylate-U-polymer-which is a polyester based on bisphenol-A and tere/isophthalates, by Unitica in 1974, 140 different types of polyarylates were reported.[163]

Polyesters have been extensively used in a variety of fields because of their excellent thermal, mechanical and electrical properties. However, polyesters have some problem regarding processability as they are insoluble in common organic solvents and possess high glass transition (Tg) and melting (Tm) temperatures. Bisphenol-A-based polyesters have high melt viscosity offering them limited injection moldability. Thus, a large amount of work has been carried out for improving processability of aromatic polyesters.

1.3.1.1 Synthesis of polyesters

The following two routes are generally used for preparation of high molecular weight aromatic polyesters.

1. Acid chloride route
2. Transesterification route

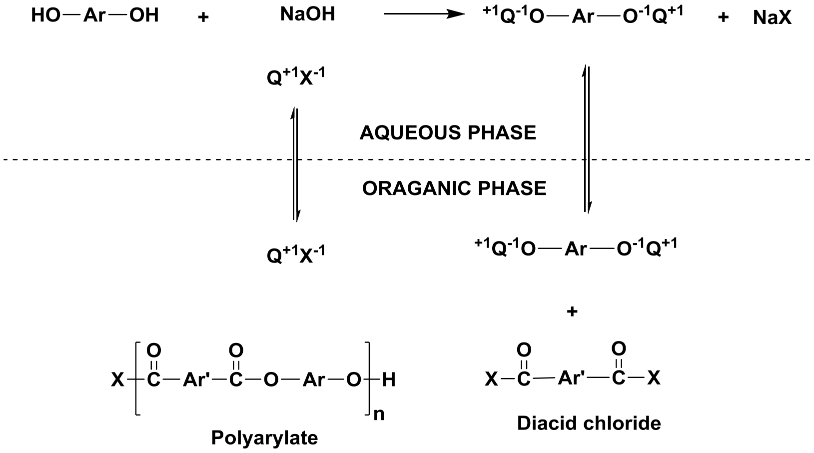
1.3.1.1.1 Acid chloride route

This is most widely applicable route for the synthesis of aromatic polyesters. The aromatic dicarboxylic acids are transformed into diacid chlorides and then condensed with diphenols. The polycondensation can be carried out by three different methods.

1.3.1.1.1a Interfacial polycondensation

The interfacial polycondensation for synthesis of aromatic polyesters was first introduced by Eareckson[164-166] and Conix[162] independently. The interfacial polymerization is typically polycondensation reaction between dialkali metal salt of a diphenol and diacid chloride(s) in the solvents such as water/dichloromethane or water/chlorobenzene.

In the process, the solution of diacid chloride in the water-immiscible solvent such as dichloromethane, chlorobenzene, etc. is added to the aqueous dialkali metal salt of diphenol under high speed stirring. The method is not suitable for preparation of aliphatic polyesters as aliphatic diols do not form alkoxide ions in aqueous medium. The polymerization reaction occurs at the interface of the two phases, therefore factors such as the speed of stirring, relative volume of the two phases, monomer concentration, phase transfer catalyst (PTC) and its concentration have profound effect on the reaction kinetics, yield and molecular weight of resulting polymer.[167] PTC helps the transport of phenoxide ions into the organic phase and also plays a role of surfactant to increase rate of reaction by enhancement of total interfacial area.[167] **Scheme 1.2** depicts a typical phase-transfer catalyzed interfacial polymerization reaction.



Scheme 1.2 Phase-transfer catalyzed interfacial polymerization reaction of bisphenol and diacid chloride

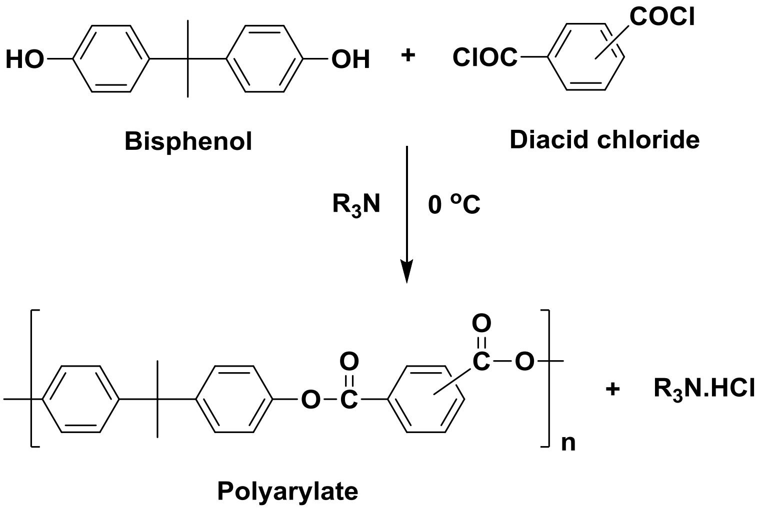
The main job of PTC is to make transportation of the anion of the bisphenolate salt into the organic phase as the ion pairs. These ion pairs combine with chloride ions present in organic phase to form the product and PTC gets regenerated back and transferred into the aqueous phase.[167, 168] The commonly used PTCs are benzyltriethylammonium chloride (BTEAC), tetraethylammonium chloride (TEAC), tetramethylammonium chloride (TMAC), benzyltriphenylphosphonium chloride (BTPPC), 15-crown-5, 18-crown-6, etc.[167] The choosing organic solvent for interfacial polycondensation is extremely important as polyesters formed should be soluble in it for achieving high molecular weight polymers. The low molecular weight polymers would be obtained when precipitation of polymer occurs during the reaction leading to lower reaction rates.

In contrast to polymerization reactions in homogeneous media, the maximum molecular weight is not necessarily achieved at the equimolar concentrations of reactants. The optimum stoichiometry of the reactants depends on the diffusion-rate of individual reactants at interface of the reaction. In literature, [169] there are reports on high molecular weight polyester synthesis with stoichiometric ratios in the range 0.58-2.0 for different diacid chloride-bisphenol.

1.3.1.1.1b Low temperature solution polycondensation

Low temperature solution polycondensations are usually carried out at room temperature or lower temperature (between -10 °C to +30 °C). In this method, polyesters are prepared by the reaction of equimolar amounts of a diacid chloride and a diol in a neutral solvent such as dichloromethane or tetrahydrofuran using a tertiary amine such as triethyl amine or pyridine, which acts as a catalyst as well as HCl acceptor. This polymerization method is also known as acceptor-catalytic polyesterification.[170]

The synthesis of polyester from bisphenol-A and terephthalic acid chloride or isophthalic acid chloride by low temperature solution polycondensation is shown in **Scheme 1.3.** The synthesis of high molecular weight polyesters is successfully achieved with pyridine alone or pyridine along with a tertiary amine in an inert organic solvent.[162, 170, 171]



Scheme 1.3 Low temperature solution polycondensation of a bisphenol and a diacid chloride

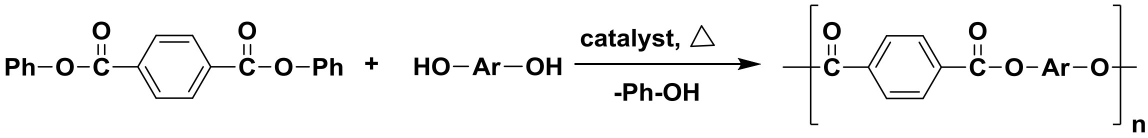
1.3.1.1.1c High temperature solution polycondensation

The polycondensation reaction between a diacid chloride and a bisphenol in the absence of an acid acceptor is sluggish at room temperature. Therefore, the polycondensation which is carried out at elevated temperatures (about 200 °C) in an inert high-boiling solvent is termed as high temperature solution polycondensation. Polyesters can also be obtained in excellent yields at 215-220 °C in dichloro-ethylbenzene as a solvent. The method does not need any acid acceptor because the evolved HCl gas is constantly taken away from the reaction mixture with the help of an inert gas flow. The *o*-dichlorobenzene with pyridine as a catalyst is found to be most effective system for synthesis of high molecular weight polymers.[172] The most commonly used high boiling solvents are nitrobenzene and o-dichlorobenzene. The various solvents which are also useful are: chlorinated benzenes (tetrachlorobenzenes), chlorinated biphenyls, chlorinated naphthalenes, chlorinated diphenylethers, and non-chlorinated aromatics like terphenyl, dibenzylbenzenes, benzophenones, etc.

1.3.1.1.2 Transesterification route

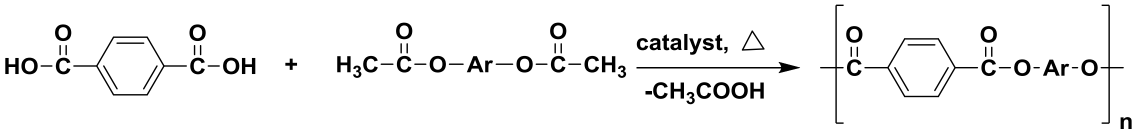
Transesterification route utilizes following reactions for synthesis of polyarylates:

1) **Reaction of diphenyl ester of aromatic dicarboxylic acid with bisphenol,**[173-175]



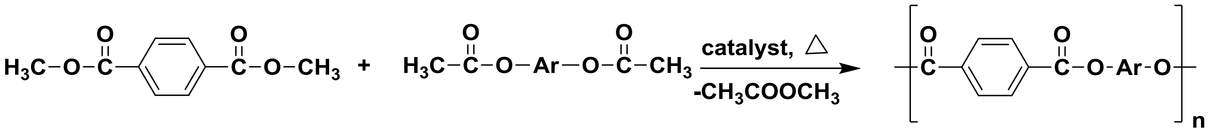
Scheme 1.4 Synthesis of polyester from diphenyl ester of aromatic dicarboxylic acid and bisphenol

2) **Reaction of aromatic dicarboxylic acid with diacetate derivative of bisphenol,**[162, 176, 177]



Scheme 1.5 Synthesis of polyester from aromatic dicarboxylic acid and diacetate derivative of bisphenol

3) **Reaction of dialkylester of dicarboxylic acid and diacetate derivative of bisphenol.**[178, 179]



Scheme 1.6 Synthesis of polyester from dialkylester of dicarboxylic acid and diacetate derivative of bisphenol

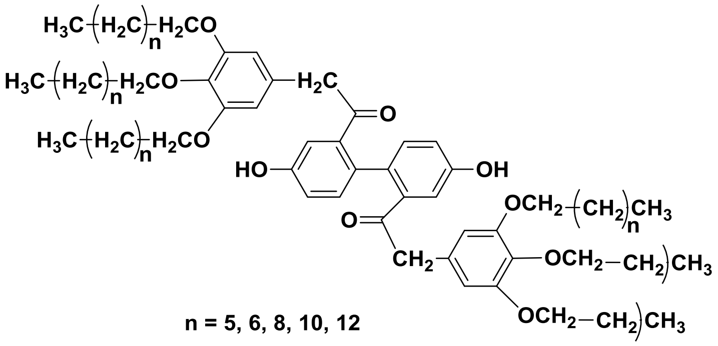
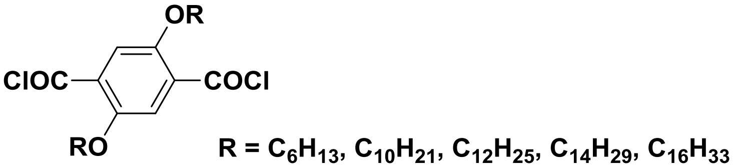
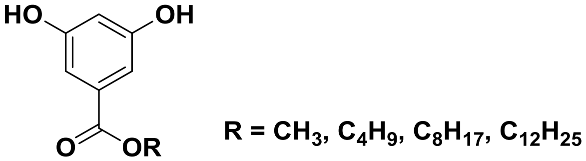
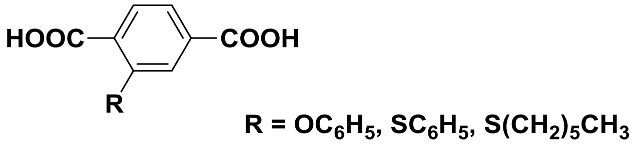
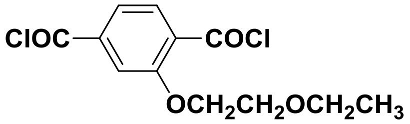
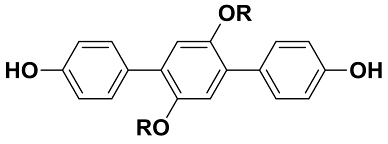
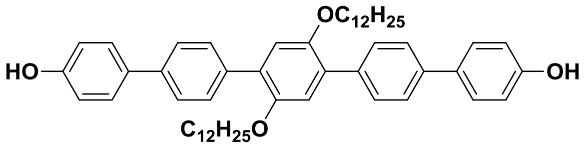
1.3.1.1.3 Miscellaneous routes for polyester synthesis

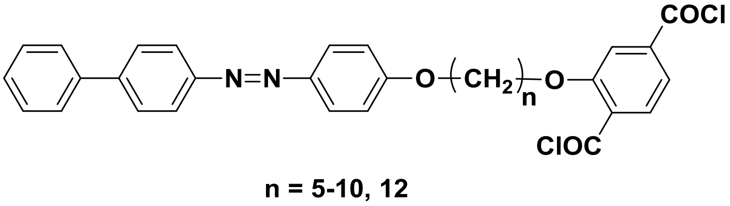
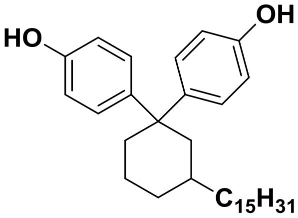
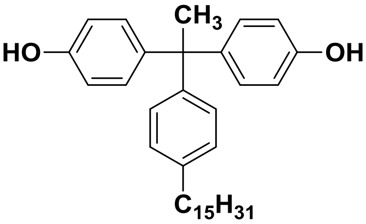
There are also some additional methods which have been applicable for synthesis of polyester such as phenol silyl ether route,[180, 181] direct esterification route,[182-184] palladium-catalyzed carbonylation route,[185] etc.

1.3.1.2 Structure-property relationship in aromatic polyesters

A large number of reports on polyarylates are available for demonstration of structure-property relationship.[178, 181, 185-187] The thermal and mechanical properties of polyesters are the function of the substituent present on the backbone and the backbone itself. Polyesters having phenyl rings or large/rigid substituents will show higher thermal properties, good solubility in common organic solvents and low crystallinity.[187] Further, the insertion of $-CF_3$ group onto the backbone of polyesters gives improved solubility as well as thermal stability.[188] Inclusion of the cardo groups into polymer backbone was found to be useful not only for increasing solubility but also for improvement in thermo-mechanical properties.[189] The *meta*-substituted monomers such as isophthalic acid, resorcinol, etc. impart kinks in the polymer backbone resulting into disrupted interchain interactions. Co-polyesters properties could be tuned in better way with varying composition of diol structure rather than that of diacid chloride structure.[190] Incorporation of pendent bulky groups or flexible chains onto the polyester backbone is found to be popular approach to improve processability. The selected bisphenols and diacid chlorides containing flexible chains used for synthesis of processable polyesters are presented in **Table 1.3**[142, 191-200]

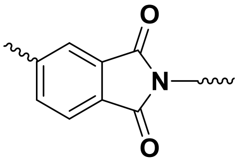
Table 1.3 List of the selected bisphenols and diacid chlorides containing flexible chains used for synthesis of polyesters

Sr. No.	Monomer structure	Reference
1	 n = 5, 6, 8, 10, 12	191
2	 R = C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$	192
3	 R = CH_3, C_4H_9, C_8H_{17}, $C_{12}H_{25}$	193
4	 R = OC_6H_5, SC_6H_5, $S(CH_2)_5CH_3$	194
5		199
7	 R = $C_{12}H_{25}$, $C_{16}H_{33}$ 	195

Sr. No.	Monomer structure	Reference
8		196
9		200
9		142

1.3.2 Polyimides

Polyimides are polymers with recurring heterocyclic imide units-

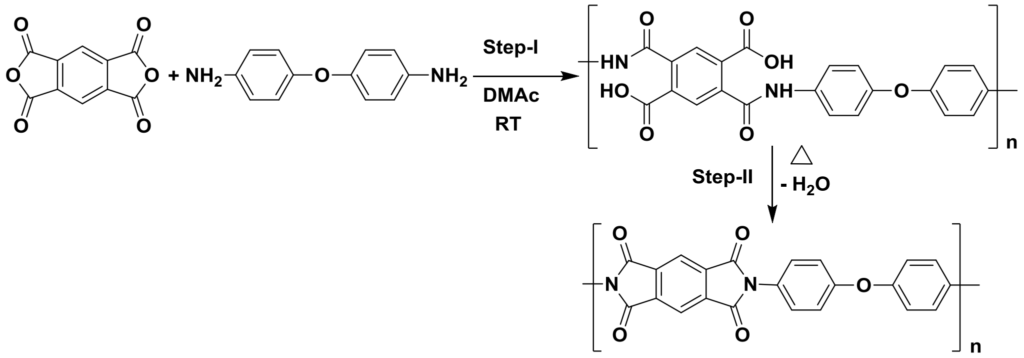


as an integral part of polymer backbone. In history, the first report related to polyimides i.e. synthesis of phthalimide derivatives by Bogert et al[201] appeared in 1908. Nextly, there was introduction of Kapton as commercial aromatic polyimide by Dupont in the early 1960s.[202] Subsequently, synthesis of various kinds of polyimides have been reported in the literature.[160, 203-209] Polyimides have scientific as well as commercial interest due to their excellent thermo-oxidative stability, superior mechanical strength, outstanding electrical properties, and high chemical resistance. In spite of processing difficulties and high cost of polyimides, they have significant applications as matrix resins, coatings, adhesives, and insulator in the automobile, aerospace and electronic-packaging industries. The various companies have commercialized polyimides with the trade names such as Kapton (DuPont), Vespel (DuPont), Pyre-ML (DuPont), Skybond (Monsanto), Apical (Kaneka), UPILEX (UBE), VTEC PI (RBI), Kaptrex (Professional Plastics) and Norton TH (Saint-Gobain).[160] However, the widespread applications of polyimides have been limited due to their insoluble and infusible nature resulting into poor processability. Therefore, large efforts have been spent to impart processability to intractable polyimides.

1.3.2.1 Synthesis of polyimides

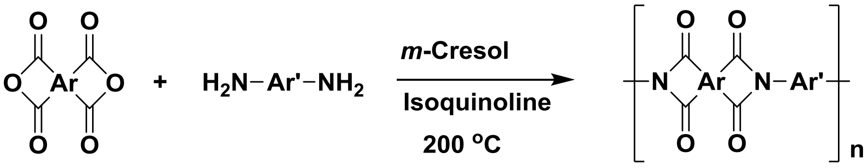
Generally, polyimides have been synthesized by polycondensation of aromatic diamines and tetracarboxylic dianhydrides. Additionally, there are number of methods reported for synthesis of polyimides, some of them are enlisted below.

1. **Two-step method *via* poly(amic acid)**



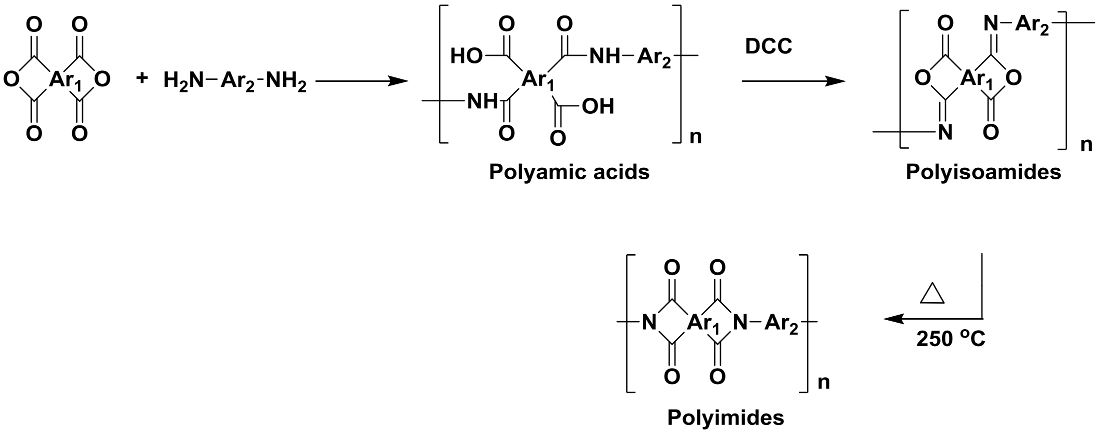
Scheme 1.7 Synthesis of Kapton by two-step method

2. **One-step high temperature solution polymerization**



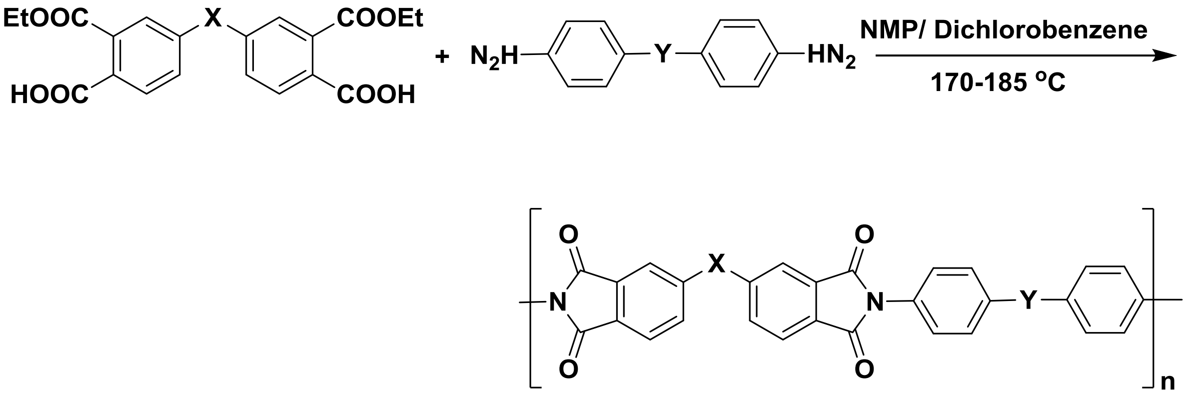
Scheme 1.8 Synthesis of polyimides by one-step high temperature solution polymerization

3. **Polyimides *via* polyisoimide precursors**[210]



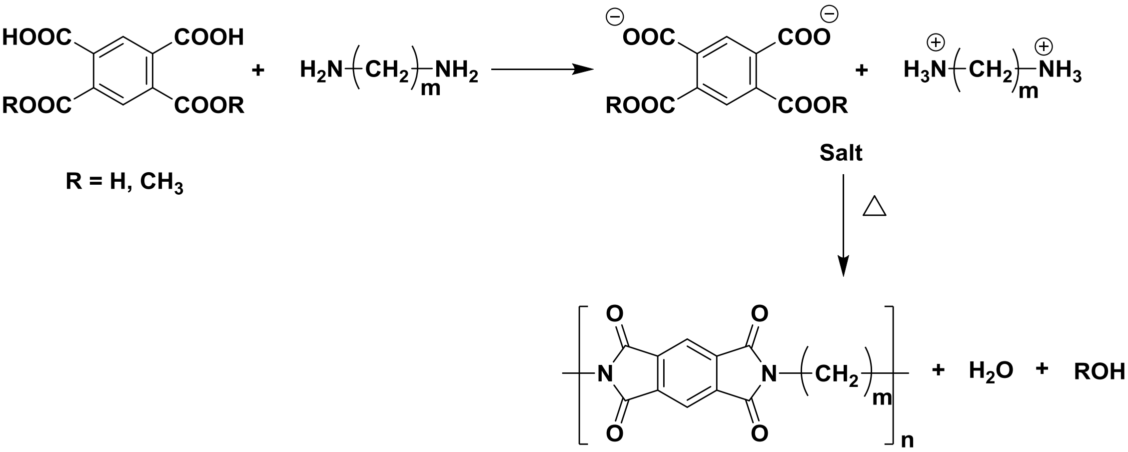
Scheme 1.9 Synthesis of polyimides *via* polyisoimide precursor

4. Polyimides from diester-acids and diamines (Ester-acid route)[211]



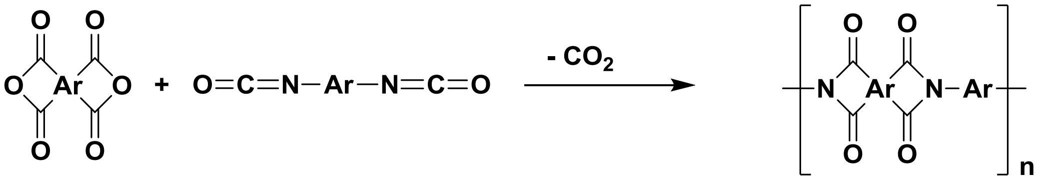
Scheme 1.10 Synthesis of polyimides by ester-acid route

5. Polyimides from tetracarboxylic acids and diamines[212]



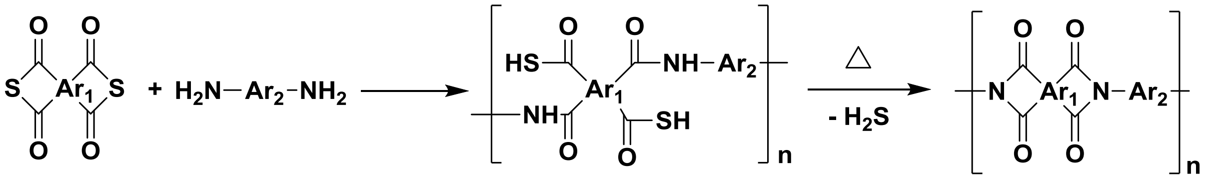
Scheme 1.11 Synthesis of polyimides from tetracarboxylic acids and diamines

6. Polyimides from diisocyanates and dianhydrides[213]



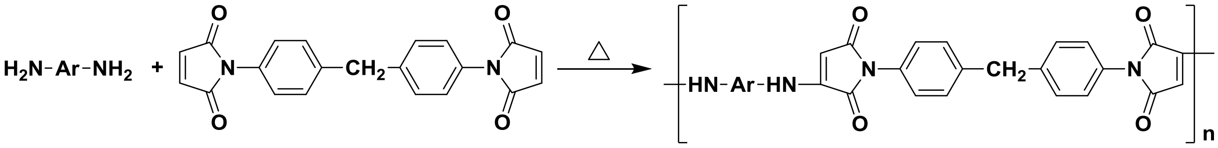
Scheme 1.12 Synthesis of polyimide from diisocyanates and dianhydrides

7. Polyimides from diamines and dithioanhydrides[214, 215]



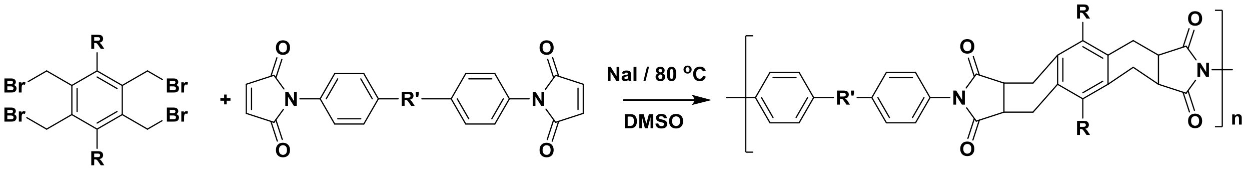
Scheme 1.13 Synthesis of polyimides from diamines and dithioanhydrides

8. Polyimides from diamines and bismaleimides (Michael addition reaction)[216]



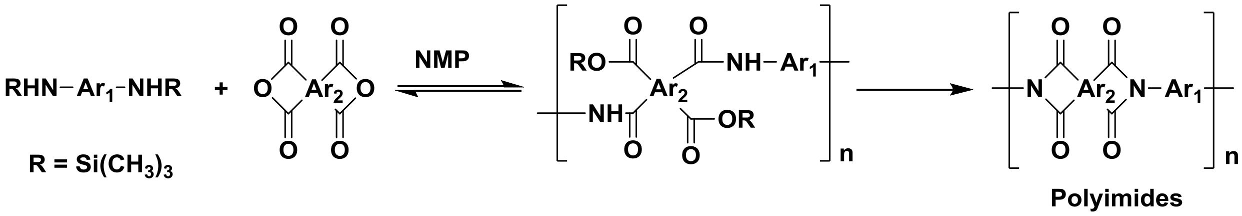
Scheme 1.14 Synthesis of polyimides by Michael addition reaction

9. Polyimides from bisdienes and dienophiles (Diels-Alder reaction)[218, 217, 218]



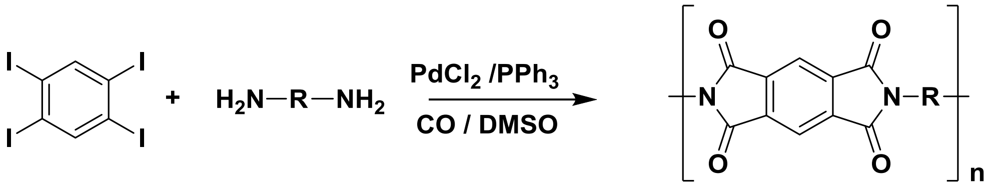
Scheme 1.15 Synthesis of polyimides by Diels-Alder reaction

10. Polyimides from silylated diamines and dianhydrides[219, 220]



Scheme 1.16 Synthesis of polyimides from silylated diamines

11. Polyimides by Pd-catalyzed carbon-carbon coupling reaction[221]



Scheme 1.17 Synthesis of polyimides by Pd-catalyzed carbon-carbon coupling reaction

Out of all these methods ‘two step method via polyamic acid’ and ‘one-step high temperature solution polymerization’ are commonly used methods and will be discussed in brief.

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

This classical method was developed at DuPont for synthesis of Kapton, the first commercial polyimide and is still popularly utilized for the synthesis of insoluble polyimides. **Scheme 1.7** illustrates the two-step method for synthesis of Kapton. The method consists of first step as polycondensation of dianhydride and diamine in polar aprotic solvents such as DMAc or NMP at ambient temperature to form processable poly(amic acid). In the second step, poly(amic acid) is converted into corresponding polyimide by imidization

1.3.2.1.1a First step: Formation of poly(amic acid)s

The first step involved the nucleophilic attack of diamine nitrogen on the carbonyl carbon of dianhydride to open the anhydride with formation of amic acid. In reaction equilibrium, the acylation of amine i.e. forward reaction is an exothermic, second order and faster than the backward reaction which is a first order reaction. As a result, high molecular weight poly(amic acid) is obtained when the reaction is carried out lower temperature and higher monomer concentrations.[209] The rate of reaction is also governed by reactivity of the monomers (nucleophilicity of amine and electrophilicity of dianhydride carbonyl carbon). Generally, the structural variations in diamine have more influence on the rate of the acylation reaction than that in dianhydride.[222] The more nucleophilic the diamine more is reactivity which can be correlated with basicity (pKa) given by Hammett equation.[223] Though aliphatic diamines are more basic, they do not form poly(amic acid)s because they have propensity to react with carboxyl group of the formed amic acid resulting into formation ionic salts and hence protonated amine group can not react with the anhydride. Further, diamines with very low basicity have too weak nucleophilicity to react with dianhydrides. Therefore, diamines with a pKa of 4.5-6 are suitable for formation of high molecular weight poly(amic acid). The reactivity of the dianhydrides could be measured on basis of electron affinity (Ea). The higher the value, greater will be the reactivity of the dianhydride.[224] The dianhydride could be activated for nucleophilic attack on the anhydride carbonyl by strong electron-withdrawing groups. The role of solvents is also important in the formation poly(amic acid)s. The commonly used solvents are N,N-dimethylacetamide, 1-methyl-2-pyrrolidinone, N,N-dimethylformamide and dimethyl sulfoxide as they are polar aprotic solvents and also able to form strong hydrogen-bonded complexes with the carboxyl group.

1.3.2.1.1b Second step: Imidization of poly(amic acid)s

Thermal imidization of poly(amic acid)s is the most commonly used method for conversion of poly(amic acid)s into corresponding polyimides and it is carried out by heating poly(amic acid)s gradually to 250-350 °C. The imidization proceeds with the evolution of solvent and water formed during cyclization reaction. Alternatively, high temperature solution imidization is utilized to obtain soluble and processable polyimides. The cyclization is carried out by heating solution of poly(amic acid) in high boiling solvents at 160-200 °C using azeotropic distillation. As compared with thermal imidization, this method allows lower temperatures as well as greater mobility to polymer chains in solution which could avoid degradation and side reactions. The chemical imidization poly(amic acid)s involves the cyclization using a chemical dehydrating agent in the presence of basic catalyst at 20-80 °C, depending upon solubility of polyimides.[225] The commonly employed dehydrating agents are acetic anhydride, propionic anhydride, *n*-butyric anhydride, etc. with basic catalyst such as pyridine, isoquinoline and triethylamine. The different methods of imidization offer polyimides with varying solubility. Generally, polyimides obtained by chemical imidization have more solubility than those obtained by thermal imidization. However, thermal imidization provides polyimides with excellent thermal properties as compared to chemical cyclization.[226]

1.3.2.1.2 One-step high temperature solution polymerization

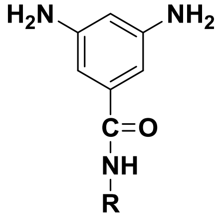
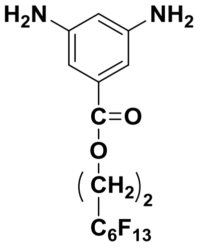
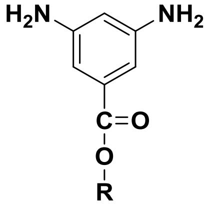
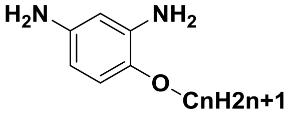
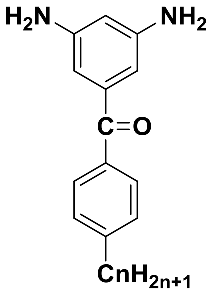
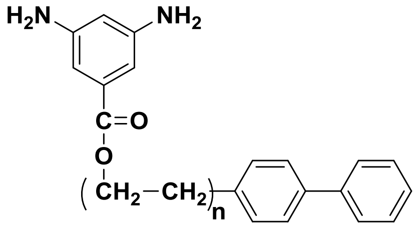
This method is used for preparation of polyimides which are soluble in high boiling solvents at polymerization reaction temperatures.[227] In the process, a stoichiometric amount of dianhydride and diamine are heated in a high-boiling solvent or mixture of solvents at temperatures above 150 °C.[228, 229] The imidization reaction at these temperatures proceeds rapidly and water generated during the reaction is distilled off constantly as an azeotropic mixture with the solvent. The solvents such as nitrobenzene, *m*-cresol, chlorinated aromatic solvents, chlorophenols and polar aprotic solvents are commonly used. Hasanain et al.[230] have utilized salicyclic acid as a solvent for synthesis of polyimides by one-step polycondesation.

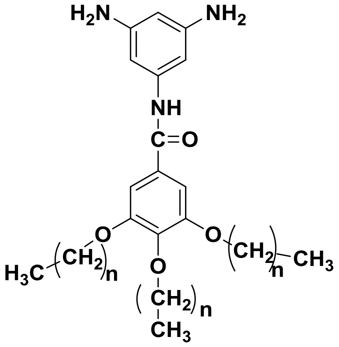
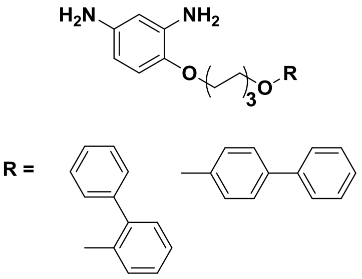
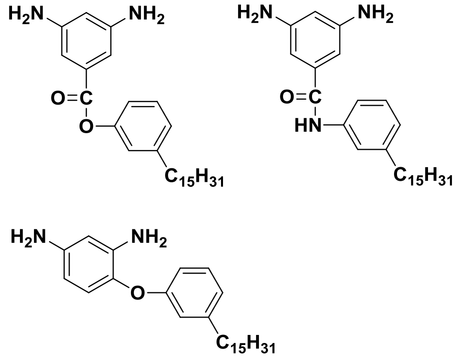
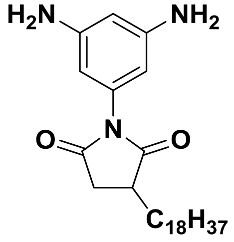
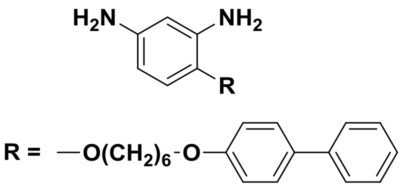
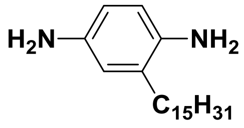
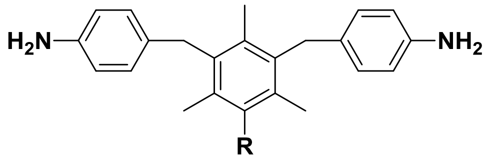
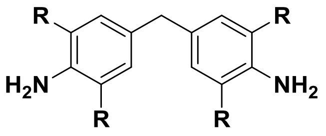
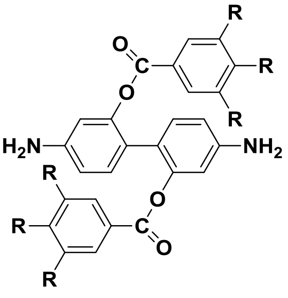
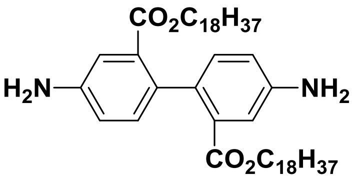
Toluene and o-dichlorobenzene are frequently used as cosolvents for azeotropic removal of water formed in condensation reaction. Unlike two-step method described above, the attainment of a high molecular weight poly(amic acid) is not necessary for this method. Imidization reaction still progresses *via* an amic acid intermediate which is present in relatively small concentration as it has short-life at higher temperatures and hence it gets rapidly imidized or decomposed to amine and anhydride. The one-step polymerization is usually carried out in the presence of quinoline, tertiary amines and dialkylaminopyridines as catalyst for imidization. In particular, the polymerization can be applicable for synthesis of polyimides from unreactive, sterically or electronically-hindered diamines and dianhydrides. The extent of imidization in polyimides obtained by one-step high temperature solution method is basically absolute or 100%. There will not be presence of ‘defect sites’ such as amic acid and isoimide units, in the resultant polyimides, which accounts for their superior physical properties over polyimides obtained by conventional two-step method. The one-step melt polymerization using the extrusion-molding method was used for preparation of polyimides having melting transitions (T_m) more than 300 °C or glass transition temperatures (T_g) more than 250 °C.[231]

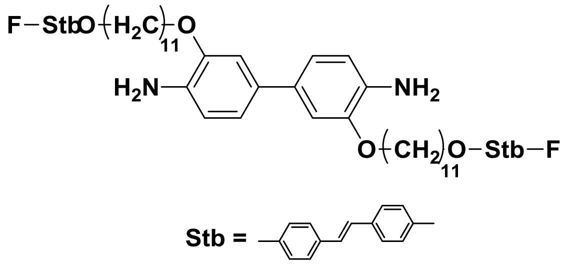
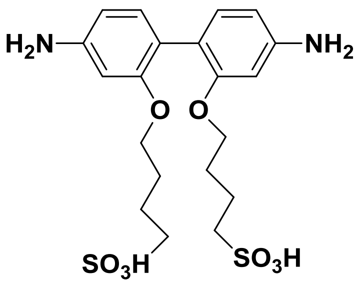
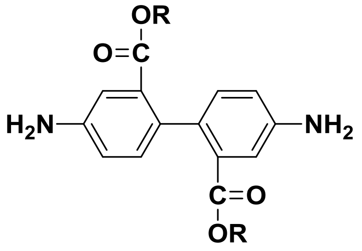
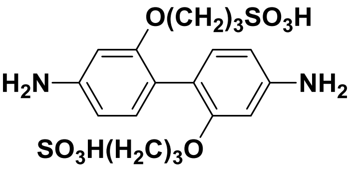
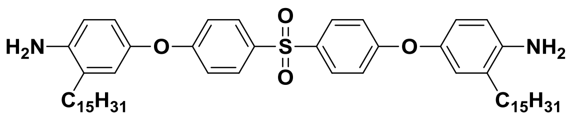
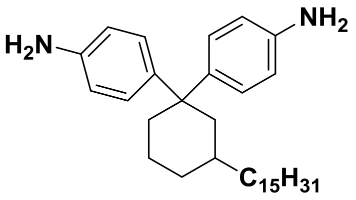
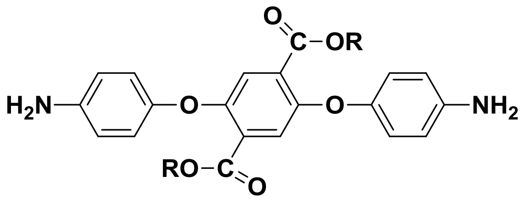
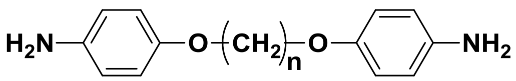
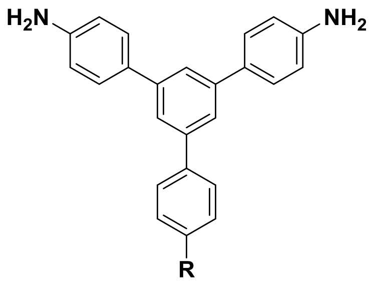
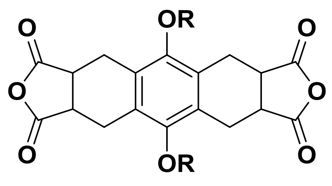
1.3.2.2 Structure-property relationship in polyimides

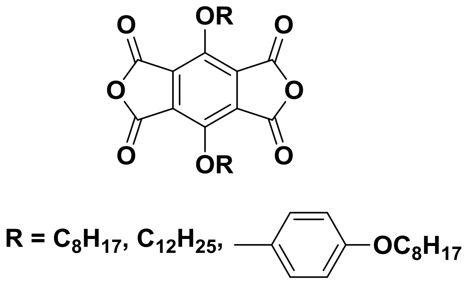
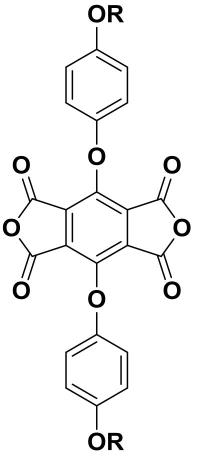
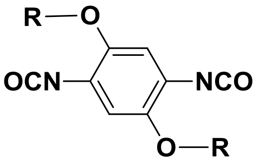
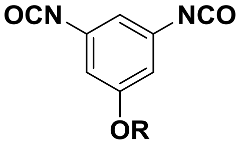
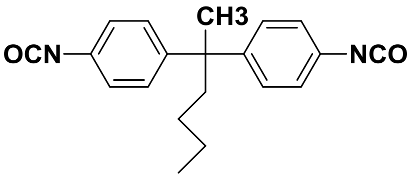
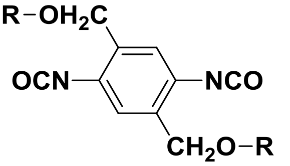
Polyimides are well known class of high performance polymers and by virtue of their high temperature stability, they have wide applications in advanced technologies e.g. spacecrafts, electronic industry, defense and consumer applications too. In spite of excellent properties, polyimides have limited solubility in common organic solvents and have high melting and glass transition temperatures because of rigid backbone as well as strong interchain interactions due to charge transfer complex (CTC) formation which pose problems during processing. Therefore, several approaches have been utilized to improve their melt and solution processability without losing their advantageous properties.[232-235] The most popular approaches are introduction of hinge atoms, flexible or kinked linkages, or non coplanar structure in the polymer backbone which reduce chain crystallinity, CTC formation and electronic polarization interactions. The variations in the structures of the diamine and dianhydride have a remarkable effect on properties of the modified polyimides. The incorporation of flexible linkages within or onto the backbone of polyimide will increase segmental motion, disrupt close chain packing and provide an additional handle for interaction with solvent, thus it offers resulting polymer with lower T_g and enhanced solubility. Therefore, large number of the efforts towards dropping the T_g and improving solubility of polyimides have centred on decreasing backbone rigidity by the incorporation of flexible linkages.[236] The selected examples of diamine, diisocyanate and dianhydride monomers containing flexible alkyl linkages used for the synthesis of polyimides are listed in **Table 1.4**.

Table 1.4 List of selected monomers containing flexible alkyl linkages used for the synthesis of polyimides

Monomer structure (Reference)	**Monomer structure (Reference)**
 R = C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ (237)	 (238)
 R = CH_3, C_4H_9, C_8H_{17}, $C_{10}H_{21}$, $C_{16}H_{33}$, $C_{18}H_{37}$ (239, 240)	 n = 6, 8, 10, 12, 14, 16 (241)
 n = 10, 11, 12, 13, 14 (242)	 n = 1, 3 (243)

Monomer structure (Reference)	**Monomer structure (Reference)**
 (244)	 (245)
 154, 246	 (247)
 (245)	 (248)
 R = C_6H_{13}, C_8H_{17} (249)	 R = CH_3, C_2H_5, $CH(CH_3)_2$ (250)
 R = $-O-(CH_2)_n-CH_3$, n = 5, 8, 10, 12, 14, 16,18 (251)	 (252)

Monomer structure (Reference)	**Monomer structure (Reference)**
 (253)	 (254)
 R = $-CH_2-(CH_2)_{n-1}-CH_3$ n = 7, 16,18 (255)	 (256)
 (156, 257)	 (200)
 R = CH_3, C_4H_9, C_8H_{17}, $C_{12}H_{25}$ (258)	 n = 2, 4, 6, 8, 10, 12 (259, 260)
 R = C_6H_{13}, $C_{12}H_{25}$ (261)	 R = C_4H_9, C_8H_{17}, $C_{12}H_{25}$ (258)

Monomer structure (Reference)	**Monomer structure (Reference)**
 (262, 263)	 R = CH_3, C_4H_9, C_8H_{17}, $C_{12}H_{25}$ (264, 265)
 R = C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$ (266)	 R = C_4H_9, C_8H_{17}, $C_{12}H_{25}$, $C_{16}H_{33}$ (267)
 (268)	 R = C_4H_9, C_6H_{13}, C_8H_{17} (269-271)

1.3.3 Polyhydrazides and poly(1,3,4-oxadiazole)s

Polyhydrazides[272] are found to be interesting polymeric materials because they have wide applications as fibers and membranes due to their excellent dyeability, improved elasticity and fair absorption characteristics. Furthermore, polyhydrazides serve as precursors to poly(1,3,4-oxadiazole)s and polytriazoles.[273] Polyhydrazides are also useful for preparation of chelating polymers since they possess hydrazide group (-CO-NH-NH-CO-) which can form complex with metal ions.[274] In general, low temperature solution polymerization,[275] interfacial polycondensation[63] and direct polycondensation using di- or triphenyl phosphate[276] have been used for the synthesis of polyhydrazides.

Poly(1,3,4-oxadiazole)s are an useful class of high performance polymers which find wide applications by virtue of high thermal stability as well as mechanical properties, in combination with opto-electronic properties owed by the 1,3,4-oxadiazole ring structure.[277]

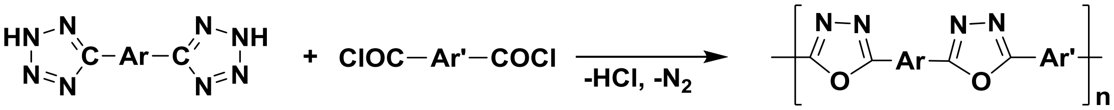
1.3.3.1 Synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s

1.3.3.1.1 Synthesis of polyhydrazides

In 1944, Moldenhnauer et al.[278] reported first synthesis of polyhydrazides by polycondensation reaction of dicarboxylic acids or their derivatives *viz.*, acid chloride with hydazine. The convenient method for preparation polyhydrazides is polycondensation of diacylhydrazides with dicarboxylic acids or their derivatives such as diester, diacid chloride, etc.[279] Generally, high molecular weight polyhydrazides are obtained by polycondensation reaction of diacid chloride and diacylhydrazide in N,N-dimethyl acetamide at low temperature[280] or by polycondensation of diacylhydrazide and dicarboxylic acid *via* Yamazaki-Higashi phosphorylation method in the presence of various condensing agents.[281, 282]

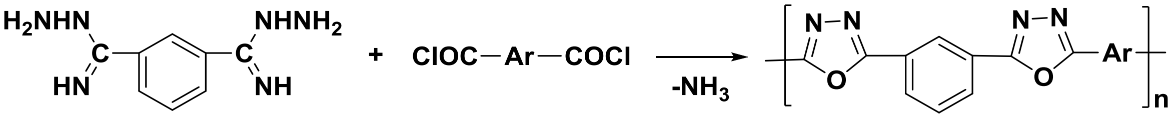
1.3.3.1.2 Synthesis of poly(1,3,4-oxadiazole)s

Poly(1,3,4-oxadiazole)s have been synthesized by different methods. Historically, various methods have been tried for the synthesis of poly(1,3,4-oxadiazole)s. **Scheme 1.18** depicts first method of synthesis by reaction of ditetrazoles and diacids,[283] However, low molecular weight polymers were obtained due to insolubility of the polymers. Thus, tetrazole monomers of various structures were polymerized to get polymer with improved solubility, but the high molecular weight polymers were not obtained.[284] Hence, the method is of historical interest only.



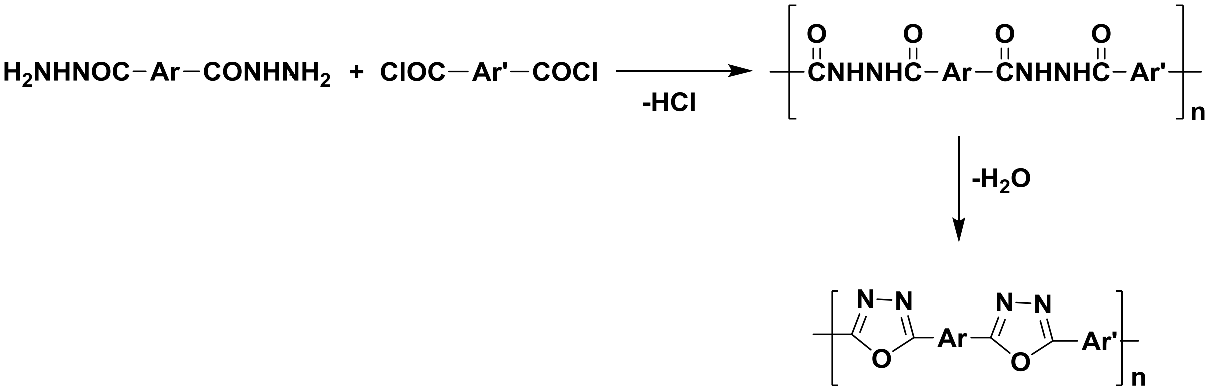
Scheme 1.18 Synthesis of poly(1,3,4-oxadiazole)s with reaction between ditetrazole and diacid chloride

In 1966, Saga and coworkers[285] reported polycondensation of bis(amidrazones) and diacid chlorides to form poly(*N*-acy1amidrazone)s which were cyclized to corresponding poly(1,3,4-oxadiazole)s. Further, a one step reaction between dicarboxylic acids and bis(amidrazones) was carried out in a mixture of methanesulfonic acid and P_2O_5 to form poly(1,3,4-oxadiazole)s (**Scheme 1.19)**[286] However, formation of low molecular weight polymers and low accessibility of the bis(amidrazone) monomers are the main limitations of the method.



Scheme 1.19 Synthesis of poly(1,3,4-oxadiazole)s using bis(amidrazones) and diacid chlorides

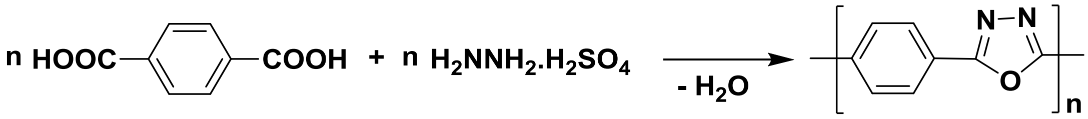
The widely used method for preparation of poly(1,3,4-oxadiazole)s involves two steps: 1) preparation of precursor polyhydrazide by polycondensation of diacylhydrazide of carboxylic acid and diacid chloride 2) cyclization of polyhydrazides to corresponding poly(1,3,4-oxadiazole)s either thermally (heating up to 300°C) or chemically (heating in dehydrating agents such as $POCl_3$), as depicted in **scheme 1.20**. The advantage of the two step method is the intermediate polyhydrazides are processable and can be obtained in high molecular weight. The method was first reported by Frazer et al.[287] in 1964 and was further investigated for a large number of monomers and various reaction conditions in different solvents *viz*., DMAc, NMP and HMPA.[288]



Scheme 1.20 Synthesis of poly(1,3,4-oxadiazole)s by two step route

The films or fibers of polyhydrazide can be converted into the corresponding poly(1,3,4-oxadiazole) by slowly heating up to 300 °C for long period (up to 100 h). The properties of poly(1,3,4-oxadiazole) obtained by thermal cyclization are mostly dependent on the cyclization temperature. It was found that kinetics of thermal cyclization of polyhydrazides follows first-order kinetic with slight deviation after completion of 80% cyclisation.[273] This indicates the cyclization proceeds with increase in rigidity in polymer chains and at the end the reaction was slowed due to limited diffusion.

One more method which has been extensively used to prepare poly(1,3,4-oxadiazole)s is one-step polycondensation of aromatic dicarboxylic acids or their derivatives such as ester, nitrile, amide, etc., with hydrazine (H_2NNH_2) or hydrazine sulfate ($H_2NNH_2.H_2SO_4$) in fuming sulfuric acid (oleum)[289] or in a mixture of strong acids[290, 291](**Scheme 1.21**)



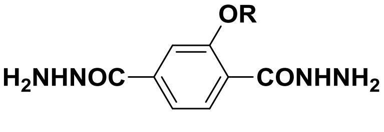
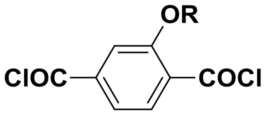
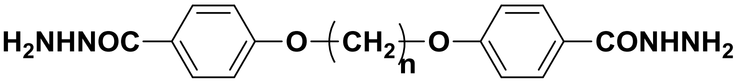
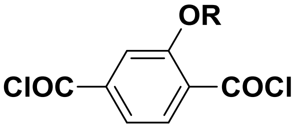
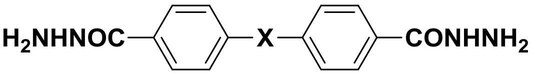
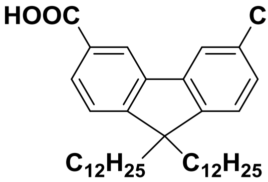
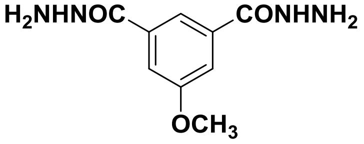
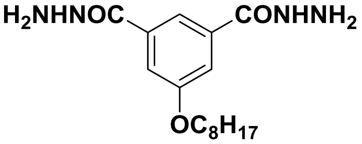
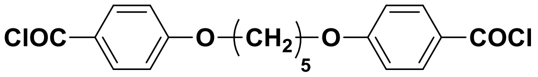
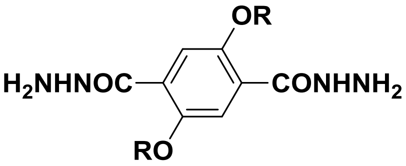
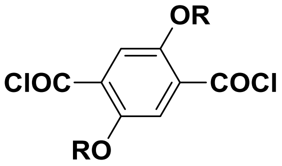
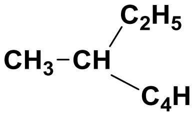
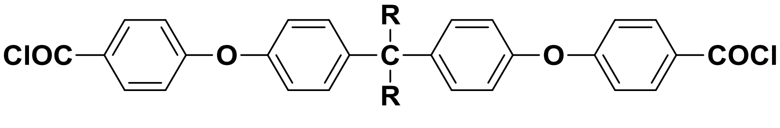
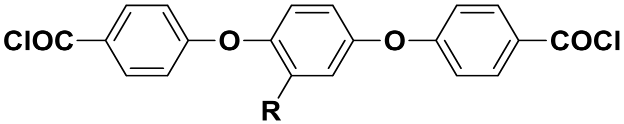
Scheme 1.21 Synthesis of poly(1,3,4-oxadiazole)s using hydrazine or hydrazine sulfate

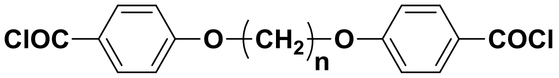
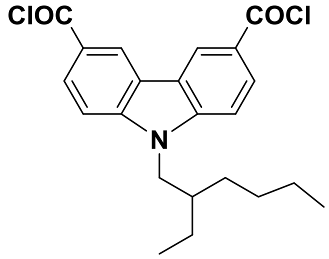
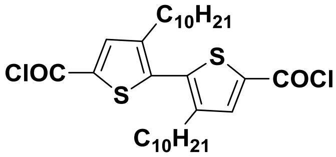
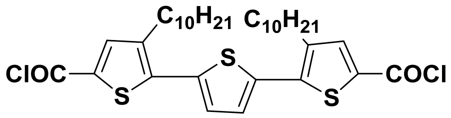
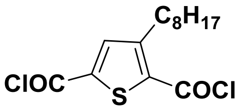
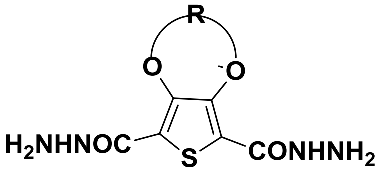
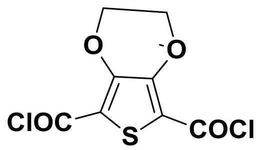
Among the methods and variations that have been investigated for the preparation of aromatic poly(1,3,4-oxadiazole)s, the most useful from a practical point of view are: 1) one-step polycondensation of dicarboxylic acids or their derivatives with hydrazine or hydrazine sulfate, and 2) two-step polycondensation of diacylhydrazides with diacid chlorides. Though the former method gives high molecular weight polymers, it is only applicable for acid stable monomer and has limited application due to strong acidic conditions. On other hand, latter method provides polymers of not only high molecular weight but also it can be used for a wide range of monomers.

1.3.3.2 Structure-property relationship in polyhydrazides and poly(1,3,4-oxadiazole)s

Polyhydrazides and poly(1,3,4-oxadiazole)s represent a special class high performance polymers so that they are utilized in small quantity for very high valued end-applications in membrane materials, opto-electronic devices, etc.[292] As poly(1,3,4-oxadiazole)s have low solubility in common organic solvents, new poly(1,3,4-oxadiazole)s containing bulky substituents on aromatic rings of backbone or bulky groups such as hexafluoroisopropylidene or diphenyl silane in the backbone or alkyl chain either as pendent or within polymer backbone with enhanced solubility in common organic solvents and hence processability were synthesized. The list of selected monomers used for synthesis of processable polyhydrazides and poly(1,3,4-oxadiazole)s is presented in **Table 1.5.**[293-307]

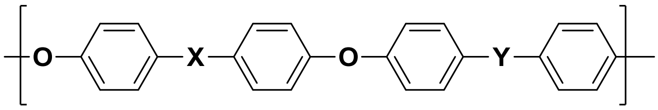
Table 1.5 List of selected monomers used for the synthesis of processable polyhydrazides and poly(1,3,4-oxadiazole)s

Sr. No.	Monomer Structure	Reference
1	  R = C_2H_5, C_5H_{11}, C_8H_{17}, $C_{10}H_{21}$	293
2	  R = C_5H_{11}, C_8H_{17}	294
3	 X = $C(CH_3)_2$, $O(CH_2)_6O$, O 	297
4	  	298
5	  R = $C_{12}H_{25}$, $C_{16}H_{33}$,  $CH_3-CH(C_2H_5)(C_4H_9)$	299-301
6	 R = CH_3, CF_3	302
7	 R = CH_3, $C(CH_3)_3$	303

Sr. No.	Monomer Structure	Reference
8	 n = 2, 4, 6, 8, 12	304
9		305
10	  	306
11	  R = $—CH_2 CH_2—$, $-(CH_2)_3-$	307

1.3.4 Poly(arylene ether)s

Poly(arylene ether)s are well known high performance engineering thermoplastics having significance in a wide range of applications *viz*., structural resins, microelectronic components, gaskets and tubing.[308] Poly(arylene ether)s have extensive applications because of their outstanding physical properties such as high modulus, toughness, good thermal and chemical stability. Generally, nucleophilic aromatic substitution (S_NAr) reaction between activated dihalides with bisphenols has been used for preparation a variety poly(arylene ether)s.[160, 309, 310]



X = -CO-, SO_2, etc.,

Y = $-C(CH_3)_2-$, $-C(CF_3)_2-$, -O-, etc

Figure 1.8 A general structure of poly(arylene ether) backbone

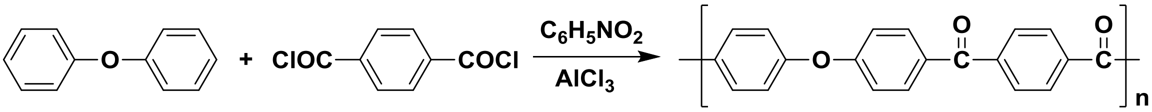
Figure 1.8 represents a general structure of poly(arylene ether) backbone, where X is usually a carbonyl or sulfonyl group derived from the activated dihalide and Y is any connecting group such as isopropylidene or a chemical bond.

1.3.4.1. Synthesis of poly(arylene ether)s

Poly(arylene ether)s can be synthesized by a variety of methods such as i) electrophilic substitution ii) nucleophilic aromatic substitution,[311, 312] iii) ring opening of arylene ether cyclics,[313-315]iv) silyl ether displacement, [316] and v) catalytic coupling.[308, 317] Out of these methods, the first two are most common and are discussed in brief below:

1.3.4.1.1 Electrophilic route

Conventionally, poly(ether ketone)s (PEKs) and poly(ether sulfone)s have been prepared by two types of reactions: Friedel-Crafts acylation or sulfonylation and nucleophilic aromatic substitution (SNAr). Generally PEKs are semicrystalline polymers with low solubility in common organic solvents. The initial research on PEKs was focused on finding a suitable solvent for their synthesis by Friedel-Crafts acylation reaction. Bonner[318] at DuPont has firstly achieved the synthesis of PEKs using terephthaloyl chloride and diphenyl ether in nitrobenzene solvent in the presence of catalysts such as aluminum chloride or antimony pentachloride **(Scheme 1.22)**. But, he could obtain low molecular weight polymers only.



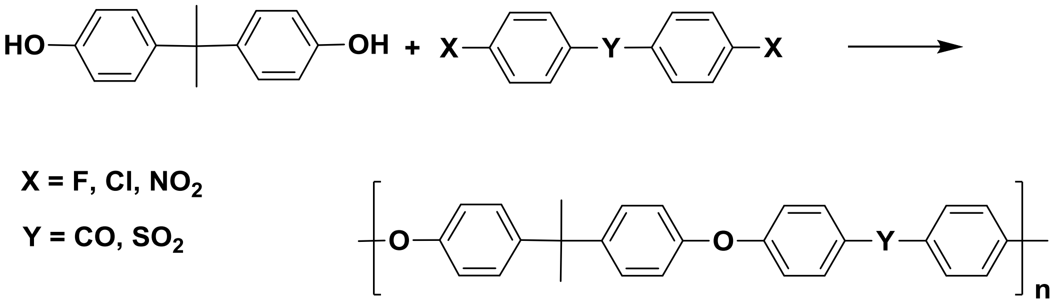
Scheme 1.22 Synthesis of poly(ether ketone ketone) *via* Friedel-Craft acylation

Further, Goodman made use of dichloromethane as the solvent and synthesized moderate molecular weight polymers.[319] *p*-Phenoxybenzoyl chloride which is an AB type monomer under these reaction condition afforded poly(ether ketone) with high molecular weight. Iwakura et al[320] demonstrated that polyphosphoric acid was useful solvent to polymerize p-phenoxybenzoic acid to PEK with moderate molecular weights. Marks et al[321] made use of HF/BF_3 as solvent and successfully synthesized high molecular weight PEK. Further, trifluoromethanesulfonic acid as solvent and catalyst for PEK synthesis was introduced by Rose.[322] However, handling of HF/BF_3 is not easy and trifluoromethanesulfonic acid is expensive, as a result both solvents are not preferred for industrial scale synthesis of PEK. Jansons et al[323] demonstrated applications of

Lewis bases like N, N-dimethyl formamide, dimethyl sulfone, tetramethylene sulfone, etc. as solvents for high molecular weight PEK synthesis. Similarly, poly(ether sulfone)s could be obtained with Friedel-Crafts sulfonylation in presence of ferric chloride in the place of aluminum chloride.

1.3.4.1.2 Nucleophilic route

This route is most commonly utilized for synthesis of poly(arylene ether)s and involves nucleophilic aromatic substitution reaction of bisphenoxide with activated dihalide. The polymerization reaction can be represented in **Scheme 1.23**



Scheme 1.23 Synthesis of poly(arylene ether)s by nucleophilic route

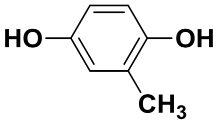
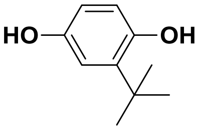
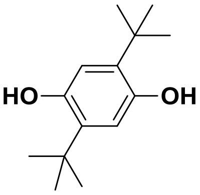
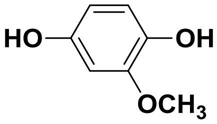
The presence of electron-withdrawing group *viz.*, carbonyl or sulfone is essential to activate aromatic dihalides. The order of reactivities in different aromatic halides is F >> Cl > Br. Generally, for strong electron-withdrawing group such as sulfone, the halide can be either -F or -Cl, but, for weak electron-withdrawing groups, halide must be -F to obtain high molecular weights. In the case less reactive dihalides like 4, 4'-dichlorobenzophenone, single electron transfer occurs as side reaction leading to low molecular weight polymers.[324, 325] Percec et al[326] attempted polymerization of dichloroketone monomers but unable to achieve high molecular weight polymers consistently.

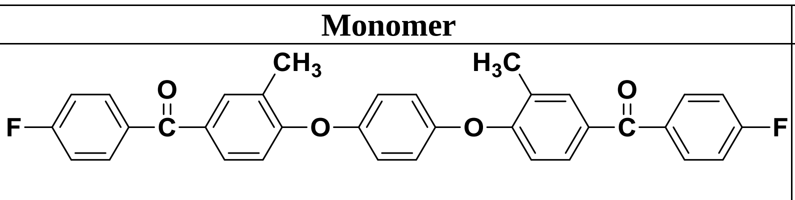
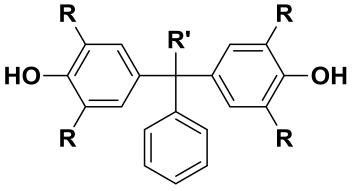
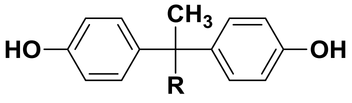
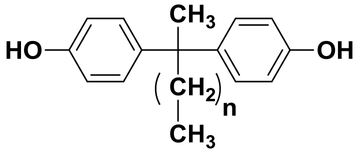
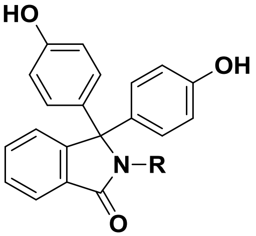
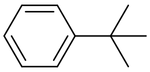
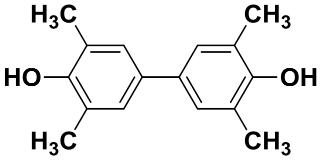
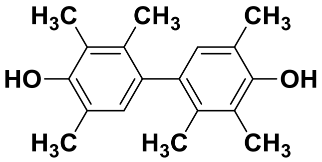
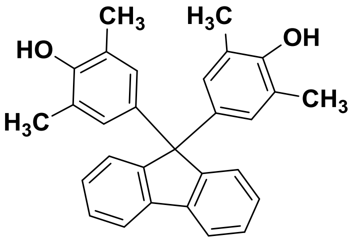
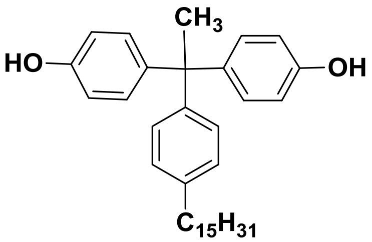
Johnson et al.[327] used dimethyl sulfoxide as a solvent, sodium hydroxide as base to form bisphenoxide salt, chlorobenzene for azeotropic distillation of water formed during reaction. However, the polymerization required bisphenol and sodium hydroxide in the strict stoichiometry as excess of sodium hydroxide can react with activated halide or ether linkages of the polymers which would reduce the molecular weights. The next limitation of the method is the insolubility of sodium hydroxide which prevents polymerization. The alkali metal carbonates *viz.*, sodium and potassium carbonate as base instead of sodium hydroxide were utilized by McGrath et al.[328] Excess carbonates can be accepted as they are poor nucleophile compared with sodium hydroxide. Kricheldorf et al[329] successfully synthesized poly(arylene ether)s using silylated bisphenols in the presence of CsF as a catalyst. The side product of the polymerization trimethylsilyl fluoride is a volatile which could be removed at high temperature. Thus, polymerization was carried out at melt condition without solvent and formation of salt.

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

Poly(arylene ether)s i.e. poly(ether ketone)s and poly(ether sulfone)s are well recognized high performance polymers because of their outstanding chemical and thermo-mechanical properties.[308, 330] However, poly(ether ketone)s have high crystallinity which hampers their solubility in common organic solvents resulting in limited applications of these materials. A variety of approaches have been introduced to modify of basic structure of PEEK in order to get different properties. The structural changes mainly focused on the ratio and order of ether/ketone linkages; introduction of *meta* kinks in backbone, incorporation of pendent alkyl or phenyl or bulky groups[331, 332] onto the polymer backbone, introduction of $-CR_2$ or sulfone groups in polymer backbone. These structural changes in PEEK, could decrease the crystallinity and offered better solubility leading them toward the wider applications. The selected examples of monomers containing flexible alkyl chains used for synthesis of poly(arylene ether)s are given in **Table 1.6.**

Table 1.6 List of selected monomers containing flexible alkyl chains used for synthesis of poly(arylene ether)s[333-342]

Sr. No.	Monomer	Reference
1		333
2		339
3		333
4		340

Sr. No.	Monomer	Reference
5		333
6	 R / R' = H, CH_3, CF_3	334
7	 R = $C_{11}H_{23}$, $C_{17}H_{35}$	335
8	 n = 2, 4	336
9	 R = CH_3 , 	337
10	 	341
11		342
12		143

1.4 Summary

1. Furans, lignin and CNSL are the major bio-based renewable sources of aromatic monomers useful for synthesis of high performance polymers and could be considered as promising feedstocks for sustainable polymer industry.
2. CNSL is an important source of natural phenols which is abundantly available and inexpensive by-product of agricultural-based Cashew Industry. CNSL has three reactive sites namely; phenolic hydroxyl group, aromatic ring and unsaturation in alkenyl side chains which provide opportunities for chemical transformations. Taking advantage of these reactive sites, a wide range of difunctional monomers have been synthesized. Still, there is a scope to explore potential use of CNSL for synthesis of difunctional monomers for high performance polymers with interesting properties such as improved solubility, melt processability, etc. Thanks to aliphatic C_{15} chain which is responsible for packing disruption in polymer chains and provides additional handle for interaction with solvents.
3. High performance polymers have diverse applications in aerospace and automotive industries, microelectronics, proton exchange membranes for fuel cells, etc. because of their excellent thermal stability, chemical resistance, mechanical strength and electrical properties. However, they have limited solubility, high glass transition temperatures (T_g) and/or melting temperatures (T_m) which restricts their widespread applications. Therefore, polymer chemistry is enriched with design and synthesis of new monomers for preparation of high performance polymers with improved processability characteristics. The study of preparations and properties of various high performance polymers has revealed structure-property relationship useful in designing and synthesis of polymers with desired properties. The incorporation of pendent flexible alkyl chains is one of the desired approaches used to improve polymer solubility and processability.

References

1. R. Hofer and M. Selig, in *Polymer Science: A Comprehensive Reference*, eds. K. Matyjaszewski and M. Moller, Elsevier, Amsterdam, 2012, pp. 5-14.
2. *Emission Scenarios Database; SRES Scenarios Version 1.1* July 2000; http://sres.ciesin.org/final_data.html.
3. C. V. Mythili, A. M. Retna and S. Gopalakrishnan, *J. Mater. Sci.*, 2004, **27**, 235-241.
4. A. Gandini, in *Biocatalysis in Polymer Chemistry*, ed. K. Loos, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, pp. 1-33.
5. D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493-1513.
6. A. Gandini, *Green Chem.*, 2010, **13**, 1061-1083.
7. A. Gandini, *Macromolecules*, 2008, **41**, 9491-9504.
8. http://www.iucn.org/.
9. A. Gandini and M. N. Belgacem, in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, 2008.
10. B. Kamm, M. Kamm, P. R. Gruber and S. Kromus, in *Biorefineries-Industrial Processes and Products*, Wiley-VCH Verlag GmbH, 2008, pp. 1-40.
11. R. Babu, K. O'Connor and R. Seeram, *Prog. Biomaterials*, 2013, **2**, 8.
12. P. T. Anastas and M. M. Kirchhoff, *Acc. Chem. Res.*, 2002, **35**, 686-694.
13. D. J. Dijkstra and G. Langstein, *Polym. Int.*, 2011, **61**, 6-8.
14. T. T. M. Tan, *J. Appl. Polym. Sci.*, 1997, **65**, 507-510.
15. A. L. Marshall and P. J. Alaimo, *Chem. Eur. J.*, 2010, **16**, 4970-4980.
16. J. Sanders, E. Scott, R. Weusthuis and H. Mooibroek, *Macromol. Biosci.*, 2007, **7**, 105-117.
17. G. John, B. Vijai Shankar, S. R. Jadhav and P. K. Vemula, *Langmuir*, 2010, **26**, 17843-17851.
18. J. C. Serrano-Ruiz, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266-5281.
19. N. Hernandez, R. C. Williams and E. W. Cochran, *Org. Biomol. Chem.*, 2014, **12**, 2834-2849.
20. R. T. Mathers, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 1-15.
21. S. A. Miller, *ACS Macro Lett.*, 2013, **2**, 550-554.

22. A. P. Dove and M. A. R. Meier, *Macromol. Chem. Phys.*, 2014, **215**, 2135-2137.
23. U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schäfer, *Angew. Chem. Inter. Ed.*, 2011, **50**, 3854-3871.
24. M. R. L. Furst, R. L. Goff, D. Quinzler, S. Mecking, C. H. Botting and D. J. Cole-Hamilton, *Green Chem.*, 2012, **14**, 472-477.
25. L. Montero de Espinosa and M. A. R. Meier, *Eur. Polym. J.*, 2011, **47**, 837-852.
26. H. Blattmann, M. Fleischer, M. Bähr and R. Mülhaupt, *Macromol. Rapid Commun.*, 2014, **35**, 1238-1254.
27. S. A. Sanchez-Vazquez, H. C. Hailes and J. R. G. Evans, *Polym. Rev.*, 2013, **53**, 627-694.
28. M. A. Mosiewicki and M. I. Aranguren, *Eur. Polym. J.*, 2013, **49**, 1243-1256.
29. L. Fertier, H. Koleilat, M. n. Stemmelen, O. Giani, C. Joly-Duhamel, V. Lapinte and J.-J. Robin, *Prog. Polym. Sci.*, 2013, **38**, 932-962.
30. F. Seniha Guner, Y. Yagci and A. Tuncer Erciyes, *Prog. Polym. Sci.*, 2006, **31**, 633-670.
31. D. Shukla, Y. S. Negi, J. S. Uppadhyaya and V. Kumar, *Polymer Reviews*, 2012, **52**, 189-228.
32. Z. S. Petrovic, *Polymer Reviews*, 2008, **48**, 109-155.
33. L. Maisonneuve, T. Lebarbe, E. Grau and H. Cramail, *Polym. Chem.*, 2013, **4**, 5472-5517.
34. M. A. R. Meier, *Macromol. Chem. Phys.*, 2009, **210**, 1073-1079.
35. M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788-1802.
36. F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup and J. P. Pascault, *Prog. Polym. Sci.*, 2010, **35**, 578-622.
37. H. R. Kricheldorf, *Polym. Rev.*, 1997, **37**, 599-631.
38. M. R. Islam, M. D. H. Beg and S. S. Jamari, *J. Appl. Polym. Sci.*, **131**, 10.1002/app.40787.
39. C. Aouf, S. Benyahya, A. Esnouf, S. Caillol, B. Boutevin and H. Fulcrand, *Eur. Polym. J.*, 2014, **55**, 186-198.

40. R. Auvergne, S. Caillol, G. David, B. Boutevin and J.-P. Pascault, *Chem. Rev.*, 2014, **114**, 1082-1115.
41. M. Fache, B. Boutevin and S. Caillol, *Eur. Polym. J.*, 2015, **68**, 488-502
42. D. J. Hayes, S. Fitzpatrick, M. H. B. Hayes and J. R. H. Ross, in *Biorefineries-Industrial Processes and Products*, eds. B. Kamm;, P. R. Gruber; and M. Kamm;, Wiley-VCH Verlag GmbH, 2008, pp. 139-164.
43. C. W. Bird and G. W. Cheeseman, *in Comprehensive Heterocyclic Chemistry,*, Eds.: Katritzky, A.R. and Rees, C.W. Vol. 4, Pergamon, Oxford, 1984, Chapters 1981.
44. Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933-1937.
45. S. F. Kirsch, *Org. Biomol. Chem.*, 2006, **4**, 2076-2080.
46. A. Gandini, *Prog. Polym. Sci.*, 2013, **38**, 1-29.
47. A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa and M. Gomes, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 295-298.
48. A. Mitiakoudis and A. Gandini, *Macromolecules*, 1991, **24**, 830-835.
49. S. Boufi, A. Gandini and M. N. Belgacem, *Polymer*, 1995, **36**, 1689-1696.
50. C. Moreau, M. Belgacem and A. Gandini, *Topics in Catalysis*, 2004, **27**, 11-30.
51. P. Sonar, T. R. B. Foong, S. P. Singh, Y. Li and A. Dodabalapur, *Chem. Commun.*, 2012, **48**, 8383-8385.
52. C. H. Woo, P. M. Beaujuge, T. W. Holcombe, O. P. Lee and J. M. J. FrÃ©chet, *J. Am. Chem. Soc.*, 2010, **132**, 15547-15549.
53. T. M. Lacerda and A. Gandini, *J. Renew. Mater.*, 2014, **2**, 2-12.
54. J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539-554.
55. J. A. Moore and J. E. Kelly, *Macromolecules*, 1978, **11**, 568-573.
56. J. A. Moore and J. E. Kelly, *J. Polym. Sci. Polymer Chem. Ed.*, 1978, **16**, 2407-2409.
57. J. A. Moore and J. E. Kelly, *Polymer*, 1979, **20**, 627-628.
58. J. A. Moore and E. M. Partain, *Macromolecules*, 1983, **16**, 338-339.
59. S. Boufi, M. N. Belgacem, J. Quillerou and A. Gandini, *Macromolecules*, 1993, **26**, 6706-6717.

60. J. A. Moore and J. E. Kelly, *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22**, 863-864.
61. S. Gharbi, A. Afli, R. E. Gharbi and A. Gandini, *Polym. Int.*, 2001, **50**, 509-514.
62. S. Gharbi and A. Gandini, *Acta Polym.*, 1999, **50**, 293-297.
63. A. Afli, S. Gharbi, R. El Gharbi, Y. Le Bigot and A. Gandini, *Eur. Polym. J.*, 2002, **38**, 667-673.
64. C. Méalares and A. Gandini, *Polym. Int.*, 1996, **40**, 33-39.
65. Z. Hui and A. Gandini, *Eur. Polym. J.*, 1992, **28**, 1461-1469.
66. N. Teramoto, Y. Arai and M. Shibata, *Carbohyd. Polym.*, 2006, **64**, 78-84.
67. C. Vilela, L. Cruciani, A. J. D. Silvestre and A. Gandini, *Macromol. Rapid Commun.*, 2011, **32**, 1319-1323.
68. C. Goussé and A. Gandini, *Polym. Int.*, 1999, **48**, 723-731.
69. C. Gousse and A. Gandini, *Polym. Bull.*, 1998, **40**, 389-394.
70. X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698-1702.
71. R. Zhang and J. A. Moore, *Macromol. Symp.*, 2003, **199**, 375-390.
72. Z. Ping, W. Linbo and L. Bo-Geng, *Polym. Degrad. Stab.*, 2009, **94**, 1261-1266.
73. C. Wang and S. Nakamura, *J. Polym. Sci. Part A: Polym. Chem.*, 1995, **33**, 2157-2163.
74. F. Chu, C. J. Hawker, P. J. Pomery and D. J. T. Hill, *J. Polym. Sci. Part A: Polym. Chem.*, 1997, **35**, 1627-1633.
75. K.-Y. Chen and C. B. Gorman, *J. Org. Chem.*, 1996, **61**, 9229-9235.
76. R. P. Fischer, G. Robert Hartranft and J. S. Heckles, *J. Appl. Polym. Sci.*, 1966, **10**, 245-252.
77. S. S. Nagane, P. S. Sane, B. V. Tawade and P. P. Wadgaonkar, WO 2014073001, 2014.
78. A. Maiorana, S. Spinella and R. A. Gross, *Biomacromolecules*, 2015, **16**, 1021-1031.
79. E. Ten and W. Vermerris, *J. Appl. Polym. Sci.*, 2015, **132**, DOI: 10.1002/app.42069.
80. http://www.lignoworks.ca/content/what-lignin.

81. S. Laurichesse and L. Averous, *Prog. Polym. Sci.*, 2014, **39**, 1266-1290.
82. E. Ten and W. Vermerris, *Polymers*, 2013, **5**, 600-642.
83. H. Lange, S. Decina and C. Crestini, *Eur. Polym. J.*, 2013, **49**, 1151-1173.
84. A. Abe, K. Dusek, S. Kobayashi, H. Hatakeyama and T. Hatakeyama, in *Biopolymers*, Springer Berlin Heidelberg, 2010, pp. 1-63.
85. M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol and B. Boutevin, *Green Chem.*, 2014, **16**, 1987-1998.
86. B. G. Harvey, A. J. Guenthner, H. A. Meylemans, S. R. L. Haines, K. R. Lamison, T. J. Groshens, L. R. Cambrea, M. C. Davis and W. W. Lai, *Green Chem.*, 2014, **17**, 1249-1258.
87. I. A. Pearl, *J. Am. Chem. Soc.*, 1952, **74**, 4260-4262.
88. I. A. Pearl, *J. Am. Chem. Soc.*, 1952, **74**, 4593-4594.
89. İ. Kaya, F. Doğan and M. Gül, *J. Appl. Polym. Sci.*, 2011, **121**, 3211-3222.
90. L. Mialon, A. G. Pemba and S. A. Miller, *Green Chem.*, 2010, **12**, 1704-1706.
91. N. Matsumi, N. Nakamura and K. Aoi, *Polym. J*, 2008, **40**, 400-401.
92. C. Pang, J. Zhang, Q. Zhang, G. Wu, Y. Wang and J. Ma, *Polym. Chem.*, 2015, **6**, 797-804.
93. C. H. R. M. Wilsens, Y. S. Deshmukh, W. Liu, B. A. J. Noordover, Y. Yao, H. E. H. Meijer and S. Rastogi, *Polymer*, 2015, **60**, 198-206.
94. J. Qin, H. Liu, P. Zhang, M. Wolcott and J. Zhang, *Polym. Int.*, 2014, **63**, 760-765.
95. J. F. Stanzione, J. M. Sadler, J. J. La Scala and R. P. Wool, *ChemSusChem*, 2012, **5**, 1291-1297.
96. S. Günther, P. Lamprecht and G. A. Luinstra, *Macromol. Symposia*, 2010, **293**, 15-19.
97. M. Neda, K. Okinaga and M. Shibata, *Mater. Chem. Phys.*, 2014, **148**, 319-327.
98. L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman and P. Dubois, *J. Mater. Chem. A*, 2015, **3**, 6012-6018.
99. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, 2014, **5**, 3142-3162.
100. V. S. Balachandran, S. R. Jadhav, P. K. Vemula and G. John, *Chem. Soc. Rev.*, 2012, **42**, 427-438.

101. C. K. S. Pillai, *Des. Monomers Polym.*, 2010, **13**, 87-121.
102. M. C. Lubi and E. T. Thachil, *Des. Monomers Polym.*, 2000, **3**, 123-153.
103. P. H. Gedam and P. S. Sampathkumaran, *Prog. Org. Coat.*, 1986, **14**, 115-157.
104. C. K. S. Pillai, *Pure Appl. Chem.*, 1998, **70**, 1249-1252.
105. G. John, B. Vijai Shankar, S. R. Jadhav and P. K. Vemula, *Langmuir*, 2010, **26**, 17843-17851.
106. G. Mele and G. Vasapollo, *Mini-Rev. Org. Chem.*, 2008, **5**, 243-253.
107. A. Kozubek, J. H. P. Tyman and R. Atta-Ur, in *Stud. Nat. Prod. Chem.* , 2005, pp. 111-190.
108. P. L. Nayak, *J. Macromol. Sci. Part C: Polym. Rev.*, 2000, **40**, 1-21.
109. R. Saladino, G. Gualandi, A. Farina, C. Crestini, L. Nencioni and A. T. Palamara, *Curr. Med. Chem.*, 2008, **15**, 1500-1519.
110. J. M. Raquez, M. Deleglise, M. F. Lacrampe and P. Krawczak, *Prog. Polym. Sci.*, 2010, **35**, 487-509.
111. G. Vasapollo, G. Mele and R. D. Sole, *Molecules*, 2011, **16**, 6871-6882.
112. J. H. P. Tyman, *Synthetic and Natural Phenols, Elsevier, Amsterdam*, 1996.
113. M. T. Harvey and C. Caplan, *Ind. Eng. Chem.*, 1940, **32**, 1306.
114. O. A. Attanasi, *Chim. Oggi*, 1983, **8**, 11-14.
115. P. K. Vemula and G. John, *Acc. Chem. Res.*, 2008, **41**, 769-782.
116. A. Kozubek, R. Zarnowski, M. Stasiuk and Gubernator, *J. Cell. Mol. Biol. Lett.*, 2001, **6**, 351-355.
117. S. Manjula and C. K. S. Pillai, *Thermochim. Acta*, 1990, **159**, 255-266.
118. J. H. P. Tyman, *Synthetic and Natural Phenols, Elsevier, Amsterdam*, 2008, ch. 13.
119. J. H. P. Tyman, *J. Am. Oil Chem. Soc.* , 1989, **66**, 533-537.
120. T. Gandhi, M. Patel and B. K. Dholakiya, *J. Nat. Prod. Plant Resour.*, 2012, **2**, 135-142.
121. A. Stadeler, *Ann. Chem. Pharm.*, 1847, **63**, 137.
122. A. R. R. Menon, C. K. S. Pillai, J. D. Sudha and A. G. Mathew, *J. Sci. Ind. Res.*, 1985, **44**, 324-338.
123. J. H. P. Tyman, D. Wielezynski and M. A. Kashani, *J. Am. Chem. Soc.*, 1978, **55**, 663-670.

124. M. T. S. Trevisan, B. Pfundstein, R. Haubner, G. Wurtele, B. Spiegelhalder, H. Bartsch and R. W. Owen, *Food Chem. Toxicol.*, 2006, **44**, 188-197.
125. J. H. P. Tyman and L. J. J. Morris, *J. Chromatogr.*, 1967, **27**, 287-288.
126. J. H. P. Tyman and N. J. Jacobs, *J. Chromatogr.*, 1971, **54**, 83-90.
127. B. G. K. Murthy, M. A. Sivasamban and J. S. Agarwal, *Ind. J. Chem.*, 1965, **3**, 33-36.
128. I. K. Varma, S. K. Bhara, M. Varma and T. S. Biddapa, *Angew. Macromol. Chem.*, 1987, **154**, 67-86.
129. J. H. P. Tyman, *J. Chromatogr.*, 1975, **111**, 285-292.
130. S. J. Krishnamurthy, *J. Ind. Chem. Soc.*, 1951, **28**, 193-197.
131. J. H. P. Tyman, *J. Chromatogr.*, 1978, **156**, 255-266.
132. J. H. P. Tyman, *Anal. Chem.*, 1976, **48**, 30-34.
133. Risfaheri, T. T. Irawadi, A. M. Nur and I. Sailah, *Indonesian J. Agri. Sci.*, 2009, **2**, 11-20.
134. P. P. Kumar, R. Paramashivappa, P. J. Vithayathil, P. V. S. Rao and A. S. Rao, *J. Agri. Food Chem.*, 2002, **50**, 4705-4708.
135. S. K. Sood, J. H. P. Tyman, A. Durrani and R. A. Johnson, *Lipids*, 1986, **21**, 241-246.
136. B. G. K. Murthy, M. A. S. Samban and J. S. Aggarwal, *J. Chromatag.*, 1968, **32**, 519-528.
137. K. I. Suresh and M. Jaikrishna, *J. Polym. Sci. Part A: Polym. Chem.*, 2005, **43**, 5953-5961.
138. P. H. Gedam, P. S. Sampathkumaran and M. A. SivaSamban, *Ind. J. Chem.*, 1972, **10**, 388-391.
139. S. Agarwal, A. Mishra and J. S. P. Rai, *J. Appl. Polym. Sci.*, 2003, **87**, 1948-1951.
140. H. P. Bhunia, G. B. Nando, A. Basak, S. Lenka and P. L. Nayak, *Eur. Polym. J.*, 1999, **35**, 1713-1722.
141. B. V. Tawade, J. K. Salunke, P. S. Sane and P. P. Wadgaonkar, *J. Polym. Res.*, 2014, **21**, 617.
142. A. S. More, P. V. Naik, K. P. Kumbhar and P. P. Wadgaonkar, *Polym. Int.*, 2010, **59**, 1408-1414

143. A. S. More, S. K. Pasale, P. N. Honkhambe and P. P. Wadgaonkar, *J. Appl. Polym. Sci.*, 2011 **121** 3689-3695.
144. A. S. More, S. K. Pasale and P. P. Wadgaonkar, *Eur. Polym. J.* , 2010, **46**, 557-567.
145. A. S. More, P. S. Sane, A. S. Patil and P. P. Wadgaonkar, *Polym. Degrad. Stab.* , 2010, **95**, 1727-1735.
146. A. S. More, A. S. Patil and P. P. Wadgaonkar, *Polym. Degrad. Stab.*, 2010, **95** 837-844.
147. N. V. Sadavarte, M. R. Halhalli, C. V. Avadhani and P. P. Wadgaonkar, *Eur. Polym. J.*, 2009, **45,** 582-589
148. N. V. Sadavarte, C. V. Avadhani, P. V. Naik and P. P. Wadgaonkar, *Eur. Polym. J.*, 2010, **46**, 1307-1315.
149. N. V. Sadavarte, S. S. Patil, C. V. Avadhani and P. P. Wadgaonkar, *High Perform. Polym.*, 2013, **25**, 735-743.
150. N. V. Sadavarte, C. V. Avadhani and P. P. Wadgaonkar, *High Perform. Polym.*, 2011, **23**, 494-505.
151. C. V. Avadhani, P. P. Wadgaonkar and S. Sivaram, *US 6255439*, 2001.
152. N. D. Ghatge and N. N. Maldar, *Polymer*, 1984, **25**, 1353-1356.
153. H. P. Bhunia, R. N. Jana, A. Basak, S. Lenka and G. B. Nando, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 391-400.
154. J. S. Mathew, S. P. Vernekar, R. Mercier and R. Kerboua, *US 6500913*, 2002.
155. A. J. Varma and S. Sivaram, *US 6451957*, 2002.
156. A. S. Jadhav, S. P. Vernekar and N. N. Maldar, *Polym. Int.*, 1993, **32**, 5-11.
157. C. K. S. Pillai, D. C. Sherrington and A. Sneddon, *Polymer*, 1992, **33**, 3968-3970.
158. A. Cyriac, S. R. Amrutha and M. Jayakannan, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 3241-3256.
159. P. E. Cassidy, *Thermally stable polymers: Synthesis and properties*, Marcel Dekker Inc., New York, 1980.
160. P. M. Hergenrother, *High Perform. Polym.*, 2003, **15**, 3-45.
161. C. W. Ulmer II, D. A. Smith, B. G. Sumpter and D. I. Noid, eds., *Computational and Theoretical Polymer Science*, 1998.
162. A. J. Conix, *Ind. Chim. Belg.*, 1957, **22**, 1457-1462.

163. V. V. Korshak, *The Chemical Structure and Thermal Characterization of Polymers*, Israel Program for Scientific Translations, Keter, London, 1971.
164. W. M. Eareckson, *J. Polym. Sci. Part A: Polym. Chem.*, 1959, **40**, 399-406.
165. E. Bucio, J. C. I. Lara-Estevez, F. A. Ruiz-Trevino and A. Acosta-Huerta, *Polym. Bull.*, 2006, **56**, 163-170.
166. S. V. Vinogradova, V. A. Vasnev and P. M. Valetskii, *Russ. Chem. Rev.*, 1994, **63**, 833.
167. S. C. Temin, in *Interfacial Syntheis, Vol II: Polymer Applications and Technology*, eds. F. Millich and C. E. J. Carraher, Marcel Dekker, New York, 1977.
168. C. M. Starks, *J. Am. Chem. Soc.*, 1971, **93**, 195-199.
169. G. Borissov and H. Sivriev, *Makromol. Chem.*, 1972, **158**, 215-222.
170. V. A. Vasnev and S. V. Vinogradova, *Russ Chem Rev*, 1979, **48**, 16-27.
171. E. Bucio, J. W. Fitch, S. R. Venumbaka and P. E. Cassidy, *Polymer*, 2005, **46**, 3971-3974.
172. H. J. Jeong, K. Iwasaki, M. A. Kakimoto and Y. Imai, *Polym J*, 1994, **26**, 379-385.
173. F. Blaschke and W. Ludwing, *US 3395119*, 1968.
174. H. Schnell, V. Boilert and G. Fritz, *US 3335167*, 1971.
175. G. M. Kosanovich and G. Salee, *US 4465819*, 1984.
176. T. S. Chung, *Polym. Eng. Sci.*, 1986, **26**, 901-919.
177. E. E. Riecke and F. L. Hamb, *J. Polym. Sci. Part A: Polym. Chem.*, 1977, **15**, 593-609.
178. G. Bier, *Polymer*, 1974, **15**, 527-535.
179. S. S. Mahajan, B. B. Idage, N. N. Chavan and S. Sivaram, *J. Appl. Polym. Sci.*, 1996, **61**, 2297-2304.
180. H. Kricheldorf and G. Schwarz, *Polym. Bull.*, 1979, **1**, 383-388.
181. H. R. Kricheldorf, Q. Z. Zang and G. Schwarz, *Polymer*, 1982, **23**, 1821-1829.
182. S. Kitayama, K. Sanui and N. Ogata, *J. Polym. Sci. Part A: Polym. Chem.*, 1984, **22**, 2705-2712.
183. F. Higashi, N. Akiyama and T. Koyama, *J. Polym. Sci. Part A: Polym. Chem.*, 1983, **21**, 3233-3239.
184. K. Matsukawa and H. Inoue, *J. Polym. Sci. Polym. Lett.*, 1990, **28**, 13-19.

185. T. Hashimoto, T. Izumitani and M. Takenaka, *Macromolecules*, 1989, **22**, 2293-2302.

186. D.-J. Liaw, *J. Polym. Sci. Part A: Polym. Chem.*, 1995, **33**, 605-613.

187. P. W. Morgan, *Macromolecules*, 1970, **3**, 536-544.

188. S.-H. Hsiao and H.-W. Chiang, *Eur. Polym. J.*, 2004, **40**, 1691-1697.

189. W. R. Krigbaum, J. Asrar, H. Toriumi, A. Ciferri and J. Preston, *J. Polym. Sci. Polym. Lett.*, 1982, **20**, 109-115.

190. B. W. Jo, R. W. Lenz and J. Jin, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 23-27.

191. D. H. Wang, S. Z. D. Cheng and F. W. Harris, *Polymer*, 2008, **49**, 3020-3028.

192. Y. H. Ahn and J. H. Chang, *Polym. Adv. Technol.*, 2008, **19**, 1479-1485.

193. S. Woo Lee and M. Ree, *J. Polym. Sci. Part A: Polym. Chem.*, 2004, **42**, 1322-1334.

194. R. Centore, A. Roviello, A. Sirigu and H. R. Kricheldorf, *Macromol. Chem. Phys.*, 1994, **195**, 3009-3016.

195. F. Kakali, J. Kallitsis, T. Pakula and G. Wegner, *Macromolecules*, 1998, **31**, 6190-6198.

196. J.-W. Lee, J.-I. Jin, B.-W. Jo, J.-S. Kim, W.-C. Zin and Y.-S. Kang, *Acta Polym.*, 1999, **50**, 399-407.

197. M. R. Pixton and D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.*, 1995, **33**, 1135-1149.

198. M. R. Pixton and D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.*, 1995, **33**, 1353-1364.

199. Y. Chen, R. Wombacher, J. H. Wendorff and A. Greiner, *Polymer*, 2003, **44**, 5513-5520.

200. R. D. Shingte, *Ph.D. Thesis submitted to University of Pune, Pune, India*, 2006.

201. M. T. Bogert and R. R. Renshaw, *J. Am. Chem. Soc.*, 1908, **30**, 1135-1144.

202. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards and K. L. Olivier, *J. Polym. Sci.*, 1965, **3**, 1373-1390.

203. C. E. Sroog, *Prog. Polym. Sci.*, 1991, **16**, 561-694.

204. M. K. Ghosh and K. L. Mittal, eds., *Polyimides, Fundamentals and Applications*, Marcel Dekker, New York, 1996.

205. P. E. Cassidy, ed., *Thermally STable Polymers* Marcel Dekker, New York, 1980.
206. R. B. Seymour and G. S. Krishenbaum, *High Performance Polymers: Their Origin and Developments*, Elsevier, New York, 1986.
207. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, eds., *Polyimides*, Blackie & Sons Ltd, Glasgow and London, 1990.
208. C. Feger, K. M. M. and J. E. McGrath, eds., *Polyimides: Materials,Chemistry and Characterization*, Elsevier, Amsterdam, 1989.
209. T. Takekoshi, in *Polyimides, Fundamentals and Applications*, eds. G. M. K and K. L. Mittal, Marcel Dekker, New York, 1996.
210. A. Mochizuki, T. Teranishi and M. Ueda, *Polym. J.*, 1994, **26**, 315-323.
211. T. M. Moy, C. D. DePorter and J. E. McGrath, *Polymer*, 1993, **34**, 819-824.
212. M. Sato, in *Handbook of Thermoplastics*, ed. O. Olabisi, Marccel Dekker, New York, 1997, p. 665.
213. H. Yeganeh, B. Tamami and I. Ghazi, *Eur. Polym. J.*, 2004, **40**, 2059-2064.
214. Y. Imai and K. Kojima, *J. Polym. Sci. Part A-1: Polym. Chem.*, 1972, **10**, 2091-2096.
215. G. S. Liou, S. H. Hsiao, M. Ishida, M. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 3815-3822.
216. S. Di Bella, G. Consiglio, N. Leonardi, S. Failla, P. Finocchiaro and I. Fragalà, *Eur. J. Inorg. Chem.*, 2004, **2004**, 2701-2705.
217. R. Gheneim, C. Perez-Berumen and A. Gandini, *Macromolecules*, 2002, **35**, 7246-7253.
218. J. H. Chi, G. J. Shin, Y. S. Kim and J. C. Jung, *J. Appl. Polym. Sci.*, 2007, **106**, 3823-3832.
219. D. M. Munoz, J. G. de la Campa, J. de Abajo and A. E. Lozano, *Macromolecules*, 2007, **40**, 8225-8232.
220. Y. Oishi, S. Onodera, J. Oravec, K. Mori, S. Ando, Y. Terui and K. Maeda, *J. Photopolym. Sci. Technol.*, 2003, **16**, 263-266.
221. R. J. Perry, S. E. Tunney and B. D. Wilson, *Macromolecules*, 1996, **29**, 1014-1020.
222. Y. J. Kim, T. E. Glass, G. D. Lyle and J. E. McGrath, *Macromolecules*, 1993, **26**, 1344-1358.

223. V. A. Zubkov, M. M. Koton, V. V. Kudryavtsev and V. M. Svetlichnyi, *Zh. Org. Khim*, 1981, **17**, 1682.

224. L. W. Frost and I. Kesse, *J. Appl. Polym. Sci.*, 1964, **8**, 1039-1051.

225. M. H. Kailani, C. S. P. Sung and S. J. Huang, *Macromolecules,* 1992, **25**, 3751-3757.

226. G.-S. Liou, S.-H. Hsiao, M. Ishida, M. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 3815-3822.

227. S. V. Vinogradova, Y. S. Vygodskii and V. V. Korshak, *Polym. Sci. U.S.S.R.*, 1970, **12**, 2254-2262.

228. F. W. Harris, in *Polyimides*, eds. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, Chapman and Hall, New York, 1990

229. T. Takekoshi, in *Polyimides: Fundamentals and Applications*, eds. M. K. Ghosh and K. L. Mittal, Marcel Dekker, New York, 1996.

230. F. Hasanain and Z. Y. Wang, *Polymer*, 2008, **49**, 831-835.

231. L. R. Schmidt, E. M. Lovgren and P. G. Meissner, *Int. Polym. Process.*, 1989, **4**, 270-276.

232. M. Ding, *Prog. Polym. Sci.*, 2007, **32**, 623-668.

233. J. de Abajo and J. G. de la Campa, *Prog. Polyimide Chem. I*, 1999, **140**, 23-59.

234. M. G. Dhara and S. Banerjee, *Prog. Polym. Sci.*, 2010, **35**, 1022-1077.

235. A. Ghosh, S. K. Sen, S. Banerjee and B. Voit, *RSC Adv.*, 2012, **2**, 5900-5926.

236. D. J. Liaw, K. L. Wang, Y. C. Huang, K. R. Lee, J. Y. Lai and C. S. Ha, *Prog. Polym. Sci.*, 2012, **37**, 907-974.

237. J. T. Jung, M. H. Yl, S. K. Kwon and K. Y. Chol, *Mol. Cryst. Liq. Cryst. Sci. Technol.*, 1999, **333**, 1-13.

238. J.-H. Kim, S.-B. Lee and S. Y. Kim, *J. Appl. Polym. Sci.*, 2000, **77**, 2756-2767.

239. Y. J. Lee, J. G. Choi, I. K. Song, J. M. Oh and M. H. Yi, *Polymer*, 2006, **47**, 1555-1562.

240. J. R. Sasthav and F. W. Harris, *Polymer*, 1995, **36**, 4911-4917.

241. L. Li, J. Yin, Y. Sui, H. J. Xu, J. H. Fang, Z. K. Zhu and Z. G. Wang, *J. Polym. Sci. Part A: Polym. Chem.*, 2000, **38**, 1943-1950.

242. Y. Tsuda, T. Kawauchi, N. Hiyoshi and S. Mataka, *Polym J*, 2000, **32**, 594-601.
243. X. Liu, H. Xiang, J. Yang and Y. Gu, *J. Appl. Polym. Sci.*, 2003, **90**, 3291-3298.
244. Y. Tsuda, M. Kojima, T. Matsuda and J. M. Oh, *Polym. J.*, 2008, **40**, 354-366.
245. S. I. Kim, M. Ree, T. J. Shin and J. C. Jung, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 2909-2921.
246. J. S. Mathew, *Ph. D. Dissertation, University of Pune, Pune, India*, 2001.
247. Y. J. Lee, Y. W. Kim, J. D. Ha, J. M. Oh and M. H. Yi, *Polym. Adv. Technol.*, 2007, **18**, 226-234.
248. N. D. Ghatge and N. N. Maldar, *Polymer*, 1984, **25**, 1353-1356.
249. F. Dumont, M. Visseaux, D. Barbier-Baudry and A. Dormond, *Polymer*, 2000, **41**, 6043-6047.
250. L. Wang, P. Chang and C. L. Cheng, *J. Appl. Polym. Sci.*, 2006, **100**, 4672-4678.
251. D. H. Wang, Z. Shen, M. Guo, S. Z. D. Cheng and F. W. Harris, *Macromolecules*, 2007, **40**, 889-900.
252. H. Yim, H. Wu, M. D. Foster, S. Z. D. Cheng and F. W. Harris, *Langmuir*, 1997, **13**, 3202-3205.
253. J. H. Park, B. H. Sohn, J. C. Jung, S. W. Lee and M. Ree, *J. Polym. Sci. Part A: Polym. Chem.*, 2001, **39**, 1800-1809.
254. Y. Yin, Q. Du, Y. Qin, Y. Zhou and K.-i. Okamoto, *J. Membr. Sci.*, 2011, **367**, 211-219.
255. H. Yim, M. D. Foster, K. McCreight, X. Jin, S. Z. D. Cheng and F. W. Harris, *Polymer*, 1998, **39**, 4675-4678.
256. Y. Yin, J. Fang, H. Kita and K.-i. Okamoto, *Chem. Lett.*, 2003, **32**, 328-329.
257. A. S. Jadhav and S. P. Vernekar, *Macromol.-New Front., Proc. IUPAC Int. Symp. Adv. Polym. Sci. Technol.*, 1998, **1**, 54.
258. Y. S. Kim and J. C. Jung, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 1764-1774.
259. M. S. Butt, Z. Akhtar, M. Zafar-uz-Zaman and A. Munir, *Eur. Polym. J.*, 2005, **41**, 1638-1646.

260. W. Zhang, H. J. Xu, J. Yin, X. X. Guo, Y. F. Ye, J. H. Fang, Y. Sui, Z. K. Zhu and Z. G. Wang, *J. Appl. Polym. Sci.*, 2001, **81**, 2814-2820.
261. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules,* 1998, **31**, 1236-1245.
262. S. W. Lee, B. Chae, B. Lee, W. Choi, S. B. Kim, S. I. Kim, S.-M. Park, J. C. Jung, K. H. Lee and M. Ree, *Chem. Mater.*, 2003, **15**, 3105-3112.
263. S. J. Lee, J. C. Jung, S. W. Lee and M. Ree, *J. Polym. Sci. Part A: Polym. Chem.*, 2004, **42**, 3130-3142.
264. K. H. Choi, K. H. Lee and J. C. Jung, *J. Polym. Sci. Part A: Polym. Chem.*, 2001, **39**, 3818-3825.
265. K. H. Lee and J. C. Jung, *Polym. Bull.*, 1998, **40**, 407-414.
266. M. Wenzel, M. Ballauff and G. Wegner, *Makromol. Chem.*, 1987, **188**, 2865-2873.
267. A. Sarkar, *Ph. D. Dissertation, University of Pune, Pune, India*, 2005.
268. N. D. Ghatge and U. P. Mulik, *J. Polym. Sci. Part A: Polym. Chem.*, 1980, **18**, 1905-1909.
269. H. Kim, Y. J. Choi, J. Jung and W. C. Zin, *Polym. Bull.*, 1997, **38**, 689-694.
270. J. Jung and S.-B. Park, *Polym. Bull.*, 1995, **35**, 423-430.
271. J. C. Jung and S.-B. Park, *J. Polym. Sci. Part A: Polym. Chem.*, 1996, **34**, 357-365.
272. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci. Part A: Polym. Chem.*, 1964, **2**, 1171-1179.
273. A. H. Frazer and I. M. Sarasohn, *J. Polym. Sci. Part A: Polym. Chem.*, 1966, **4**, 1649-1664.
274. A. H. Frazer and T. A. Reed, *J. Polym. Sci. Part C: Polym. Symp.*, 1967, **19**, 89-94.
275. J. Preston, W. B. Black and W. L. Hofferbert, *J. Macromol. Sci: Part A - Chem.*, 1973, **7**, 45-65.
276. F. Higashi and M. Ishikawa, *J. Polym. Sci. Polym. Chem.*, 1980, **18**, 2905-2907.
277. M. J. Nanyan and J. I. Kroschwitz, eds., *Encyclopedia of polymer science and engineering 2nd edition,* John Wiley & Sons Inc., New York, 1982.
278. O. Moldenhauer and H. Back, *US 2349979* 1944.

279. E. J. Vandeberg and C. G. Overberger, *Science*, 1963, **141**, 176-177.

280. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci. Part A: General Papers*, 1964, **2**, 1147-1156.

281. V. P. Ubale, A. D. Sagar, N. N. Maldar and M. V. Birajdar, *J. Appl. Polym. Sci.*, 2001, **79**, 566-571.

282. V. A. E. Shaikh, V. P. Ubale, N. N. Maldar, S. V. Lonikar, C. R. Rajan and S. Ponrathnam, *J. Appl. Polym. Sci.*, 2006, **100**, 73-80.

283. C. J. Abshire and C. S. Marvel, *Makromol. Chem.*, 1961, **44**, 388-397.

284. M. Bruma, G. Neamtu and I. Sava, *J. Macromol. Sci. Chem.*, 1985, **22**, 833-847.

285. M. Saga and T. Shono, *J. Polym. Sci. Part B: Polym. Lett.*, 1966, **4**, 869-873.

286. M. Ueda and M. Oda, *Polym J*, 1989, **21**, 193-197.

287. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci. Part A: General Papers*, 1964, **2**, 1181-1183.

288. I. Sava, B. Schulz, S. Zhu and M. Bruma, *High Perform. Polym.*, 1995, **7**, 493-501.

289. Y. Iwakura, K. Uno and S. Hara, *J. Polym. Sci. Part A: Polym. Chem.*, 1965, **3**, 45-54.

290. E. R. Hensema, J. P. Boom, M. H. V. Mulder and C. A. Smolders, *J. Polym. Sci. Part A: Polym. Chem.*, 1994, **32**, 513-525.

291. B. Schulz and E. Leibnitz, *Acta Polym.*, 1992, **43**, 343-347.

292. B. Schulz, M. Bruma and L. Brehmer, *Adv. Mater.*, 1997, **9**, 601-613.

293. M. Gillo, P. Iannelli, P. Laurienzo, M. Malinconico, A. Roviello, P. Mormile and L. Petti, *Chem. Mater.*, 2002, **14**, 1539-1547.

294. D. Capitani, P. Laurienzo, M. Malinconico, N. Proietti and A. Roviello, *J. Polym. Sci. Part A: Polym. Chem.*, 2003, **41**, 3916-3928.

295. S. Zhu, B. Schulz, M. Bruma and L. Brehmer, *Polym. Adv. Technol.*, 1996, **7**, 879-887.

296. C. J. Thaemlitz and P. E. Cassidy, *Polymer*, 1992, **33**, 206-208.

297. N. C. Yang, Y. H. Park and D. H. Suh, *J. Polym. Sci. Part A: Polym. Chem.* , 2003, **41**, 674-683.

298. M. A. M. Nasr, A. A. Kassem, A. E. Madkour and M. Z. M. Ali Ahmed, *React. Funct. Polym.*, 2005, **65**, 219-228.

299. E. R. Hensema, M. E. R. Sena, M. H. V. Mulder and C. A. Smolders, *J. Polym. Sci. Part A: Polym. Chem.*, 1994, **32**, 527-537.
300. S. Janietz and S. Anlauf, *Macromol. Chem. Phys.*, 2002, **203**, 427-432.
301. S. Janietz, S. Anlauf and A. Wedel, *Synth. Met.*, 2001, **122**, 11-14.
302. S.-H. Hsiao and C.-H. Yu, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 1847-1854.
303. S. H. Hsiao, L. R. Dai and M. H. He, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 1169-1181.
304. G. Avitabile, G. Gentile, P. Laurienzo, M. Malinconico, E. Martuscelli, F. Riva and M. G. Volpe, *J. Polym. Sci. Part B: Polym. Phys.*, 1999, **37**, 1687-1701.
305. H. Meng, Z. K. Chen and W. Huang, *J. Phys. Chem. B*, 1999, **103**, 6429-6433.
306. W. Huang, H. Meng, W. L. Yu, J. Pei, Z. K. Chen and Y. H. Lai, *Macromolecules*, 1999, **32**, 118-126.
307. U. P. Ojha, K. Krishnamoorthy and A. Kumar, *Synth. Met.*, 2003, **132**, 279-283.
308. R. J. Cotter, *Engineering Thermoplastics, A Handbook of Poly(arylene ether)s*, Gordon and Breach, Postfach, Switzerland, 1995.
309. P. A. Stainland, G. Alleb and B. J.C., eds., *Comprensive Polymer Science*, Pergamon Press, New York, 1989.
310. J. W. Labadie, J. L. Hedric and M. Ueda, eds., *Step Growth Polymers for High Performance Materials, New Synthetic Method, ACS Symposium Series 624*, American Chemical Society, Washington, 1996.
311. R. N. Johnson and A. G. Farnham, *J. Polym. Sci. Part A-1: Polym. Chem.*, 1967, **5**, 2415-2427.
312. B. K. Mandal and S. Maiti, *Eur. Polym. J.*, 1986, **22**, 447-450.
313. H. M. Colquhoun, C. C. Dudman, M. Thomas, C. A. O'Mahoney and D. J. Williams, *J. Chem. Soc. Chem. Commun.*, 1990, 336-339.
314. M. Chen and H. W. Gibson, *Macromolecules*, 1996, **29**, 5502-5504.
315. D. Xie and H. W. Gibson, *Macromol. Chem. Phys.*, 1996, **197**, 2133-2148.
316. H. R. Kricheldorf, U. Delius and K. U. Tonnes, *New Polym. Mater.*, 1988, **1**, 127-141.

317. I. Colon and G. T. Kwiatkowski, *J. Polym. Sci. Part A: Polym. Chem.*, 1990, **28**, 367-383.
318. W. H. Bonner, *US 3065205*, 1962.
319. I. Goodman, M. J. E. and W. Russell, *GB 971227*, 1964.
320. Y. Iwakura, K. Uno and T. Takiguchi, *J. Polym. Sci. Part A-1: Polym. Chem.*, 1968, **6**, 3345-3355.
321. B. M. Marks, *US 3441538*, 1964.
322. J. B. Rose, *EP 63874*, 1982.
323. V. Jansons and K. Dahl, *Makromol. Chem. Macromol. Symp.*, 1991, **51**, 87-101.
324. V. Percec, R. S. Clough, M. Grigoras, P. L. Rinaldi and V. E. Litman, *Macromolecules*, 1993, **26**, 3650-3662.
325. V. Percec, R. S. Clough, P. L. Rinaldi and V. E. Litman, *Macromolecules*, 1991, **24**, 5889-5892.
326. V. Percec, M. Grigoras, R. S. Clough and J. Fanjul, *J. Polym. Sci. Part A: Polym. Chem.*, 1995, **33**, 331-344.
327. R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale and C. N. Merriam, *J. Polym. Sci. Part A-1: Polym. Chem.*, 1967, **5**, 2375-2398.
328. D. K. Mohanty, Y. Sachdeva, J. L. Hedrick, J. F. Wolfe and J. E. McGrath, , . *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.*, 1984, **25**, 19.
329. H. R. Kricheldorf and G. Bier, *Polymer*, 1984, **25**, 1151-1156.
330. W. L. Jeff, L. H. James and U. Mitsuru, in *Step-Growth Polymers for High-Performance Materials*, eds. J. L. Hedrick and J. W. Labadie, American Chemical Society, 1996, pp. 210-225.
331. P. N. Honkhambe, N. S. Bhairamadgi, M. V. Biyani, P. P. Wadgaonkar and M. M. Salunkhe, *Eur. Polym. J.*, 2010, **46**, 709-718.
332. S. Kawasaki, M. Yamada, K. Kobori, F. Jin, Y. Kondo, H. Hayashi, Y. Suzuki and T. Takata, *Macromolecules*, 2007, **40**, 5284-5289.
333. Y. Taguchi, H. Uyama and S. Kobayashi, *J. Polym. Sci. Part A: Polym. Chem.*, 1996, **34**, 561-565.
334. X. C. Ge, Y. Xu, M. Xiao, Y. Z. Meng and A. S. Hay, *Eur. Polym. J.*, 2006, **42**, 1206-1214.

335. S. Gronewald, P. E. Cassidy, J. W. Fitch, J. Arbaugh, H. Herbold and D. Jurek, *High Perform. Polym.*, 2001, **13**, S117-S121.

336. U. Hoffmann, M. Klapper and K. Mullen, *Polym. Bull.*, 1993, **30**, 481-488.

337. G. Chen, X. Zhang, S. Zhang, T. Chen and Y. Wu, *J. Appl. Polym. Sci.*, 2007, **106**, 2808-2816.

338. D. Liu and Z. Wang, *Polymer*, 2008, **49**, 4960-4967.

339. W. Risse and D. Y. Sogah, *Macromolecules*, 1990, **23**, 4029-4033.

340. S. Zhang, L. Fu, J. Liu, D. Yang, Z. Gao, M. Jia, Y. Zheng and Z. Wu, *Macromol. Chem. Phys.*, 2000, **201**, 649-655.

341. F. Keitoku, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 1994, **32**, 317-322.

342. X. Shang, X. Li, M. Xiao and Y. Meng, *Polymer*, 2006, **47**, 3807-3813.

Chapter 2

Scope and Objectives

It is difficult to imagine modern human life without the use of polymers. Polymers have applications in food packaging, clothing, drugs, electronic circuits, energy devices, automobile and aviation industries and so on. Polymers are utilized in submarines moving at bottom of deep sea to satellite revolving in the space and their use is necessary not only for lavish human life but also to fulfill fundamental human needs. History tells that man has made widespread utilization of bio-based polymers such as animal skin, plant fiber, flax, ramie, jute, silk, cotton, shellac, natural rubber, celluloid (thermoset derived from camphor and cellulose), cellophane (produced from cellulose), soybean-based composites, etc., throughout his journey. However, in 21st century there have been major developments in petroleum refining and synthetic chemistry as a result of industrial revolution which gave birth to polymer technologies producing a variety synthetic polymers such as Bakelite, nylons, polyesters, synthetic rubbers, polyolefins, and so on.[1, 2] The production of these polymers has grown to such an extent that, the present age is known as 'Polymer Age'

In recent years, depletion of petroleum resources and environmental awareness has been turning the attention of polymer chemists to produce monomers and polymers from renewable resource materials. However, at present the renewable biopolymers have higher cost and limited applications as compared to petroleum-based polymers. Therefore, synthesis of low cost and scalable monomers and polymers from non-edible renewable biomass is the challenge to polymer chemists worldwide. In this context, monomers and polymers derived from renewable resources viz., monosaccharides, fatty acids, starch, cellulose, lactic acid, natural amino acids, etc. have been reported in the literature.[3-6] However, there have been several difficulties in production of chemicals and monomers from the biomass, particularly extraction or isolation of such chemicals from biomass. Therefore, the concept of the bio-refinery is very crucial for exploitation of biomass into monomers and polymers.[7]

For synthesis of bio-based monomers and polymers, generally following two approaches are utilized: i) synthesis of polymers composed of entirely renewable materials and ii) synthesis of partially renewable polymers in combination with petroleum-based components. Further, depending upon the end application, there have been efforts: a) to reproduce existing petroleum-based monomers ('drop-in' substitute or bioreplacement), b) to obtain new monomers providing new polymers which could mimic commodity polymers and c) to synthesize newer polymers with advantageous properties over petroleum-based polymers i.e. bioadvantaged polymers.[3, 8] The production of polymers from biomass should be knowledge intensive and take advantage of the structure of the biomass.[9]

High performance/ high temperature polymers is one of the speciality and well recognized areas of polymer science for more than 60 years.[10] Generally, aromatic difunctional monomers are required for the preparation of high performance polymers. There is a great interest to find biobased alternative building-blocks for the synthesis of high performance polymers. However, most of the renewable resources mentioned earlier provide aliphatic monomers and polymers. Aromatic difunctional monomers can be derived from renewable resources such as lignin, cashew nut shell liquid (CNSL) and tannin.[11, 12] Lignin and CNSL are of particular interest as they are the sources of natural phenols and have been utilized to obtain aromatic difunctional monomers.

CNSL is a non-edible oil and is the by-product of agro-based cashew processing industry. CNSL contains various phenols with a long unsaturated 15- carbon chain. The extraction, purification, composition and chemistry of CNSL has been thoroughly reviewed in the literature.[11, 13, 14] The reactivity of phenolic hydroxyl group, aromatic ring and unsaturation in side chain makes CNSL an interesting raw material for synthesis of polymers and additives for polymers. A great deal of research work is being devoted for utilization of CNSL as a promising alternative for petroleum-based derivatives. CNSL has found applications in phenolic resins, break linings, surface coatings, etc.[14-18] CNSL has been used in the preparation of many speciality materials such as liquid crystalline polyesters, polyurethanes, phenalkamine cross-linking agents, cross-linkable polyphenols and various speciality polymers and additives.[11, 19]

The important features of CNSL as a versatile starting material are: inexpensive, abundant availability and chemically reactive nature. The polymers derived from CNSL exhibit flexibility due to the presence of long C-15 hydrocarbon chain resulting in improved processability. Although there are number of literature reports on utilization CNSL, many areas remained which are yet to utilize this attractive raw material. The previous work from our group has resulted into utilization of CNSL as a starting material for synthesis of difunctional monomers for preparation of high performance polymers with improved solubility and processability.[11] Thus, design and synthesis of difunctional step-growth monomers containing special structural features starting from CNSL is an interesting strategy.

High performance polymers such as polyesters, polyimides, poly(1,3,4-oxadiazole)s, poly(arylene ether)s, etc. exhibit unique combination of properties such as high thermal stability, high mechanical properties and excellent chemical resistance.[10] These polymers find applications in aviation, automobile and electronic industries. However, the poor solublity in common organic solvents, coupled with high melting (T_m) and glass transition temperature (T_g) results in poor processability which results from the presence of rigid backbone and strong interchain interactions from symmetrical and polar groups. Solubility / processability of these polymers can be improved by (i) introducing flexible linkages in the polymer backbone; (ii) introducing monomer with crank shaft or bent units along the backbone or (iii) the use of bulky side groups or flexible side chains.[20, 21] These approaches work by forcing the chains apart and lead to the improved solubility and better processability. The objective of processability thus could be achieved with design and synthesis of difunctional monomers containing special structural features that disturb chain packing and structural regularity in polymer backbone.

Additionally, the present work was devoted for the synthesis of cyanate ester and bismaleimide with wider processing window (temperature gap between melting and curing temperatures) based on monomers containing pentadecyl chain.[22] Also it was anticipated that the incorporation of pentadecyl chain in thermosetting resins viz., cyanate esters, bismaleimide and epoxy resins would lead to improved toughnesss and impact strength.

The present work involved utilization of 3-pentadecyl phenol as a starting material which in turn is obtained from CNSL- a renewable resource material. The difunctional monomers were designed in such way that they possess one or more of the structural features such as: i) presence of flexible ether linkage, ii) non-symmetry in the structure and iii) the naturally gifted pendent pentadecyl chain. Thus, overall objectives of the present thesis are:

1. Design and synthesis of new difunctional monomers such as bisphenol, diamine, diacid, dialdehyde and diacylhydrazide containing flexible ether linkages and pendent pentadecyl chain starting from renewable resource material-CNSL.
2. Synthesis of difunctional monomers viz., dibromide, diacid, diacylhydrazide and diphenol containing biphenylene unit and pendent pentadecyl chain(s) starting from CNSL.

3. Synthesis of thermoplastics viz., polyesters, polyimides, poly(arylene ether)s, polyhydrazides, poly(1,3,4-oxadiazole)s and thermosets viz., cyanate ester, bismaleimide and epoxy resin using selected synthesized monomers.
4. To investigate the effect of pendent pentadecyl chains and flexible ether linkages primarily on the polymer properties such as solubility, crystallinity, thermal properties, etc.

References

1. N. Hernandez, R. C. Williams and E. W. Cochran, *Org. Biomol. Chem.*, 2014, **12**, 2834-2849.
2. R. Hofer and M. Selig, in *Polymer Science: A Comprehensive Reference*, eds. K. Matyjaszewski and M. Moller, Elsevier, Amsterdam, 2012, pp. 5-14.
3. R. T. Mathers, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 1-15.
4. A. Gandini, M. N. Belgacem and M. N. B. Gandini, in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, 2008, pp. 273-288.
5. A. Gandini, *Macromolecules*, 2008, **41**, 9491-9504.
6. M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788-1802.
7. B. Kamm, M. Kamm, P. R. Gruber and S. Kromus, in *Biorefineries-Industrial Processes and Products*, Wiley-VCH Verlag GmbH, 2008, pp. 1-40.
8. S. A. Miller, *ACS Macro Lett.*, 2013, **2**, 550-554.
9. J. Sanders, E. Scott, R. Weusthuis and H. Mooibroek, *Macromol. Biosci.*, 2007, **7**, 105-117.
10. P. E. Cassidy, *Thermally stable polymers: Synthesis and properties*, Marcel Dekker Inc., New York, 1980.
11. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, 2014, **5**, 3142-3162.
12. R. Auvergne, S. Caillol, G. David, B. Boutevin and J.-P. Pascault, *Chem. Rev.*, 2014, **114**, 1082-1115.
13. C. K. S. Pillai, *Des. Monomers Polym.*, 2010, **13**, 87-121.
14. M. C. Lubi and E. T. Thachil, *Des. Monomers Polym.*, 2000, **3**, 123-153.
15. K. I. Suresh and V. S. Kishanprasad, *Ind. Eng. Chem. Res.*, 2005, **44**, 4504-4512.

16. A. H. Tullo, *Chem. Engg News*, 2008, **86**, 26-27.
17. G. Mele and G. Vasapollo, *Mini-Rev. Org. Chem.*, 2008, **5**, 243-253.
18. P. H. Gedam and P. S. Sampathkumaran, *Prog. Org. Coat.*, 1986, **14**, 115-157.
19. V. S. Balachandran, S. R. Jadhav, P. K. Vemula and G. John, *Chem. Soc. Rev.*, 2012, **42**, 427-438.
20. C. W. Ulmer II, D. A. Smith, B. G. Sumpter and D. I. Noid, eds., *Computational and Theoretical Polymer Science*, 1998.
21. P. Hergenrother and W. Volksen, in *High Perform. Polym.*, Springer Berlin Heidelberg, 1994, pp. 111-164.
22. A. D. Kulkarni, B. V. Tawade and P. P. Wadgaonkar, *High Perform. Polym.*, 2013, **25**, 278 - 286.

Chapter 3

Synthesis and Characterization of Condensation Monomers Starting from CNSL

3.1 Introduction

The structure of the monomer plays a pivotal role in deciding the properties of polymer and with the selection of appropriately designed monomers the properties of polymer could be tailored.[1, 2] Therefore, synthesis of polymers exhibiting targeted properties is usually pioneered with the synthesis of desired monomers. A variety of difunctional monomers have been synthesized to modify the properties of high performance/ thermally stable polymers and address the issues such as insolubility in common organic solvents and higher transition temperatures (T_g and T_m) which are generally encountered with these polymeric materials.[3] The polymer chemistry is enriched with the outstanding approaches devoted for incorporating the structural features in the monomer structure that lead to improved processability of high performance polymers.[4] These structural features in monomers have also opened the opportunities for newer applications for high performance polymers in the areas such as automobile, aerospace, electronics, membranes, energy devices, etc.[5]

There has been a constant search for new difunctional monomers such as bisphenols, diamines, diacids, dialdehydes, diisocyanates, etc. for synthesis of high performance polymers with modified structures. Moreover, the cost and availability of raw materials as well as energy and environmental concerns are crucial factors for introduction of new monomers and polymers in the market.

In last two to three decades, extensive research efforts in alternative chemicals derived from renewable resource materials have been encouraged due to the predicted shortage of fossil resources and their unstable prices. Therefore, synthesis of monomers and polymers from renewable resource materials has become an interesting topic of research for polymer scientists worldwide. In this respect, monomers and polymers derived from renewable resources such as monosaccharides, plant oils, starch, cellulose, lactic acid, natural amino acids, etc. have been reported in the literature.[6, 7] These aforementioned renewable resources provide aliphatic monomers and polymers. Aromatic difunctional monomers are desirable for synthesis of high performance/high temperature polymers. Lignin and CNSL are the two viable sources of natural phenols and these have been exploited to obtain aromatic difunctional monomers useful for synthesis of high performance polymers.[8, 9]

In this dissertation, new difunctional monomers viz; dialdehyde, bisphenols, diamine, dihalide, dinitrile, diacids and diacylhydrazides were synthesized starting from 3-pentadecyl phenol which in turn is obtained from CNSL-a renewable resource material. **(Figure 3.1)**

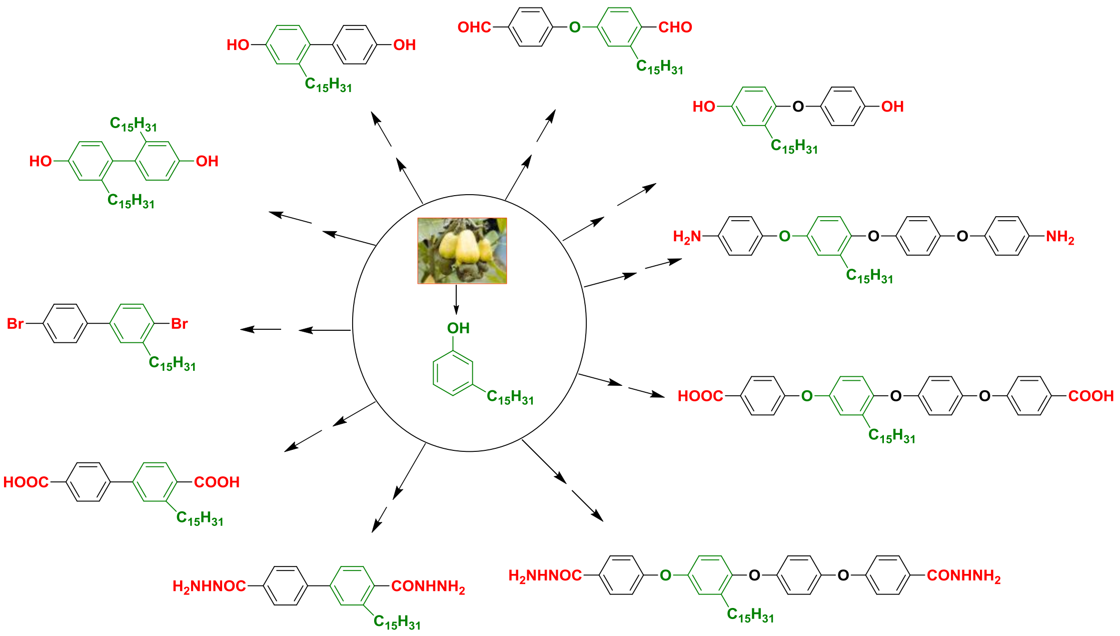


Figure 3.1 CNSL-derived difunctional monomers

3.2 Experimental

3.2.1 Materials

3-Pentadecyl phenol, copper powder, bromobenzene, copper cyanide, palladium-on-carbon, ruthenium-on-carbon, n-butyl lithium, calcium hydride, N-bromo succinimide, 4-methoxy phenol, tetra-n-butylphosphonium bromide, 4-fluorobenzonitrile, 4-methoxy phenyl boronic acid, tetrakis(triphenyl phosphine)palladium, bis(1,5-cyclooctadiene)nickel, 1,5-cyclooctadiene, bipyridine, phenyl boronic acid and ethylene glycol (Aldrich Chemicals) were used as received. Methyl iodide, trifluoromethane sulfonic anhydride, thionyl chloride, copper cyanide, ferric chloride and iodine were procured from Spectrochem. Bromine, ammonia solution, copper sulfate, hydrochloric acid, sulfuric acid, pyridine, triethyl amine, ethanol, glacial acetic acid, 1-chloro-4-nitrobenzene, hydrobromic acid, silica gel and celite (Merck, India and E-Merck Germany) were used as received. Potassium hydroxide, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate, potassium carbonate and magnesium sulfate (Loba Chemie) were used as received. Hydrazine hydrate (99%) (S.D. Fine., India) was used as received. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[10]

3.2.2 Measurements

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

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

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

3.3 Preparations

3.3.1 Synthesis of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde:

3.3.1.1 Synthesis of 3-pentadecyl phenol

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

Yield: 480 g (95%);

M.P.: 50-51°C (Lit. M.P.: 50-51°C)[11]

3.3.1.2 Synthesis of 1-pentadecyl-3-phenoxy benzene

Into a 1000 mL two necked round bottom flask fitted with a Dean and Stark assembly with a reflux condenser were taken 3-pentadecyl phenol (100 g, 0.33 mol), potassium hydroxide (22.06 g, 0.39 mol), N,N-dimethylacetamide (300 mL) and toluene (150 mL). The reaction mixture was refluxed for 7 h and the by-product water formed was removed from the reaction mixture azeotropically. After completion of the reaction, the solvents were distilled off and the dark sticky product was dried under reduced pressure. The product obtained was potassium salt of 3-pentadecyl phenol.

Into a 1000 mL round bottom flask containing potassium salt of 3-pentadecyl phenol (111 g, 0.32 mol) was added bromobenzene (50.88 g, 0.32 mol), followed by addition of Cu powder (2.22 g, 2 wt%) and N,N-dimethylacetamide (150 mL). The reaction mixture was refluxed for 10 h. After completion of the reaction, the obtained dark colored reaction mixture was poured into water (500 mL); the Cu salts were removed by filtration. The filtrate was extracted with ethyl acetate (2 x 100 mL) washed with water (3 x 100 mL) and ethyl acetate solution was dried over sodium sulfate. The solvent evaporation yielded crude 1-pentadecyl-3-phenoxy benzene. Pure 1-pentadecyl-3 –phenoxy benzene was obtained by silica gel (60- 120 mesh) column chromatography (eluent: pet ether).

Yield: 74 g (60 %);

M.P. 32 °C (Lit. M.P.: 32 ºC)[12]

IR (cm^{-1}): 1250 (Ar-O-Ar stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.84 - 7.34 (m, 9 H), 2.57 (t, 2 H), 1.57-1.61 (m, 2 H), 1.20-1.32 (m, 24 H), 0.88 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 157.4, 157.0, 145.0, 129.6, 129.4, 123.4, 122.9, 119.0, 118.7, 116.0, 35.8, 31.9, 31.3, 29.7, 29.5, 29.4, 22.7, 14.2

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

Into a 500 mL three necked round bottom flask equipped with a stirrer, a condenser, a dropping funnel and a thermometer were placed 1-pentadecyl-3-phenoxy benzene (25.0 g, 66 mmol) and dichloromethane (150 mL). Bromine (22.08 g, 0.14 mol) was added to the reaction mixture while protecting from light. The top of the condenser was equipped with a trap to absorb HBr released during reaction. The reaction mixture was maintained at a temperature between -5 to 0 °C during the addition of bromine. After completion of bromine addition, the reaction mixture was stirred at the same temperature for 1h and then overnight at room temperature. After completion of the reaction, excess of bromine and HBr were neutralized with 10% aqueous ammonia (100 mL). The two phases formed in the reaction mixture were separated, and the organic layer was washed with water (2 x 300 mL). The dichloromethane solution was dried over sodium sulfate, filtered and dichloromethane was removed by distillation on a rotary evaporator. Pure 1-bromo-4-(4’-bromophenoxy)-2-pentadecyl benzene was obtained by silica gel (60-120 mesh) column chromatography (eluent: pet ether).

Yield: 30 g. (85 %);

M.P. 43 °C (Lit. M.P.: 43 ºC)[12]

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40-7.49 (m, 3 H), 6.85-6.89 (m, 3H), 6.69 (dd, 1H), 2.67 (t, 3H), 1.56-1.60 (m, 2H), 1.20-1.32 (m, 24H), 0.88 (t, 3H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 156.2, 155.9, 144.0, 133.7, 132.7, 120.7, 120.3, 118.3, 117.9, 115.9, 36.3, 31.9, 29.7, 29.6, 29.4, 22.7, 14.1

3.3.1.4 Synthesis of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde

Into a 250 mL three necked round bottom flask equipped with a magnetic stirring bar were taken 1-bromo-4-(4-bromophenoxy)-2-pentadecylbenzene (5.38 g, 10.0 mmol) and dry tetrahydrofuran (50 mL) and reaction mixture was cooled to -78 °C under nitrogen atmosphere. n-BuLi (13.75 mL, 1.6 M in hexane, 22.0 mmol) was added to the reaction mixture which was followed immediately by addition of dry N,N-dimethylformamide (3.1 mL, 40.0 mmol). The resulting mixture was stirred at -78 ˚C for 30 min and then warmed to room temperature and stirred for additional 1h. Subsequently, the mixture was stirred with 1M aqueous HCl (20 mL) for 10 min**,** then the mixture was concentrated and the residue was dissolved in ethyl acetate. The ethyl acetate solution was washed with saturated aqueous $NaHCO_3$ solution, brine, and dried over $MgSO_4$. The solvent was removed and the residue was purified by silica gel column chromatography, using silica gel and a mixture of pet ether and ethyl acetate (10:1, (v:v)) as an eluent to give 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde.

Yield: 2.61 g (60 %);

M.P.: 52 °C

IR (cm^{-1}): 1700 (-C=O stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 10.22 (s, 1 H), 9.97 (s, 1 H), 7.80-7.99 (m, 3 H), 7.10- 7.20 (m, 2 H), 6.85-7.03 (m, 2 H), 3.09 (t, 2 H), 1.50 -1.72 (m, 2 H), 1.20-1.37 (m, 24 H), 0.83-0.93 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 190.7, 190.6, 161.2, 160.0, 148.9, 133.9 132.3, 132.0, 129.9, 120.9, 119.2, 116.8, 32.5, 32.1, 31.9, 29.7, 29.4, 22.7, 14.12

3.3.2 Synthesis of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

3.3.2.1 Synthesis of 3-pentadecyl anisole

Into a 1000 mL round bottom flask equipped with a magnetic stirrer bar were placed 3-pentadecyl phenol (100 g, 0.33 mol), dimethyl sulfoxide (400 mL), potassium hydroxide (20.16 g, 0.36 mol) and methyl iodide (22.5 mL, 0.36 mol) and the mixture was stirred at room temperature for 12 h. The reaction mixture was treated with water and 3-pentadecyl anisole was extracted with ethyl acetate, washed with brine solution and dried over sodium sulfate. 3-Pentadecyl anisole was purified by column chromatography (eluent: petroleum ether).

Yield: 100 g, (95 %)

M.P.: 28 °C (Lit. M. P.: 27-28 °C)[13]

IR (cm^{-1}): 1261 (Ar-O-C stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15 - 7.23 (m, 1H), 6.71 - 6.79 (m, 3H), 3.80 (s, 3H), 2.58 (t, 2H), 1.54 - 1.75 (m, 2H), 1.25-130 (m, 24H), 0.88 (t, 3H)

^{13}C NMR (50 MHz, $CDCl_3$) δ 159.54, 144.63, 129.12, 120.85, 114.18, 110.76, 55.09, 36.03, 31.92, 31.40, 29.67, 29.52, 29.36, 22.69, 14.12

3.3.2.2 Synthesis of 4-bromo-3-pentadecyl anisole

Into a 500 mL round bottom flask equipped with a magnetic stirrer bar were added 3-pentadecyl anisole (50 g, 0.157 mol), dry acetone (300 mL), and N-bromo succinimide (27.94 g, 0.157 mol). Hydrochloric acid (0.15 mL, 1.57 mmol) was added to the reaction mixture at room temperature. The resulting yellow solution was stirred until the solution became colorless. The acetone was removed in vacuum and 150 mL of hexane was added. After cooling the mixture in an ice bath, the succinimide was removed by filtration. Removal of hexane under vacuum yielded the crude product. 4-Bromo-3-pentadecyl anisole was purified by column chromatography (eluent: petroleum ether).

Yield: 56 g, (90 %)

M.P.: 40 °C

IR (cm^{-1}): 801 (C-Br stretching), 1243 (Ar-O-C stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 (d, 1 H), 6.76 (d, 1 H), 6.61 (dd, 1 H), 3.78 (s, 3 H), 2.67 (t, 2 H), 1.51 - 1.67 (m, 2 H), 1.20 - 1.41 (m, 24 H), 0.89 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 158.83, 143.15, 133.11, 115.95, 114.93, 112.77, 55.35, 36.40, 31.92, 29.89, 29.68, 29.36, 22.69, 14.11

3.3.2.3 Synthesis of 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene

Into a 500 mL two necked round bottom flask fitted with a Dean and Stark assembly with a reflux condenser were taken 4-methoxy phenol (12.9 g, 0.080 mol), potassium hydroxide (5.3 g, 0.088 mol) N,N-dimethylacetamide (75 mL) and toluene (50 mL). The reaction mixture was refluxed for 7 h and the by-product water formed was removed from the reaction mixture azeotropically. After completion of reaction, toluene was distilled off and the reaction mixture was cooled to room temperature. Into the solution of potassium salt of 4-methoxy phenol in N,N-dimethylacetamide was added 4-bromo-3-pentadecyl anisole (30 g, 0.075 mol), followed by Cu powder (0.300 g, 2 wt %) and N,N-dimethylacetamide (25 mL). The reaction mixture was heated at reflux for 6 h. After completion of the reaction, the obtained dark colored reaction mixture was poured into water (100 mL) and the Cu salts were removed by filtration. The filtrate was extracted with ethyl acetate (2 x 25 mL), washed with saturated aqueous sodium chloride solution (2 x 20 mL) followed by water (3 x 20 mL) and dried over sodium sulfate. Solvent evaporation yielded crude 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene which was purified by column chromatography (eluent: petroleum ether: ethyl acetate:: 90:10, v/v)

Yield: 20 g (60 %).

IR (cm^{-1}): 1209 (Ar-O-Ar stretching) and 1260 (Ar -O-C stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.82 (bs, 4 H), 6.80 - 6.77 (m, 2 H), 6.67 (dd, 1 H), 3.79 (s, 3H), 3.78 (s, 3H), 2.56 (t, 2 H), 1.66 - 1.51 (m, 2 H), 1.25 (bs., 24 H), 0.88 (t, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.63, 154.75, 152.58, 148.62, 135.61, 120.44, 118.01, 115.79, 114.69, 111.73, 55.63, 55.54, 35.87, 31.90, 29.96, 29.68, 29.56, 29.42, 22.68, 14.12

3.3.2.4 Synthesis of 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP):

Into a 250 mL round bottom flask equipped with a magnetic stirrer bar were taken 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene (4.40 g, 10 mmol), tetra-n-butylphosphonium bromide (6.78 g, 20 mmol) and 48% HBr (40 mL) and the reaction mixture was heated at reflux temperature for 6 h. Water (100 mL) was added to the reaction mixture and the mixture was extracted with ethyl acetate. The ethyl acetate solution was washed with brine, dried over sodium sulfate and concentrated in vacuum to obtain crude HPPDP which was purified by column chromatography (eluent: petroleum ether:ethyl acetate :: 70:30 v/v).

Yield: 3.3 g (80%);

M.P.: 76 ˚C

IR (cm^{-1}): 3325 (Phenolic O-H); 1204 (Ar-O-Ar stretching)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.78 (d, 4 H), 6.75 -6.70 (m, 2 H), 6.61 (dd, 1 H), 4.58 (bs, 2 H), 2.51 (t, 2 H), 1.65 -1.56 (m, 2 H), 1.33 - 1.11 (m, 24 H), 0.87 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 152.52, 151.43, 150.44, 148.51, 135.92, 120.68, 118.16, 116.89, 116.10, 113.44, 31.91, 29.96, 29.68, 29.56, 29.42, 22.68, 14.12

3.3.3 Synthesis of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline

3.3.3.1 Synthesis of 4-(4-nitrophenoxy)-1-(4-(4-nitrophenoxy)phenoxy)-2-pentadecylbenzene

Into a 250 mL round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser were placed 4-(4-hydroxyphenoxy)-3-pentadecylphenol (8.16 g, 0.026 mol), *p*-chloronitrobenzene (8.19 g, 0.052 mol), potassium carbonate (7.75 g, 0.056 mol) and anhydrous N,N-dimethylformamide (90 mL). The mixture was refluxed under the stream of nitrogen for 10 h. The reaction mixture was then cooled to room temperature and poured into water (500 mL). The product was extracted with ethyl acetate, washed with water and brine. The ethyl acetate solution was dried over sodium sulfate and concentrated in vacuum to obtain crude product. 4-(4-Nitrophenoxy)-1-(4-(4-nitrophenoxy) phenoxy)-2-pentadecylbenzene was purified by column chromatography. (Eluent: pet ether: ethyl acetate; 90:10; v:v)

Yield: 15.20 g (90 %)

IR: 1513, 1341 cm^{-1} (asymmetric and symmetric stretching of -NO_2, respectively)

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 8.21 (dd, 4H), 6.93-7.05 (m, 11H), 2.63 (t, 2H), 1.59 (m, 2H), 1.20-1.30 (m, 24H), 0.87 (t, 3H)

^{13}C NMR (50MHz, $CDCl_3$) δ = 163.7, 163.6, 155.2, 151.5, 150.5, 149.5, 142.5, 136.9, 125.9, 122.6, 122.0, 120.9, 119.0, 116.7, 116.6, 31.9, 30.1, 29.8, 29.7, 29.5, 29.3, 22.7, 14.1

3.3.3.2. Synthesis of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser were placed 4-(4-nitrophenoxy)-1-(4-(4-nitrophenoxy)phenoxy)-2-pentadecylbenzene (10.46 g, 0.016 mol), ethanol (100 mL) and 10 wt% Pd/C (0.2 g). To the reaction mixture was added hydrazine hydrate (6 mL) dropwise over a period of 1 h at reflux temperature under inert atmosphere. The mixture was refluxed for additional 4 h. The completion of reaction was confirmed by TLC and reaction mixture was poured into water. The product was extracted with dichloromethane, dried over sodium sulfate and purified by column chromatography over basic alumina. (eluent: dichloromethane)

Yield: 8.57 g (90 %)

IR: 3441, 3344 cm^{-1} (N-H stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.77-6.89 (m, 10H), 6.65-6.69 (m, 5H), 3.56 (br. s., 4H), 2.54 (t, 2H), 1.55 (m, 2H), 1.20-1.30 (m, 24H), 0.88 (t, 3H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 154.4, 153.4, 149.5, 149.2, 142.3, 120.5, 120.4, 120.3, 119.4, 118.7, 118.2, 116.2, 115.7, 31.9, 30.1, 30.0, 29.7, 29.5, 29.4, 22.6, 14.1

3.3.4 Synthesis of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide

3.3.4.1. Synthesis of 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile

Into a 100 mL two necked round bottom flask equipped with a nitrogen inlet, a reflux condenser and a magnetic stirrer were placed 4-(4-hydroxyphenoxy)-3-pentadecylphenol (20 g, 0.064 mmol), 4-fluorobenzonitrile (16.12 g, 0.13 mmol), potassium carbonate (17.98 g, 0.13 mmol) and *N*,*N*-dimethyl formamide (200 mL). The reaction mixture was refluxed for 6 h under nitrogen atmosphere. The reaction mixture was cooled and poured into water and the product was extracted with ethyl acetate, washed with brine and dried over sodium sulfate. The filtered ethyl acetate solution was concentrated under reduced pressure to get crude 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile which was purified by silica gel column chromatography using a mixture of pet ether and ethyl acetate (90:10; v:v) as an eluent.

Yield: 35 g (90%)

IR (cm^{-1}): 2227 (-CN stretching)

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 7.61 (dd, 4H), 6.98-7.03 (m, 11H), 2.62 (t, 2H), 1.58 (m, 2H), 1.24 (bs., 24H), 0.87 (t, 3H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 161.9, 155.1, 151.4, 150.6, 149.6, 136.8, 134.1, 122.5, 121.9, 120.9, 119.0, 118.8, 117.5, 117.4, 105.7, 31.9, 31.1, 29.9, 29.7, 29.4, 22.7, 14.1

3.3.4.2 Synthesis of 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid

Into a 250 mL single necked round bottom flask equipped with a magnetic stir bar and a reflux condenser were added 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile (15 g, 0.024 mol), potassium hydroxide (20.59 g, 0.37 mol), ethylene glycol (200 mL) and water (40 mL). The reaction mixture was refluxed for 24 h. After completion of reaction, the reaction mixture was diluted with water and poured into excess of concentrated hydrochloric acid. Crude 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid precipitated as a grey solid which was filtered and thoroughly washed with water. The product was dissolved in aqueous potassium hydroxide solution and was precipitated by addition of concentrated hydrochloric acid (pH=2). The solid was filtered and washed repeatedly with water and dried. 4-(4-(4-(4-Carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid was purified by silica gel column chromatography (eluent: pet ether: ethyl acetate, 80:20, v/v).

Yield: 14 g (88 %)

M.P.: 112 °C

IR (cm^{-1}): 1684 (-C=O stretching)

^{1}H NMR: (200 MHz, $CDCl_3$) δ = 8.07 (dd, 4H), 6.93-7.04 (m, 11H), 2.62 (t, 2H), 1.60 (m, 2H), 1.24 (bs., 24H), 0.86 (t, 3H)

^{13}C NMR (50 MHz, DMSO-d_6) δ = 166.3, 161.1, 161.0, 154.0, 150.5, 150.1, 149.4, 135.4, 131.2, 124.6, 121.6, 120.8, 118.6, 118.2, 116.3 116.1, 30.9, 28.9, 28.6, 28.4, 28.3, 28.22, 21.7, 13.5

3.3.4.3 Synthesis of methyl 4-(4-(4-(4-(methoxycarbonyl) phenoxy)-2-pentadecyl phenoxy) phenoxy) benzoate

Into a 250 mL two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid (14.0 g, 21.4 mmol) and 3 drops of N,N-dimethylformamide. Thionyl chloride (100 mL) was added dropwise over a period of 30 minutes and the reaction mixture was refluxed for 6 h. Excess thionyl chloride was removed by distillation under reduced pressure and to the residue was added dry toluene (25 mL). Toluene was distilled off under reduced pressure to remove the traces of thionyl chloride. This procedure was repeated twice.

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a reflux condenser and two dropping funnels was placed 4-[4’-(chlorocarbonyl)phenoxy]-2-pentadecyl benzoyl chloride (15.10 g, 29.9 mmol). Pyridine (4.73 g, 59.8 mmol) and methanol (75 mL) were added dropwise to the reaction mixture over a period of 10 minutes and the reaction mixture was refluxed for 5 h. Excess methanol was removed by distillation under reduced pressure. The obtained brown colored solution was extracted with ethyl acetate (2 x 200 mL), washed with saturated aqueous sodium chloride solution (2 x 100 mL) followed by water (3 x 100 mL) and dried over sodium sulfate. Solvent evaporation yielded crude methyl 4-(4’-methoxycarbonyl)phenoxy)-2-pentadecyl benzoate. Pure 4-(4’-methoxy carbonyl)phenoxy)-2-pentadecyl benzoate was obtained after silica gel (60-120 mesh) column chromatography (eluent: pet ether:ethyl acetate; 85:15; v/v).

Yield: 12.6 g (85%)

M. P. 65 °C

IR (cm^{-1}): 1714 (-C=O stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.0 (dd, 4H), 6.86-7.05 (m, 11H), 3.90 (d, 6H), 2.61 (t, 2H), 1.60 (m, 2H), 1.20-1.30 (m, 24H), 0.87 (t, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 162.3, 162.2, 154.8, 151.3, 151.1, 150.3, 136.5, 131.7, 124.3, 124.2, 122.2, 121.6, 120.8, 118.8, 118.7, 116.8, 116.7, 52.0, 31.9, 30.1, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1

3.3.4.4 Synthesis of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide

Into a 250 mL two necked round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed methyl 4-(4-(4-(4-(methoxycarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzoate (5 g, 7.35 mmol) and ethanol (50 mL). Hydrazine hydrate (99 %) (7.49 mL, 464 mmol) was added dropwise to the reaction mixture over a period of 15 minutes and reaction mixture was refluxed overnight. The solid that separated out was filtered and dried. Crude 4-(4-(4-(4-(hydrazinecarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide was purified by recrystallization from ethanol.

Yield: 4.5 g (90 %);

M.P. 146 ^{o}C

IR (cm^{-1}): 1602 (-C=O stretching), 3250-3350 ($-NH_2$ and –NH-)

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.71 (s, 2H), 7.82 (dd, 4H), 6.90-7.08 (m, 11H), 4.47 (br. s., 4H), 2.53 (t, 2H), 1.50 (m, 2H), 1.17 (br, s., 24H), 0.80 (t, 3H)

^{13}C NMR (126 MHz, DMSO-d_6) δ = 165.4, 160.1, 159.9, 154.3, 151.4, 150.3, 135.8, 129.1, 127.8, 127.7, 121.9, 121.5, 121.1, 118.7, 116.9, 116.7, 31.4, 29.4, 29.1, 28.9, 28.8, 28.7, 22.2, 14.0

3.3.5 Synthesis of 3-pentadecyl 4,4' biphenol

3.3.5.1 Synthesis of 4, 4'-dimethoxy-2-pentadecyl-1,1'-biphenyl

Into a 250 mL Schlenck tube equipped with a magnetic stirring bar were added 4-bromo 3-pentadecyl anisole (7.94 g, 20 mmol), 4-methoxy phenyl boronic acid (4.55 g, 30 mmol), potassium carbonate (8.29 g, 60 mmol), tetrakis(triphenyl phosphine)palladium (0.231 g, 0.2 mmol) and dry toluene (100 mL). The reaction mixture was degassed three times by freeze-pump-thaw cycles followed by purging with nitrogen. The nitrogen purging was continued for an hour. The reaction mixture was heated at 110 °C for 24 h. After completion of the reaction (TLC), the reaction mixture was allowed to attain room temperature. Water (50 mL) and ethyl acetate (50 mL) were added. The organic layer was washed with water and brine solution and concentrated to get crude product. The crude product was purified by column chromatography on silica gel using pet ether as an eluent.

Yield: 6.5 g (76%)

IR (cm^{-1}): 1605 (-C=C- stretching), 1281 (ArO-CH_3 stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.99 (d, 2 H), 6.81 (d, 2 H), 6.73 (dd, 2 H), 3.84 (s, 6 H), 2.30 (dt, 5 H), 1.38 - 1.43 (m, 4 H), 1.15 - 1.25 (m, 48 H), 0.88 (t, 6 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 158.53, 142.55, 133.23, 131.19, 114.14, 110.25, 55.11, 33.34, 31.92, 30.67, 29.69, 29.44, 29.36, 28.01, 22.68, 14.10

3.3.5.2 Synthesis of 3-pentadecyl 4, 4' biphenol

Into a 500 mL three necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser were added 4,4'-dimethoxy-2-pentadecyl-1,1'-biphenyl (13 g, 30 mmol), glacial acetic acid (100 mL) and 48% hydrobromic acid (60 mL). The solution was heated at reflux for 12 h. Thereafter, most of the solvent was removed by distillation under reduced pressure. Water (100 mL) was added and the mixture was heated under reflux until all the solids were dissolved. The solution was decolorized with charcoal and allowed to cool to afford 3-pentadecyl 4,4’ biphenol. The pure product was obtained by recrystallisation form a mixture of dichloromethane:pet ether (50:50, v/v)

Yield: 10 g (82 %)

M.P.: 101 °C

IR (cm^{-1}): 3281 (-O-H stretching), 1604 (-C=C- stretching)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.93 (d, 2 H), 6.74 (d, 2 H), 6.65 (dd, 2 H), 4.70 (br. s., 2 H), 2.23 - 2.31 (m, 4 H), 1.37 - 1.40 (m, 4 H), 1.31 - 1.14 (m, 48 H), 0.88 (t, 6 H)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.39, 142.86, 133.22, 131.39, 115.21, 112.07, 33.14, 31.92, 30.57, 29.70, 29.49, 29.37, 22.69, 14.12

3.3.6 Synthesis of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

3.3.6.1 Synthesis of 4,4'-dimethoxy-2,2’-dipentadecyl-1,1'-biphenyl

Into a 100 mL Schlenck tube equipped with a magnetic stirring bar were added 4-bromo-3-pentadecyl anisole (2 g, 5 mmol), bis(1,5-cyclooctadiene)nickel [Ni(COD)$_2$] (1.38 g, 5 mmol), 1,5- cyclooctadiene (COD) (0.23 mL, 5 mmol), bipyridine (0.78 g, 5 mmol) and toluene (20 mL). The tube was degassed three times by freeze-pump-thaw cycles followed by purging with nitrogen. The nitrogen purging was continued for an hour. The reaction mixture was heated at 80 °C for 6 h. After completion of the reaction (TLC), the reaction mixture was allowed to attain room temperature. The reaction mixture was filtered through a celite plug and the residue was washed with pet ether. After solvent evaporation, the product was purified by flash column chromatography (pet ether:dichloromethane; 90:10. v/v)

Yield: 1.20 g (75 %)

IR (cm^{-1}): 1278 (-O-C stretching), 1610 (-C=C- stretching of biphenyl)

^{1}HNMR ($CDCl_3$ 400Mz) δ = 6.99 (d, 2H), 6.81 (d, 2H), 6.73 (dd, 2H), 3.84 (bs, 6H), 2.29 (m, 4H), 1.41 (m, 4H), 1.14-1.30 (m, 48H), 0.88 (t, 6H)

^{13}CNMR ($CDCl_3$ 100Mz) δ = 158.53, 142.55, 133.23, 131.19, 114.14, 110.25, 55.11, 33.34, 31.92, 30.67, 29.69, 29.44, 29.36, 28.01, 22.68, 14.10

3.3.6.2 Synthesis of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

Into a 100 mL three necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser were added 4,4'-dimethoxy-2,2’-dipentadecyl-1,1'-biphenyl (1 g, 1.57 mmol), glacial acetic acid (25 mL) and 48% hydrobromic acid (10 mL). The solution was heated at reflux for 12 h. Thereafter, most of the solvent was removed by distillation under reduced pressure, 10 mL of water was added and the mixture was heated under reflux until all the solids were dissolved. The solution was decolorized with charcoal and allowed to cool to afford 3-pentadecyl 4,4’ biphenol. The pure product was obtained by recrystallisation from a mixture of dichloromethane:pet ether (40:60; v/v)

Yield: 0.75 g (78 %)

M.P.: 109 °C

IR: 3300 (-O-H stretching)

^{1}H NMR ($CDCl_3$ 400 MHz) δ = 6.93 (d, 2H), 6.74 (d, 2H), 6.65 (dd, 2H), 4.70 (bs, 2H), 2.26 (m, 4H), 1.39 (m, 4H), 1.14-1.30 (m, 48H), 0.88 (t, 6H)

^{13}C NMR ($CDCl_3$ 100 MHz) δ = 145.39, 142.86, 133.22, 131.39, 115.21, 112.07, 33.14, 31.92, 29.70, 29.37, 22.69, 14.12

3.3.7 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

3.3.7.1 Synthesis of 3-pentadecyl triflate

Into a 250 mL two necked round bottom flask equipped with an addition funnel and a magnetic stirring bar were added 3-pentadecyl phenol (30.4 g, 10 mmol), dichloromethane (100 mL) and pyridine (1.6 mL) and the solution was cooled at 0 °C. Trifluoromethane sulfonic anhydride (20.15 mL, 12 mmol) was added dropwise and the mixture was warmed to room temperature. The reaction was continued further for 1h. The reaction mixture was diluted with diethyl ether (200 mL), quenched with 10 % hydrochloric acid and washed successively with saturated sodium bicarbonate solution and brine. After drying over sodium sulfate, the solvent was evaporated and the product was purified by column chromatography on silica gel using petroleum ether as an eluent to obtain the pure product.

Yield: 40 g (92 %)

IR (cm^{-1}): 1142 (-S=O stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.28 - 7.42 (m, 1 H), 7.14 - 7.25 (m, 1 H), 7.03 - 7.14 (m, 2 H), 2.65 (t, 2 H), 1.70 - 1.57 (m, 2 H), 1.27 (br. s, 24 H), 0.89 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 149.66, 145.99, 129.86, 120.43, 121.10, 118.35, 35.61, 31.93, 31.08, 29.68, 29.54, 29.37, 29.12, 22.69, 14.09

3.3.7.2 Synthesis of 3-pentadecyl biphenyl

Into a 250 mL Schlenck tube equipped with a magnetic stirring bar were added 3-pentadecyl triflate (20 mmol, 8.72g), phenyl boronic acid (3.66 g, 30 mmol), potassium carbonate (8.29 g, 60 mmol), tetrakis(triphenyl phosphine)palladium (0.231 g, 0.2 mmol) and dry toluene (100 mL). The tube was degassed three times by freeze-pump-thaw cycles followed by purging with nitrogen. The nitrogen purging was continued for an hour. The reaction mixture was then heated at 110 °C for 24 h. After completion of reaction (TLC), the reaction mixture was allowed to attain room temperature. Water (50 mL) and ethyl acetate (50 mL) were added. The organic layer was washed with water and brine solution and concentrated to get crude product. 3-Pentadecyl biphenyl was purified by column chromatography on silica gel using pet ether as an eluent.

Yield: 6.1g (84 %)

IR (cm^{-1}): 2926 (-C-H stretching), 1599 (C=C stretching), 754 (=C-H bending)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.56 - 7.67 (m, 2 H), 7.30 - 7.52 (m, 6 H), 7.19 (d, 1 H), 2.69 (t, 2 H), 1.60 - 1.75 (m, 2 H), 1.23 - 1.39 (m, 24 H), 0.90 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 143.42, 141.45, 142.15, 128.66, 127.35, 127.18, 124.47, 36.09, 31.93, 31.60, 29.70, 29.55, 29.39, 22.70, 14.13

3.3.7.3 Synthesis of 4,4’-dibromo 3-pentadecyl biphenyl

Into a 250 mL three necked round bottom flask equipped with a water condenser, a dropping funnel and a thermometer were added 3-pentadecyl biphenyl (1 g, 2.75 mmol), dichloromethane (10 mL), ferric chloride (1 mol%, 10 mg) and iodine

(15 mg, 1 mol%). Bromine (0.93 g, 5.78 mmol) was added drop wise to the reaction mixture while reaction mixture was maintained at ambient temperature by controlling addition rate. The reaction mixture was stirred for 5 h at room temperature and was heated at reflux for 1h. Thereafter, reaction mixture was allowed to attain room temperature, the excess of bromine and iodine were destroyed by 10% sodium sulfate solution. The dichloromethane solution was washed with water until neutral and with brine and then dried over sodium sulfate. The product was purified by column chromatography on silica gel using pet ether as an eluent.

Yield: 1.2 g (85 %)

M. P.: 46 °C

IR (cm^{-1}): 784 (C-Br stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.54 - 7.60 (m, 3 H), 7.37 - 7.44 (m, 3 H), 7.21 (dd, 2 H), 2.77 (t, 2 H), 1.57 – 1.64 (m, 2 H), 1.22-1.39 (m, 24 H), 0.88 (m, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 142.68, 139.21, 133.16, 131.92, 128.66, 128.53, 125.77, 123.94, 121.77, 36.35, 31.93, 30.02, 29.70, 29.60, 29.46, 22.70, 14.13

3.3.7.4 Synthesis of 4, 4’ dicyano 3-pentadecyl 1,1’biphenyl

Into a 250 mL three necked round bottom flask equipped with a magnetic stirring bar and a reflux condenser were added 4, 4’ dibromo 3-pentadecyl 1,1’ biphenyl (5.22 g, 10 mmol), copper cyanide (3.58 g, 4 mmol) copper sulfate (0.5 g) and N,N-dimethylformamide (100 mL). The reaction mixture was refluxed overnight. After completion of reaction, the brown colored solution was poured into concentrated hydrochloric acid (50 mL) and the solution was extracted with ethyl acetate (2 x 100 mL), washed with brine solution (3 x 50 mL) followed by water (3 x100 mL) and dried over sodium sulfate. The solvent evaporation yielded crude 4, 4’ dicyano 3-pentadecyl 1,1’-biphenyl. The pure product was obtained by silica gel column chromatography (eluent pet ether/ ethyl acetate) followed by recrystallization from a mixture pet ether: dichloromethane; 90:10; (v:v).

Yield: 2 g (48 %)

M.P.: 93 °C

IR (cm^{-1}): 2228 (-CN group stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.66 - 7.79 (m, 5 H), 7.46 - 7.51 (m, 2 H), 2.90 (t, 2 H), 1.68 -1.74 (m, 2 H), 1.25 - 1.35 (m, 24 H), 0.87 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.77, 143.85, 143.35, 133.43, 132.76, 128.22, 127.93, 125.14, 118.45, 117.76, 112.35, 112.18, 34. 77, 31.88, 30.99, 29.63, 29.49, 29.32, 22.65, 14.09

3.3.7.5 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid

Into a 250 mL round bottom flask equipped with a magnetic stirring bar were added 4, 4' dicyano 3-pentadecyl 1,1'-biphenyl (2 g, 4.82 mmol), potassium hydroxide (4.06 g, 72.41 mmol), ethylene glycol (100 mL) and water (20 mL). The reaction mixture was heated at 180 °C for 24 h. After completion of reaction, the reaction mixture was poured into excess of water and acidified with concentrated hydrochloric acid to precipitate the product. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid was filtered and washed with water. The obtained solid was dissolved in aqueous potassium hydroxide solution and was precipitated by addition of concentrated hydrochloric acid (pH=2). The solid was filtered and washed repeatedly with water and dried.

Yield: 1.8 g (87 %)

M.P.: > 300 °C

IR (cm^{-1}): broad peak 3100-3500 (O-H stretching)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, 2 H), 8.02 (d, 1 H), 7.77 (d, 2 H), 7.60 (br. s., 1 H), 7.57 (d, 2 H), 3.10 (t, 2 H), 1.62 -1.68 (m, 2 H), 1.25-1.35 (m, 24 H), 0.88 (t, 3 H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.69, 167.52, 146.93, 145.17, 144.05, 132.78, 131.18, 130.70, 127.94, 125.25, 35.67, 33.04, 30.98, 30.83, 30.67, 30.49, 25.48, 23.74, 14.61

3.3.7.6 Synthesis of dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate

Into a 250 mL single necked round bottom flask containing 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid (2 g, 4.42 mmol) were added methanol (50 mL) and concentrated sulfuric acid (1 mL). The reaction mixture was refluxed for 24 h. After completion of reaction, the reaction mixture was poured into water and the product dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate was extracted with ethyl acetate. The ethyl acetate solution was washed with water (3 x 50 mL). Finally, ethyl acetate solution was washed with brine and dried over sodium sulfate. The crude product was purified by silica gel column chromatography using pet ether:ethyl acetate (90:10;v:v) followed by recrystallisation from dichloromethane:methanol (95:5;v:v) mixture.

Yield: 1.8 g (85 %)

MP: 65 °C

IR (cm^{-1}): 1721 (Ester –C=O carbonyl stretching)

^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.12 (d, 2 H), 7.96 (d, 1 H), 7.68 (d, 2 H), 7.46 7.48 (m, 2 H), 3.92 – 3.95 (m, 6 H), 3.02 (t, 2 H), 1.61 -1.63 (m, 2 H), 1.25 – 1.31 (m, 24 H), 0.88 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 154.39, 142.86, 133.22, 131.39, 115.21, 112.07, 33.14, 31.92, 30.57, 29.70, 29.49, 29.37, 22.69, 14.12

3.3.7.7 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

Into a 100 mL two necked round bottom flask equipped with a reflux condenser and a magnetic stirring bar were added dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate (1 g, 2.08 mmol) and methanol (10 mL). The compound was dissolved by heating and hydrazine hydrate (5 mL, 310 mmol) was added at the same temperature. The reaction mixture was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and water was added. The precipitated solid was filtered and washed with water. The crude product was recrystallized from methanol to get pure 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide.

Yield: 0.9 g (90%)

M.P.: 213 °C

IR (cm^{-1}): 3299 (-NH_2 and –NH- stretching), 1602 (-C=O, stretching)

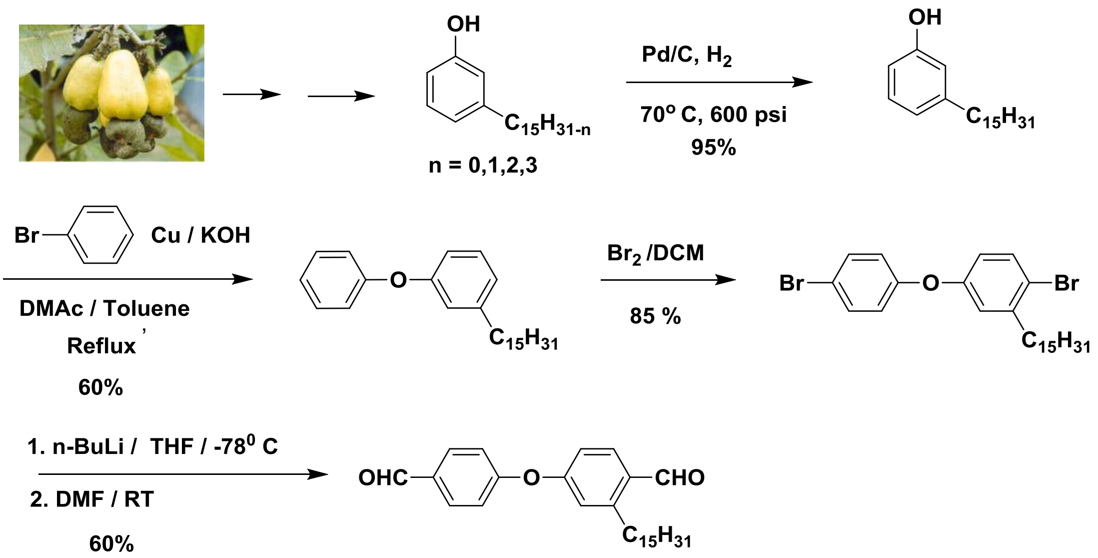
^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.89 (s, 1 H), 8.67 (s, 1 H), 7.90 (d, 2 H), 7.70 (d, 2 H), 7.48 – 7.55 (m, 2 H), 7.39 (d, 1 H), 4.27 (br. s., 4 H), 2.86 (t, 2 H), 1.73 (br. s., 2 H), 1.29 (br. s., 24 H), 0.88 (t, 3 H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 144.01, 143.65, 142.21, 136.03, 134. 00, 129.56, 128.98, 128.55, 127.68, 124.91, 34.58, 33.04, 30.83, 30.68, 30.49, 26.01, 25.88, 25.68, 25.48, 25.28, 25.09, 14.61

3.4 Results and Discussion

3.4.1 Synthesis of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde

Scheme 3.1 outlines route for the synthesis of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde starting from CNSL.



Scheme 3.1 Synthesis of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde starting from CNSL

The synthesis of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde involved four steps. In the first step, cardanol obtained from CNSL was hydrogenated at 600 psi in a Parr reactor using Pd/C as a catalyst to obtain 3-pentadecyl phenol.[11] In the second step, 1-pentadecyl 3-phenoxybenzene was prepared by the reaction of 3-pentadecyl phenol with bromobenzene in the presence of potassium hydroxide and Cu as a catalyst under classical Ullmann etherification reaction conditions.[14-16] 1-Pentadecyl 3-phenoxy benzene was selectively brominated at *para-para'* positions with bromine in dichloromethane to obtain 1-bromo 4-(4-bromophenoxy) 2-pentadecyl benzene.[17] Further, 1-bromo 4-(4-bromophenoxy) 2-pentadecyl benzene was lithiated using n-butyl lithium in tetrahydrofuran solution, followed by formylation with DMF to give the desired dialdehyde.[18] The dialdehyde and intermediates involved in its synthesis were purified by column chromatography and were characterized by spectroscopic methods.

Figure 3.2 shows FT-IR spectrum of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde. The appearance of absorption band at 1700 cm^{-1} confirmed the formation of aldehyde.

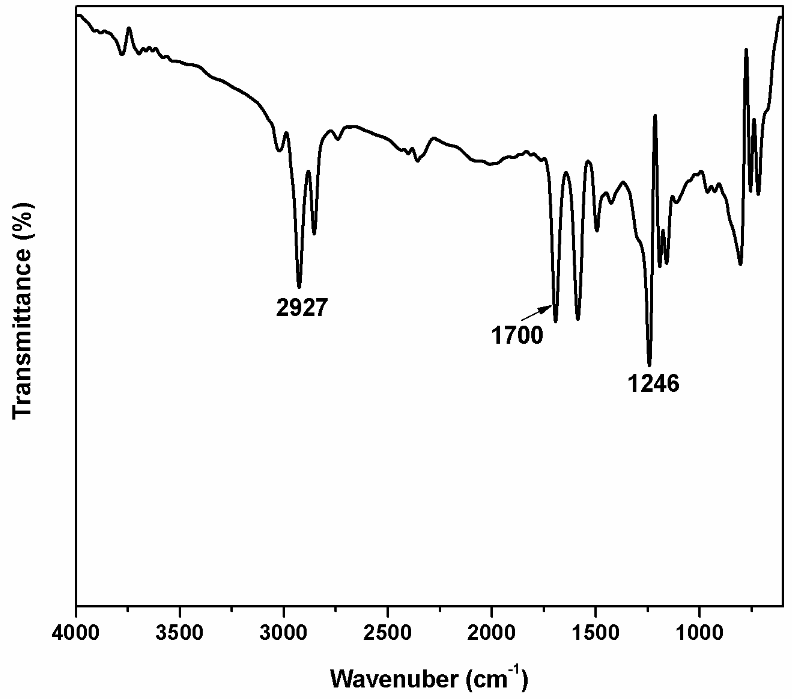


Figure 3.2 FT-IR spectrum of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde

Figure 3.3 shows ^{1}H NMR spectrum of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde. The two aldehydic protons appeared as two distinct singlets at 10.22 and 9.97 δ ppm. The appearance of two different signals for the two aldehydic protons is due to the existence of non-symmetry in the monomer. The presence of pentadecyl chain on only one aromatic ring in the monomer makes the monomer non-symmetric and consequently the two aromatic rings are magnetically nonequivalent. Three aromatic protons *ortho* to aldehyde group appeared as a multiplet in the range 7.85-7.94 δ ppm, while remaining aromatic protons appeared as a multiplet in the range 6.92–7.18 δ ppm. The benzylic –CH_2 appeared as a triplet at 3.0 δ ppm. The methylene protons *β* to aromatic ring appeared as a multiplet in the range 1.54-1.64 δ ppm. The other methylene protons exhibited a multiplet over the range 1.20–1.28 δ ppm. The terminal –CH_3 showed a triplet at 0.87 δ ppm.

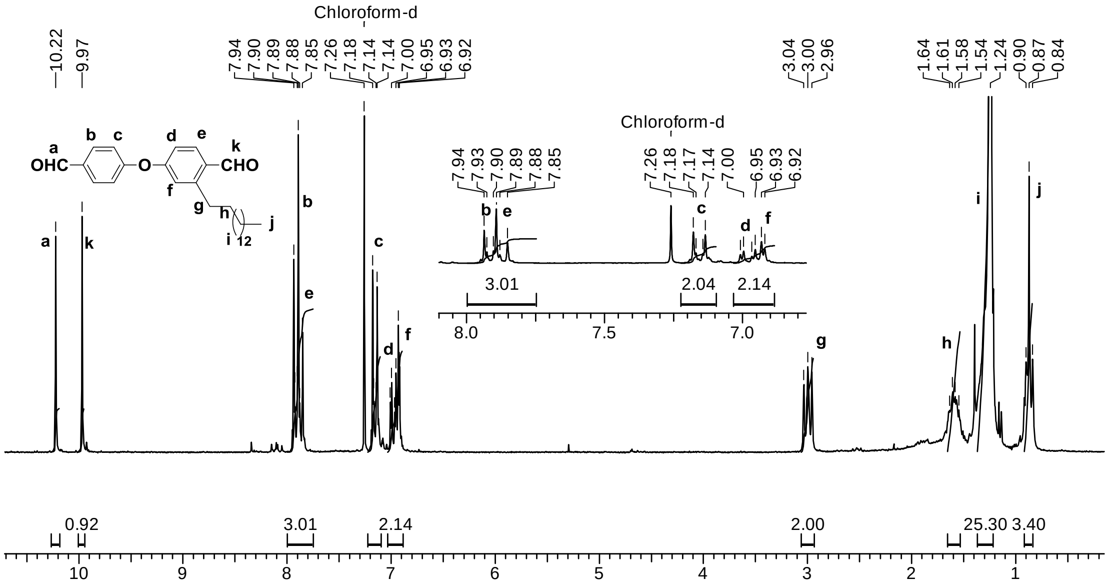


Figure 3.3 ^{1}H NMR spectrum (in CDCl$_3$) of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde

^{13}C NMR spectrum of 4-(4-formylphenoxy)-2-pentadecylbenzaldehyde is shown in **Figure 3.4.** In ^{13}C NMR spectrum, carbonyl carbons of the aldehyde group resonated at 190.67 and 190.59 δ ppm. Aromatic carbons *ortho* to carbonyl carbon appeared at 133.91 (C8) and 132.02 (C4) δ ppm. The appearance of two different signals for carbonyl–carbons and carbons adjacent to carbonyl groups is due to the existence of non-symmetry in the monomer. The spectral data corresponding to other carbon atoms was in good agreement with the proposed structure.

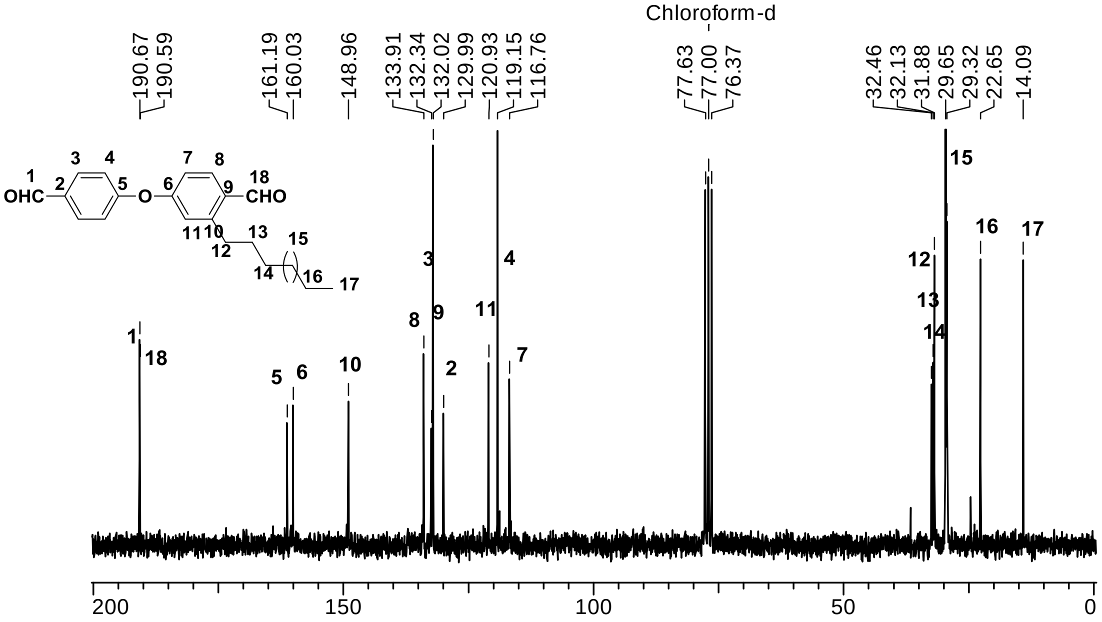
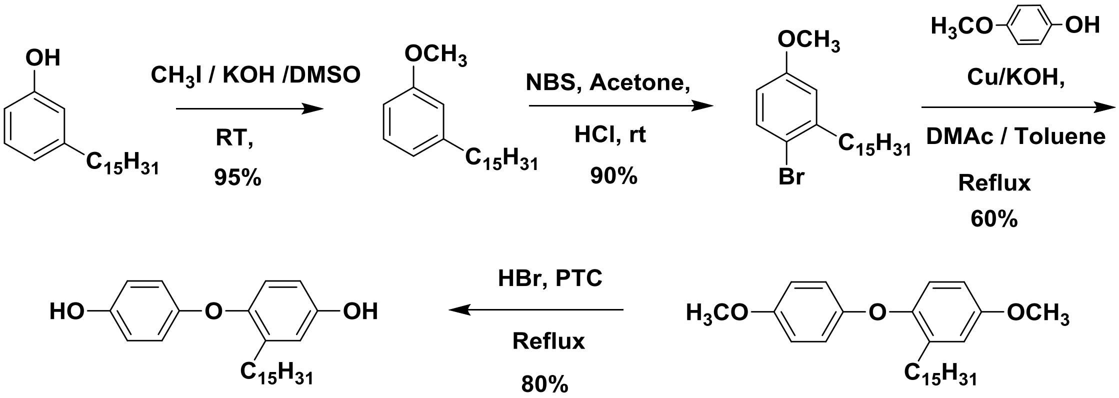


Figure 3.4 ^{13}C NMR spectrum (in CDCl$_3$) of 4-(4-formylphenoxy)- 2-pentadecylbenzaldehyde

3.4.2 Synthesis of 4-(4-hydroxyphenoxy)-3-pentadecylphenol from 3-pentadecyl phenol

Scheme 3.2 depicts route for synthesis of 4-(4-hydroxyphenoxy)-3-pentadecylphenol starting from 3- pentadecyl phenol which in turn is obtained from CNSL.



Scheme 3.2 Synthesis of 4-(4-hydroxyphenoxy)-3-pentadecylphenol starting from 3-pentadecyl phenol

The synthesis of 4-(4-hydroxyphenoxy)-3-pentadecylphenol involved four steps. The first step involved methyl ether protection of phenolic –OH with methyl iodide as the methylating agent in the presence of potassium hydroxide and dimethyl sulfoxide as a solvent.[13] 3-Pentadecyl anisole was brominated using N-bromosuccinimide, catalytic HCl and acetone as a solvent to give 4-bromo 3-pentadecyl anisole.[18, 19] Further, 4-bromo 3-pentadecyl anisole was treated with monomethyl ether of hydroquinone in the presence of potassium hydroxide and Cu as a catalyst under classical Ullmann etherification reaction conditions to form 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene. Then 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene on demethylation by standard procedure[2021] in the presence of HBr and tetra n-butyl phosphonium bromide as a phase transfer catalyst afforded 4-(4-hydroxyphenoxy)-3-pentadecylphenol. The bisphenol and intermediates involved in the synthesis were purified by column chromatography and were characterized by IR and NMR spectroscopy.

^{1}H NMR spectrum of 3-pentadecyl anisole is represented in **Figure 3.5.** In aromatic region, a multiplet in the range 7.15-7.23 δ ppm could be assigned to the proton *meta* to methoxy group and other three protons exhibited a multiplet in the range 6.71-6.79 δ ppm. The peak at 3.80 δ ppm is due to methoxy group protons.

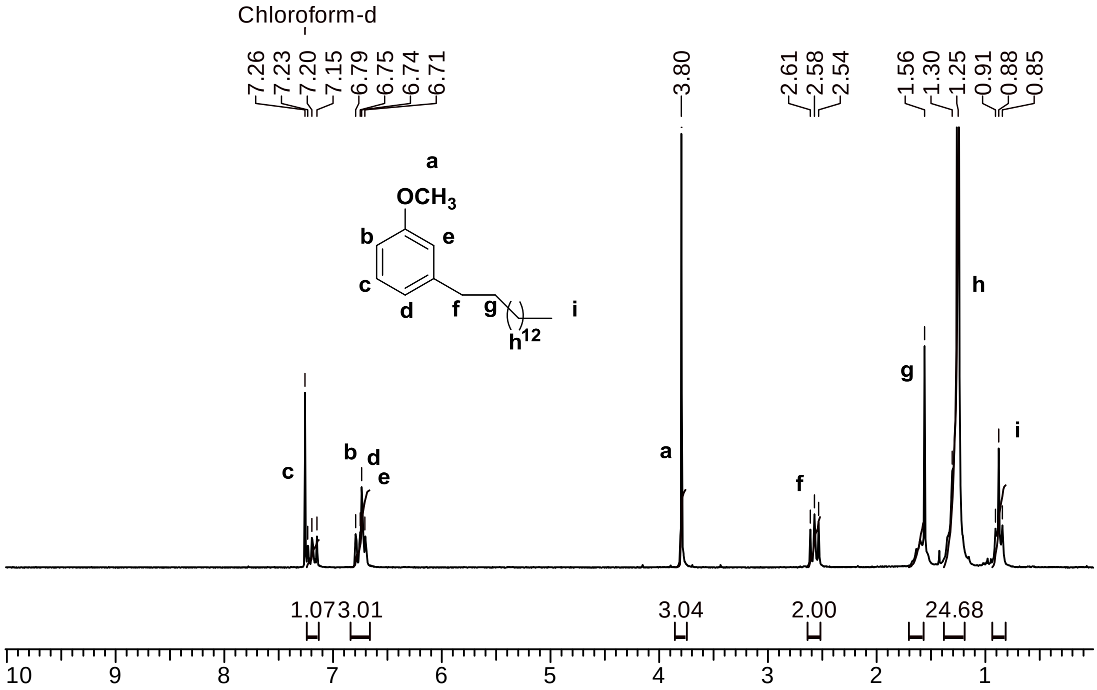


Figure 3.5 ^{1}H NMR spectrum (in CDCl$_3$) of 3-pentadecyl anisole

^{13}C NMR spectrum of 3-pentadecyl anisole along with assignments is reproduced in **Figure 3.6.**

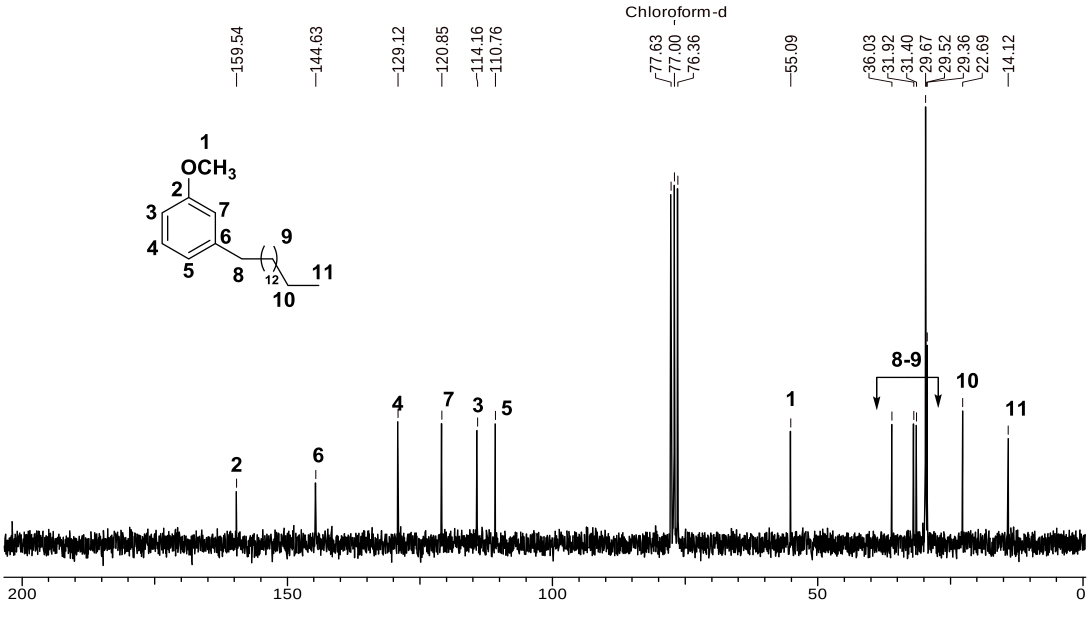


Figure 3.6 ^{13}C NMR spectrum (in CDCl$_3$) of 3-pentadecyl anisole

^{1}H NMR spectrum of 4-bromo 3-pentadecyl anisole is shown in **Figure 3.7.** The proton *ortho* to bromine appeared as a doublet at 7.40 δ ppm. The protons *ortho* to methoxy group, d and b exhibited a doublet 6.67 δ ppm and a doublet of doublet at 6.61 δ ppm, respectively. The methoxy group protons appeared at 3.78 δ ppm. The peaks in the aliphatic region are due to the pentadecyl chain

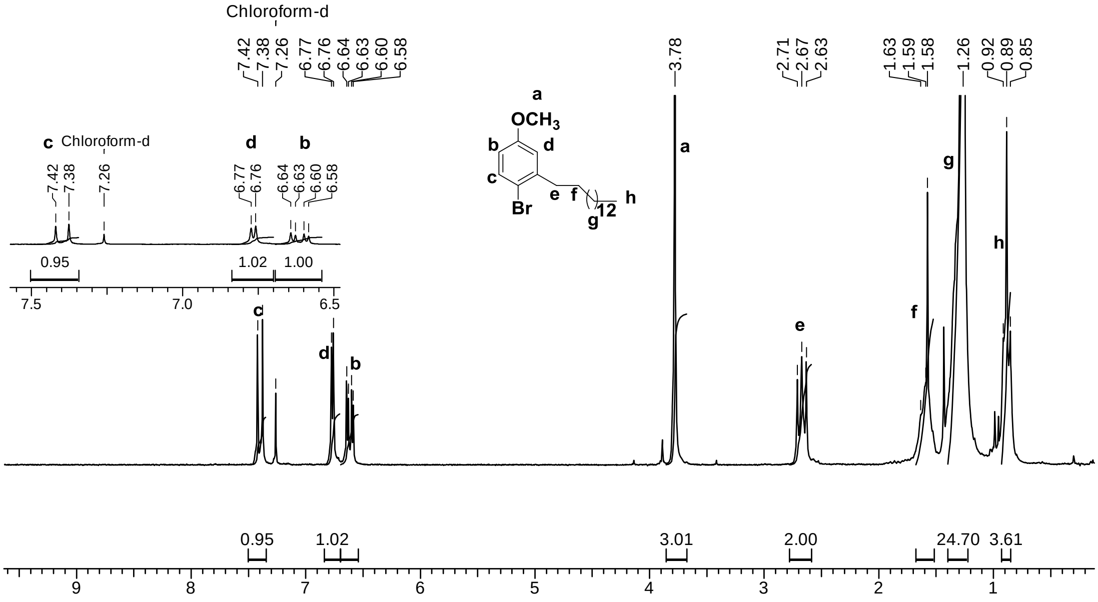


Figure 3.7 ^{1}H NMR spectrum (in CDCl$_3$) of 4-bromo 3-pentadecyl anisole

^{13}C NMR spectrum of 4-bromo 3-pentadecyl anisole along with assignments is represented in **Figure 3.8** and assignments are in good agreement with the structure.

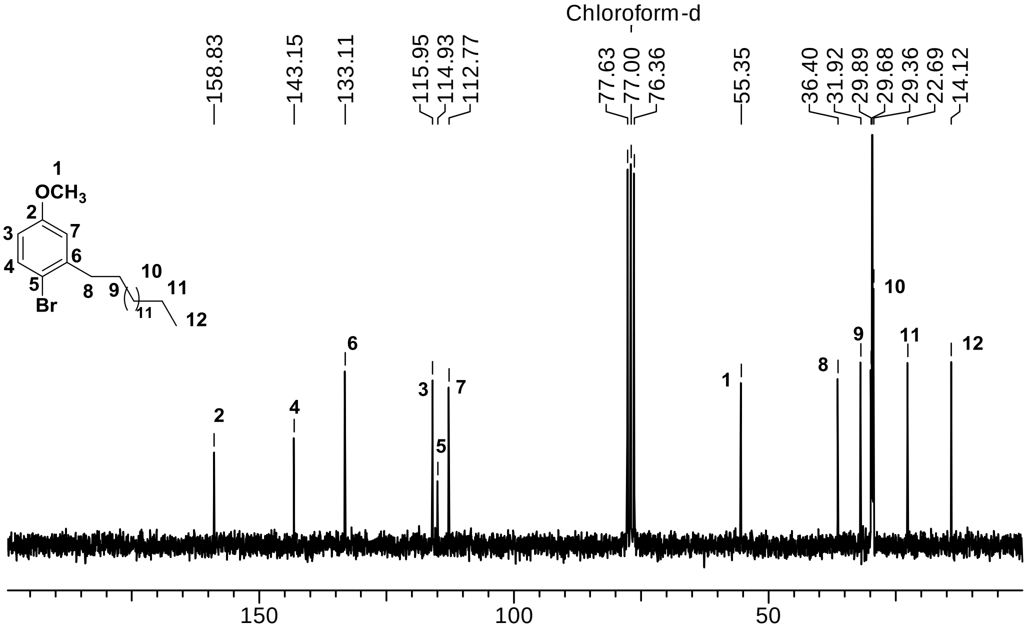


Figure 3.8 ^{13}C NMR spectrum (in CDCl$_3$) of 4-bromo 3-pentadecyl anisole

^{1}H NMR spectrum of 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene is represented in **Figure 3.9.** The four protons of aromatic ring without pentadecyl chain exhibited a singlet at 6.82 δ ppm. The multiplet in the region 6.80-6.77 δ ppm could be attributed to the protons c and d whereas doublet of doublet at 6.69 is due to the proton c. The methoxy groups appeared at two distinct singlets at 3.78 and 3.79 δ ppm due to the non-symmetry in the structure. The protons of pentadecyl chain appeared in the aliphatic region.

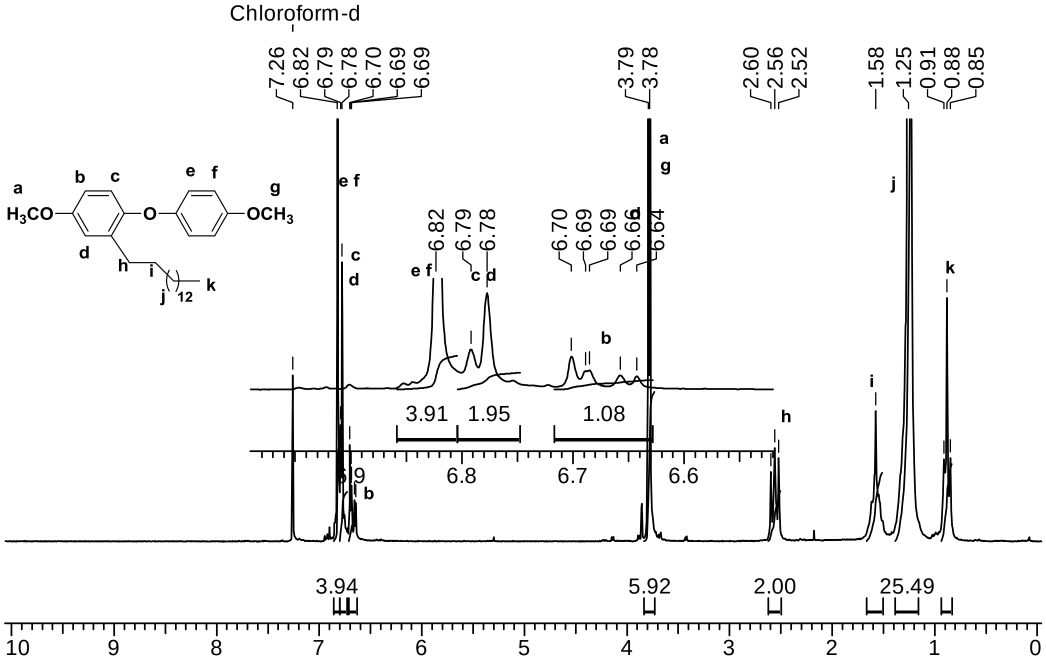


Figure 3.9 ^{1}H NMR spectrum (in $CDCl_3$) of 4-methoxy-1-(4-methoxyphenoxy)-2-pentadecylbenzene

FT-IR spectrum of 4-(4-hydroxyphenoxy)-3-pentadecylphenol is reproduced in **Figure 3.10**, which showed a broad absorption band at 3325 cm^{-1} due to the phenolic hydroxyl group. The band at 1204 cm^{-1} corresponds to C–O–C stretching.

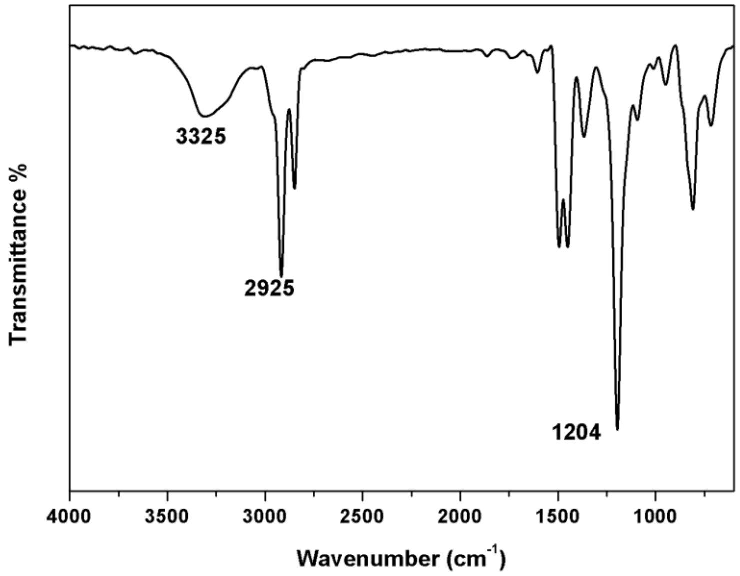


Figure 3.10 FT-IR spectrum of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

^{1}H NMR spectrum of 4-(4-hydroxyphenoxy)-3-pentadecylphenol along with assignments is presented in **Figure 3.11.**

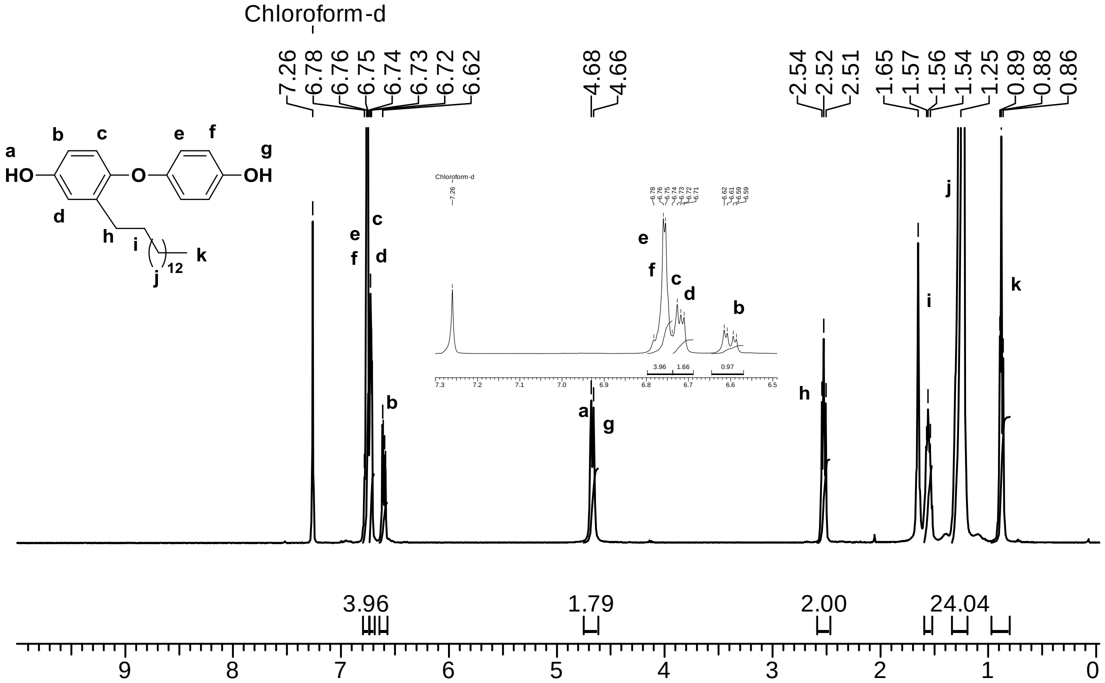


Figure 3.11 ^{1}H NMR spectrum (in CDCl$_3$) of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

In the NMR spectrum, a multiplet in the region 6.74-6.78 δ ppm is due to four aromatic protons of the aromatic ring without pentadecyl chain, the multiplet in the region 6.73-6.70 δ ppm is due to two aromatic protons which are *ortho* and *meta* to the pentadecyl chain and the doublet of doublet at 6.61 δ ppm is due to the proton *para* to the pentadecyl chain. The phenolic –OH groups appeared as two distinct peaks at 4.66 and 4.68 δ ppm, the benzylic protons showed a triplet at 2.52 δ ppm and the remaining protons of the pentadecyl chain appeared in aliphatic region.

^{13}C NMR spectrum of 4-(4-hydroxyphenoxy)-3-pentadecylphenol along with assignments is represented in **Figure 3.12** and assignments are in good agreement with the structure.

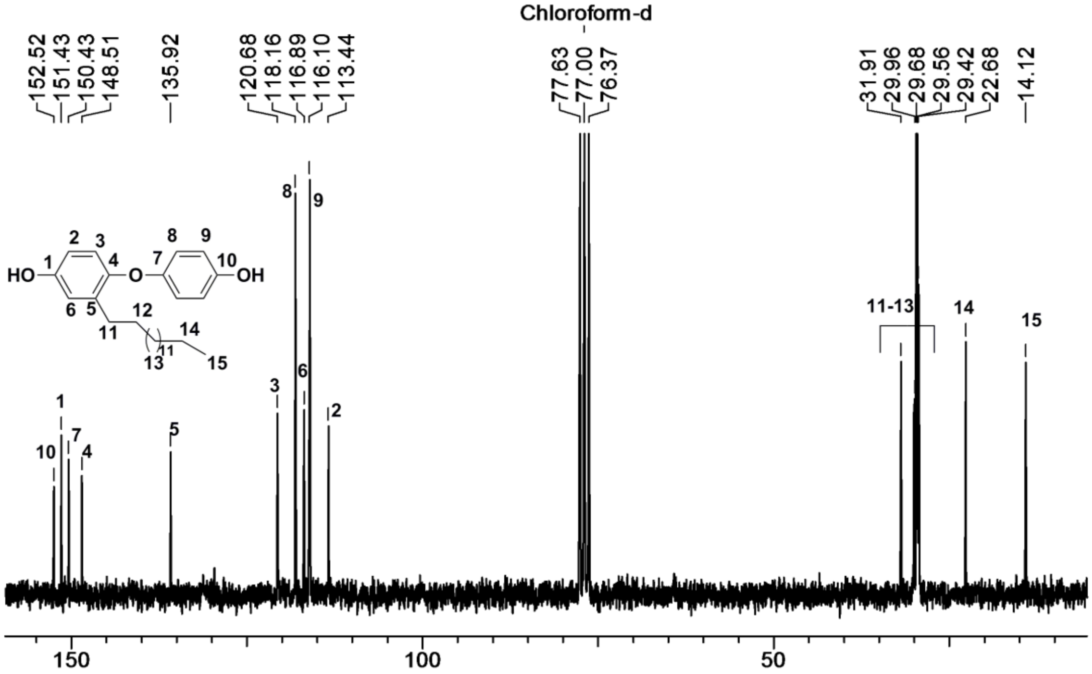


Figure 3.12 ^{13}**C NMR spectrum (in CDCl$_3$) of 4-(4-hydroxyphenoxy)-3-pentadecylphenol**

^{1}H-^{1}H COSY-NMR spectrum of 4-(4-hydroxyphenoxy)-3-pentadecylphenol is given in **Figure 3.13** which clearly confirms the molecular structure.

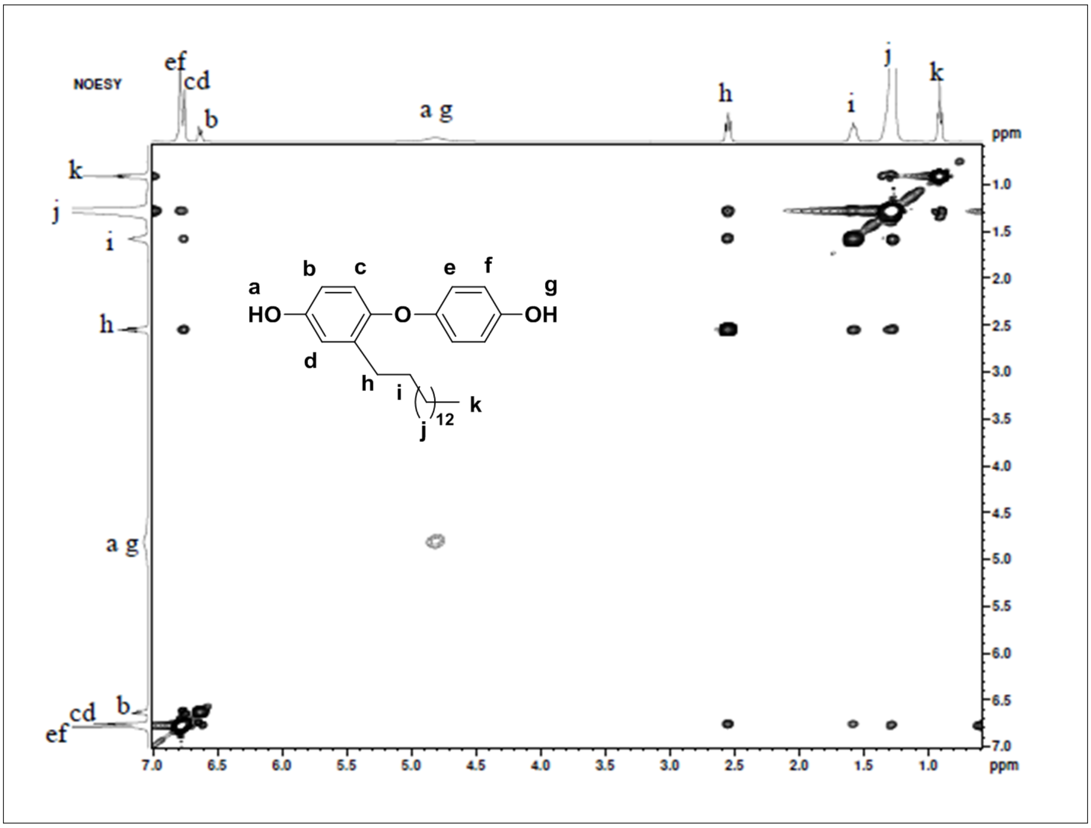
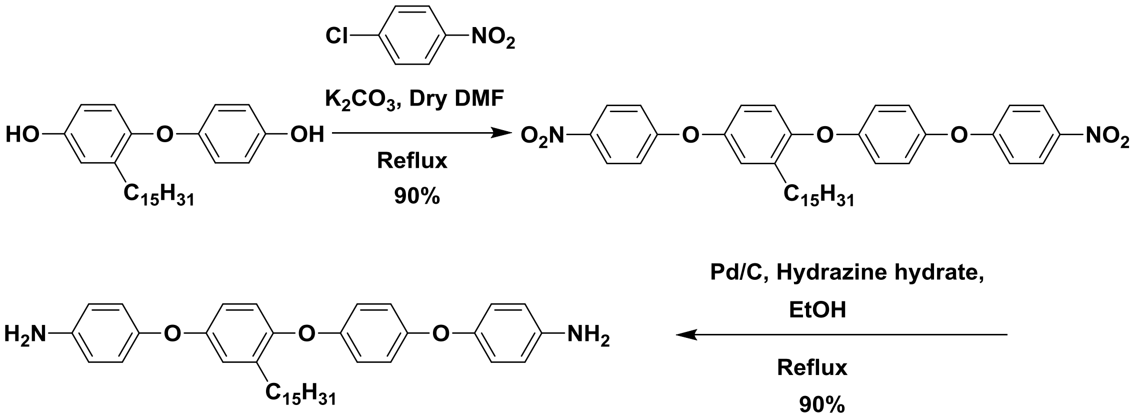


Figure 3.13 ^{1}**H-**^{1}**H COSY-NMR spectrum of 4-(4-hydroxyphenoxy)-3-pentadecylphenol**

3.4.3 Synthesis of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline

Scheme 3.3 outlines route for synthesis of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline starting from 4-(4-hydroxyphenoxy)-3-pentadecylphenol.



Scheme 3.3 Synthesis of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline

The dinitro compound viz., 4-(4-nitrophenoxy)-1-(4-(4-nitrophenoxy)phenoxy)-2-pentadecylbenzene was prepared by nucleophilic halo displacement of *p*-chloronitrobenzene with 4-(4-hydroxyphenoxy)-3-pentadecylphenol in the presence of potassium carbonate. The reaction was carried out using N, N-dimethylformamide as a solvent at reflux temperature. The diamine was obtained by reduction of dinitro compound using hydrazine hydrate and Pd/C as catalyst in refluxing ethanol.[22]

^{1}H NMR spectrum of 4-(4-nitrophenoxy)-1-(4-(4-nitrophenoxy)phenoxy)-2-pentadecylbenzene is shown in **Figure 3.14**. The four aromatic protons *ortho* to the nitro group appeared as a multiplet in the region 8.17-8.25 δ ppm, while remaining 11 aromatic protons appeared as a multiplet in the region 6.96-7.05 δ ppm. The benzylic methylene protons exhibited a triplet at 2.63 δ ppm. The methylene protons β to aromatic ring appeared as a multiplet in the range 1.56-1.62 δ ppm, the remaining methylene protons of the pentadecyl chain appeared as a multiplet in the range 1.20-1.28 δ ppm and a triplet at 0.87 is due to methyl protons of the pentadecyl chain.

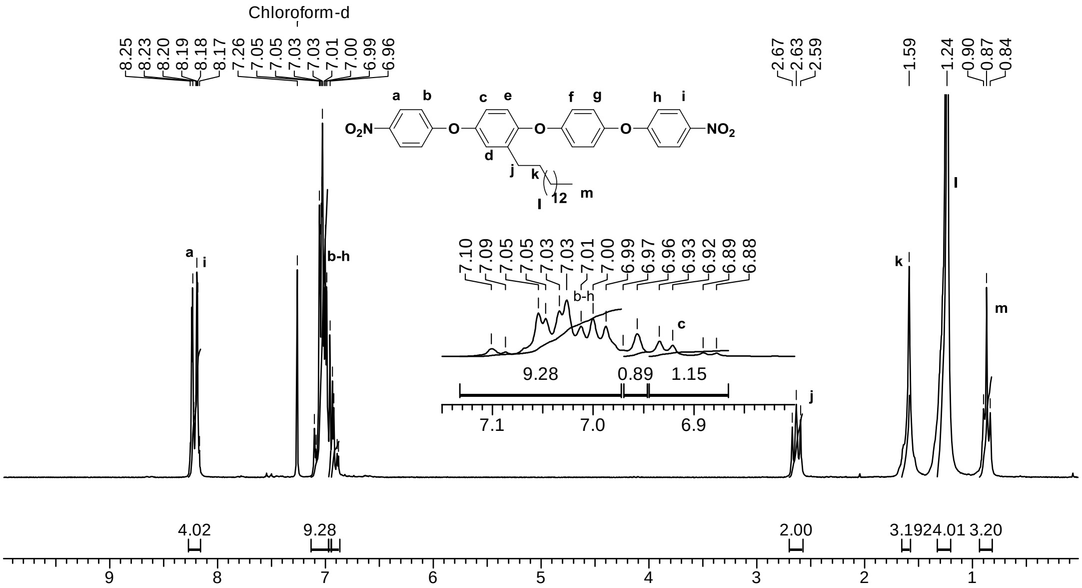


Figure 3.14 ^{1}H **NMR spectrum (in** $CDCl_3$**) of 4-(4-nitrophenoxy)-1-(4-(4-nitrophenoxy)phenoxy)-2-pentadecylbenzene**

FT-IR spectrum of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline is shown in **Figure 3.15.** The absorption peaks at 3441, 3344 and 3309 cm^{-1} are due to -N-H bond stretching of the $–NH_2$ group.

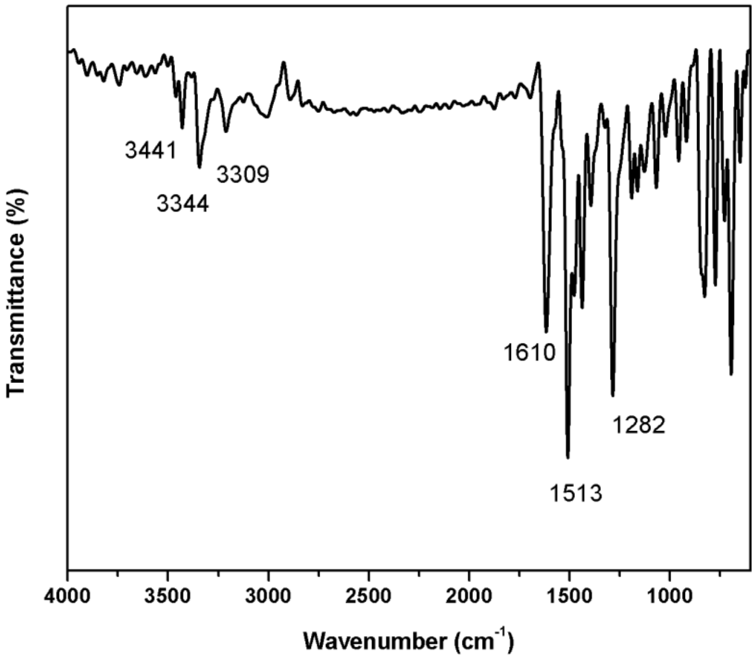


Figure 3.15 FT-IR spectrum of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline

^{1}H NMR spectrum of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline is shown in **Figure 3.16**

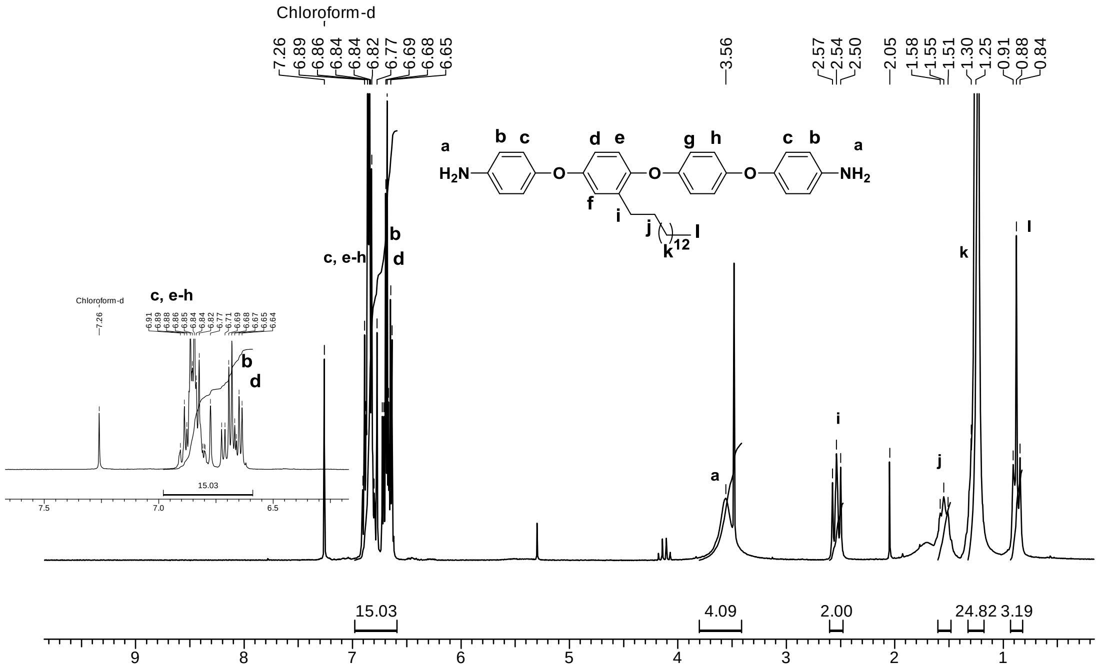


Figure 3.16 ^{1}**H NMR spectrum (in CDCl**$_3$**) of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline**

In ^{1}H NMR spectrum of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline, the appearance of a broad singlet at 3.56 δ ppm is due to the four protons of amino group which confirms the formation of the multiring diamine. The protons *ortho* to amino groups appeared as a multiplet in the range 6.64-6.71 δ ppm and the other aromatic ring protons exhibited a multiplet in the range 6.77-6.91 δ ppm. The upfield shift in four aromatic *ortho* protons is observed as electronegative –NO_2 group was converted into electron donating –NH_2 group. Also there was observation of slight upfield shift with other protons. The benzylic methylene protons appeared in the dinitro compound at 2.63 δ ppm exhibited upfield shift and appeared at 2.54 δ ppm, the methylene protons β to the aromatic ring appeared as a multiplet in the range 1.51-1.58. The terminal methyl protons exhibited a triplet at 0.88 δ ppm.

^{13}C NMR spectrum of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline along with assignments is shown in **Figure 3.17**

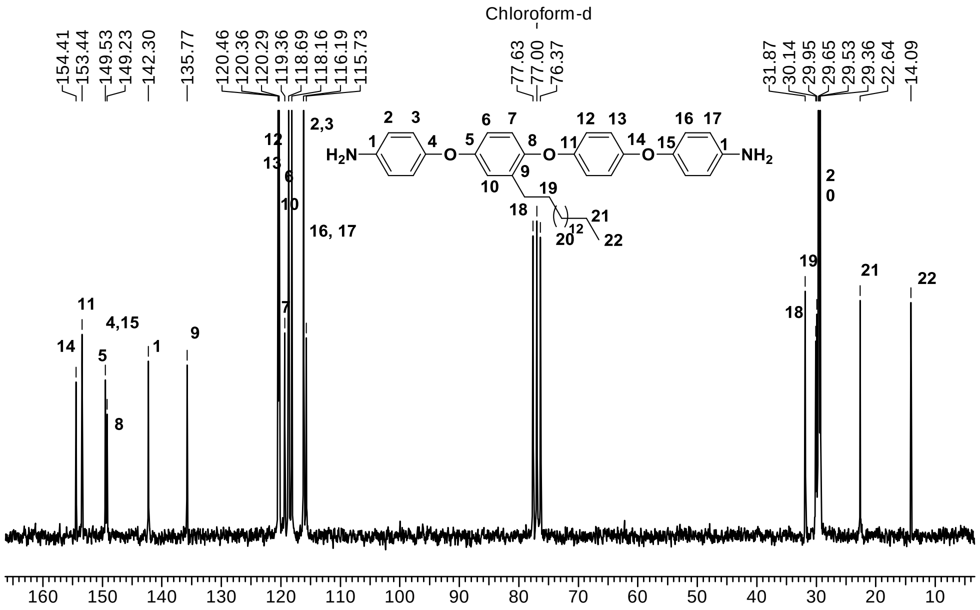
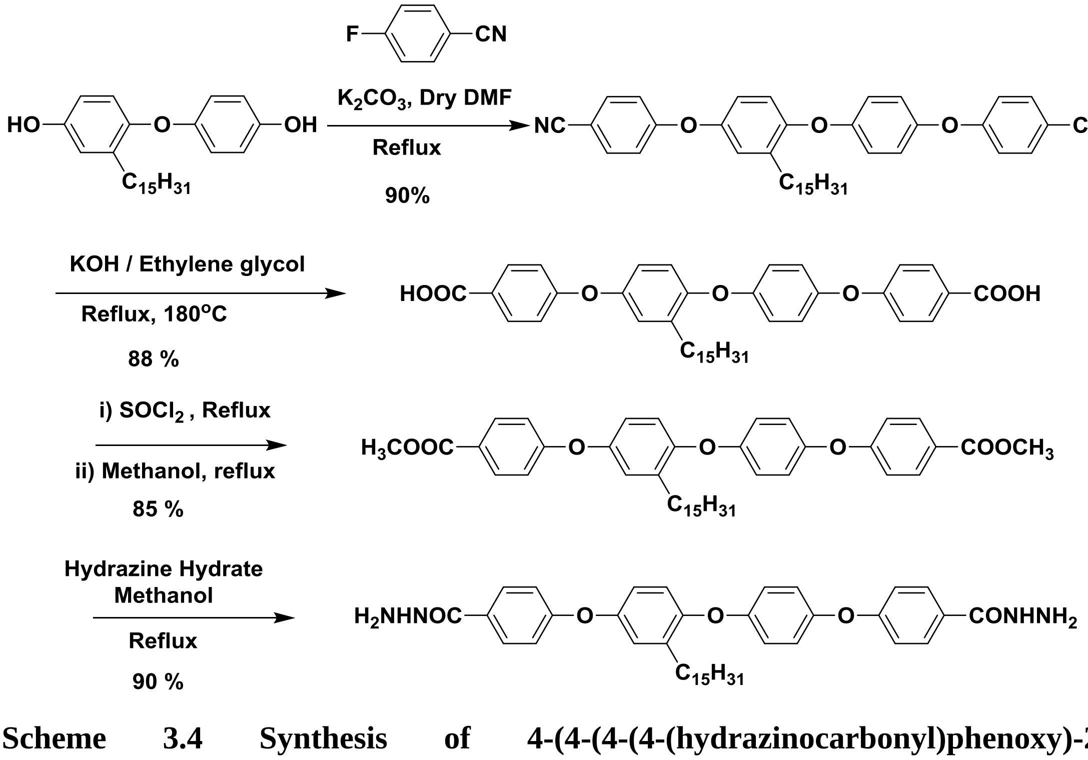


Figure 3.17 ^{13}C NMR spectrum (in $CDCl_3$) of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy) aniline

3.4.4 Synthesis of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy) phenoxy) benzohydrazide

Scheme 3.4 depicts route followed for synthesis of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide starting from 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP).



Scheme 3.4 Synthesis of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide

4-(4-(4-(4-(Hydrazinocarbonyl) phenoxy)-2- pentadecyl phenoxy) phenoxy) benzohydrazide was synthesized from HPPDP in four steps. 4-(4-(4-(4-Cyanophenoxy)-2- pentadecylphenoxy) phenoxy) benzonitrile was synthesized by nucleophilic fluoro displacement of 4-fluorobenzonitrile with HPPDP. In the reaction, dipotassium salt of HPPDP was prepared *in situ* by reaction of HPPDP with K_2CO_3 in refluxing DMF and it was refluxed with p-fluorobenzonitrile.[23, 24] The intermediate 4-(4-(4-(4-cyanophenoxy)-2- pentadecylphenoxy) phenoxy) benzonitrile was then converted into 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid by alkaline hydrolysis using potassium hydroxide and ethylene glycol as a solvent. The diacid was treated with thionyl chloride to obtain diacid chloride which was not isolated but directly transformed into diester by reaction with methanol. The diester viz. methyl 4-(4-(4-(4-(methoxycarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzoate was purified by column chromatography. The diester was converted into 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide by hydrazinolysis with hydrazine hydrate (99%) in methanol.[16, 25]

^{1}H NMR spectrum of 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile is presented in **Figure 3.18.**

In the aromatic region, protons *ortho* to –CN group exhibited two doublets at 7.60 and 7.61 δ ppm. This could be attributed to non-symmetry in the structure. The rest of the aromatic protons appeared as multiplet over the range 6.88- 7.03 δ ppm. In aliphatic region triplet at 2.62 δ ppm corresponds to benzylic –CH_2 of pentadecyl group, the methylene protons β to the aromatic ring exhibited a multiplet in the range 1.45-1.62 δ ppm and multiplet in the range 1.21-1.28 δ ppm could be assigned to the remaining methylene protons of the pentadecyl chain. The terminal methyl group protons of pentadecyl chain exhibited a triplet at 0.87 δ ppm

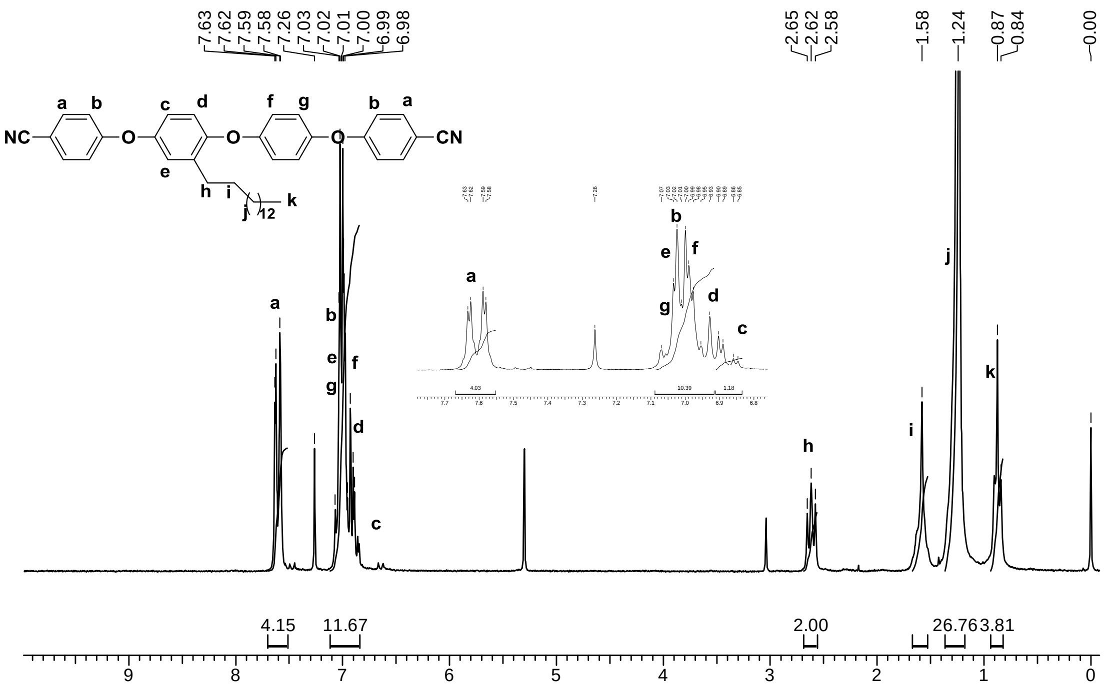


Figure 3.18 ^{1}H NMR spectrum (in CDCl$_3$) of 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile

^{13}C NMR spectrum of 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile along with assignments is reproduced in **Figure 3.19.**

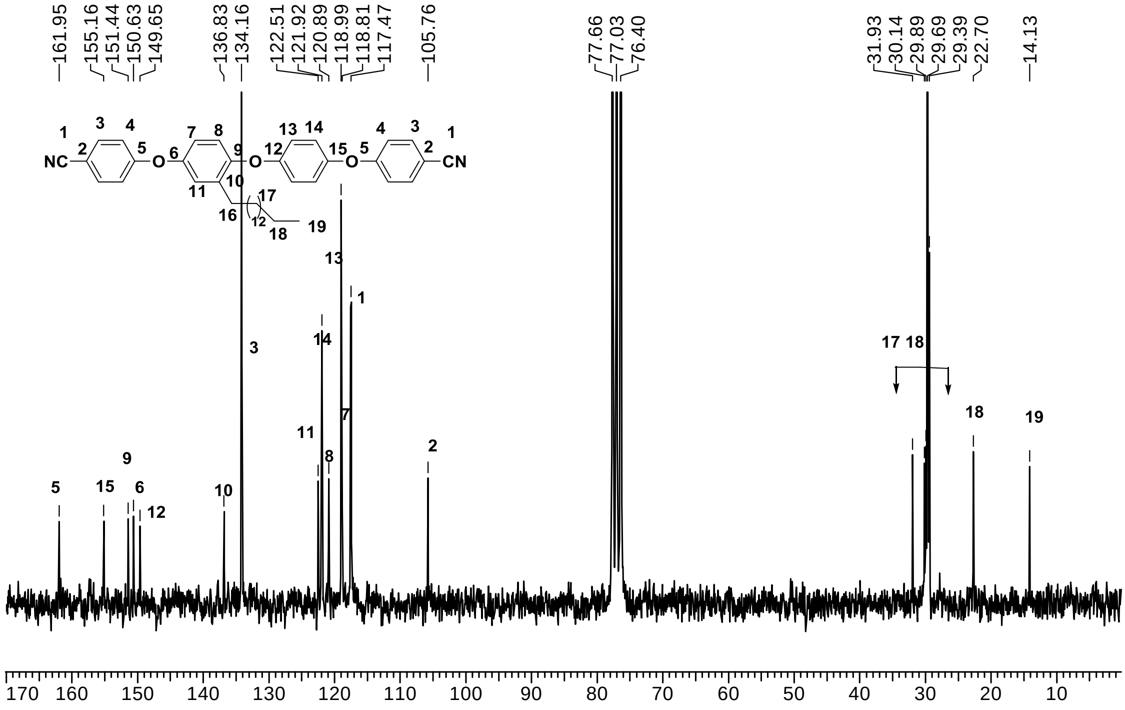


Figure 3.19 ^{13}C NMR spectrum (in CDCl$_3$) of 4-(4-(4-(4-cyanophenoxy)-2-pentadecylphenoxy)phenoxy)benzonitrile

^{1}H NMR spectrum of 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid along with assignments is presented in **Figure 3.20.** The four aromatic protons, *ortho* to carboxylic acid group exhibited two doublets at 8.07 and 8.08 δ ppm while rest of aromatic protons exhibited multiplet over the range 6.93- 7.04 δ ppm. The protons of benzylic –CH$_2$ of pentadecyl chain appeared as a triplet at 2.62 δ ppm and methylene protons β to the aromatic ring appeared as multiplet in the range 1.56-1.64 δ ppm. The remaining methylene protons of the pentadecyl chain exhibited a multiplet in the range 1.21-1.28 δ ppm and terminal methyl group protons exhibited a triplet at 0.87 δ ppm.

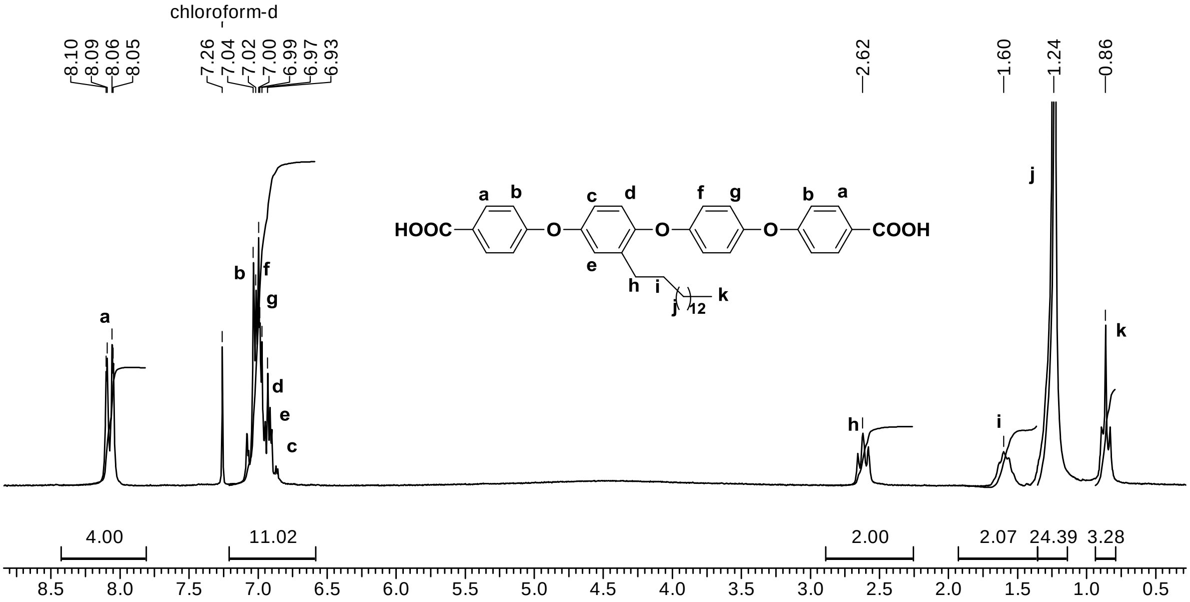


Figure 3.20 ^{1}H NMR spectrum (in CDCl$_3$) of 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid

^{13}C NMR spectrum of 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy) benzoic acid along with assignments is represented in **Figure 3.21.**

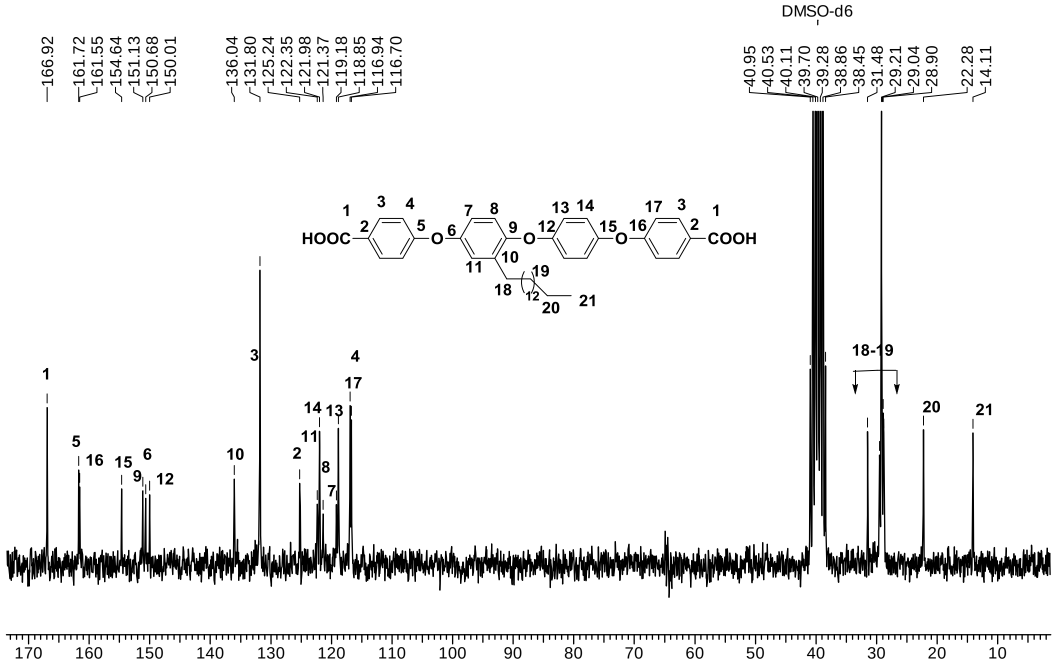


Figure 3.21 ^{13}C NMR spectrum (in DMSO-d$_6$) of 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid

^{1}H NMR spectrum of 4-(4-(4-(4-(methoxycarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzoate is represented in **Figure 3.22**.

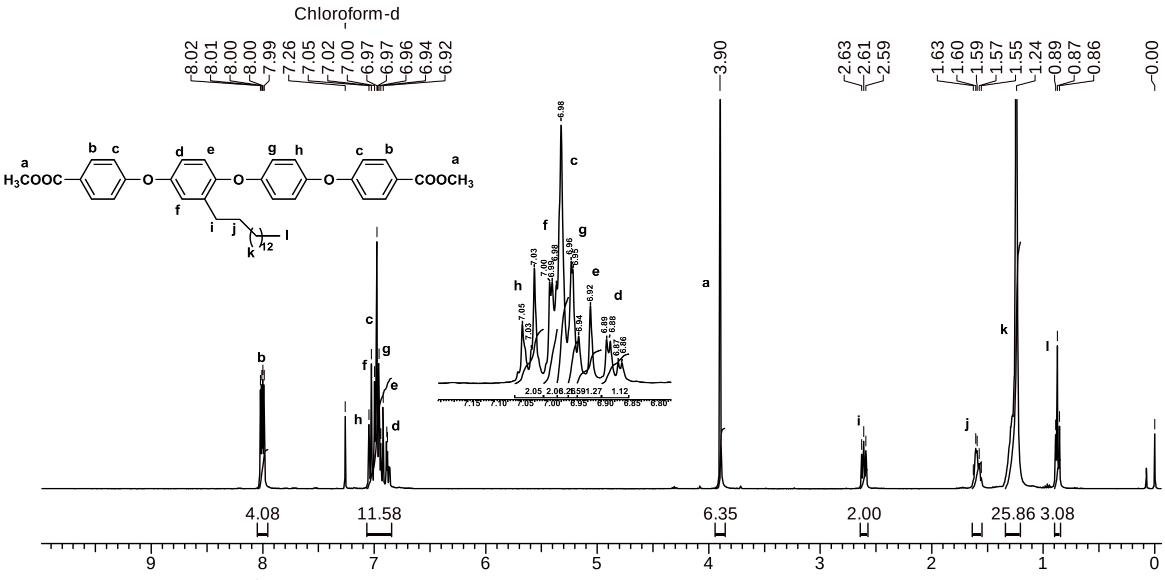


Figure 3.22 ^{1}H NMR spectrum (in CDCl$_3$) of 4-(4-(4-(4-(methoxycarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzoate

The two doublets at 8.0 and 8.01 δ ppm are attributed to protons *ortho* to ester group and remaining aromatic protons appeared as a multiplet in the region 6.92-7.05 δ ppm. The methyl group protons of ester function exhibited a singlet at 3.90 δ ppm. The aliphatic protons of benzylic –CH_2, -CH_2 β to aromatic ring and remaining methylene group protons appeared as a triplet at 2.61, multiplet in region 1.55-1.63

and 1.20-1.28 δ ppm, respectively. The terminal –CH_3 group showed a triplet 0.87 δ ppm.

^{13}C NMR spectrum of 4-(4-(4-(4-(methoxycarbonyl) phenoxy)-2-pentadecylphenoxy) phenoxy)benzoate along with assignments is shown in **Figure 3.23.** The carbonyl carbon and methyl carbon of ester group exhibited peaks at 166.58 and 51.98 δ ppm, respectively.

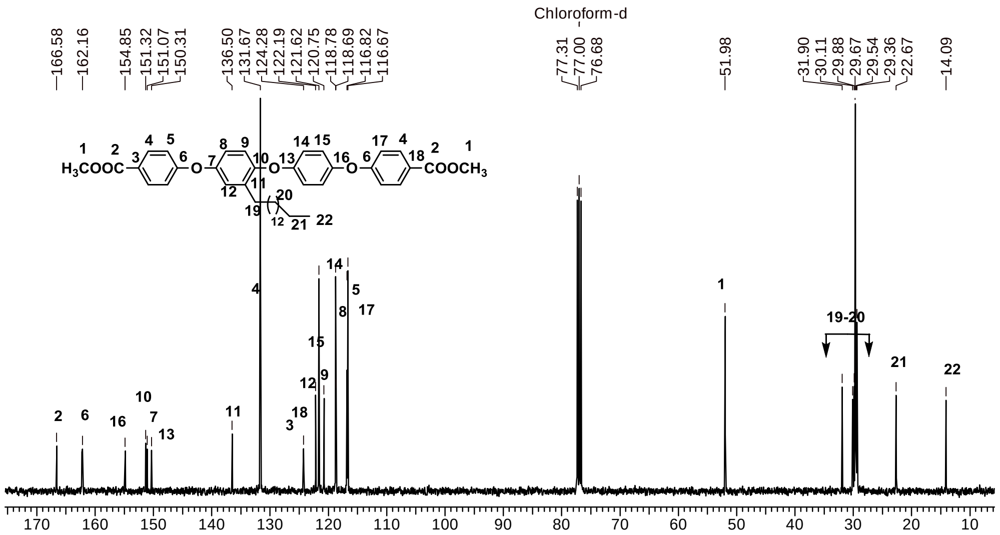


Figure 3.23 ^{13}C NMR spectrum (in $CDCl_3$) of 4-(4-(4-(4-(methoxycarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzoate

Figure 3.24 depicts FT-IR spectrum of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide. FT-IR spectrum showed absorption band at 3307 and 1602 cm^{-1} corresponding to –N-H and –C=O stretching of acyl hydrazide groups. The absorption band at 1231 cm^{-1} could be attributed to ether linkages.

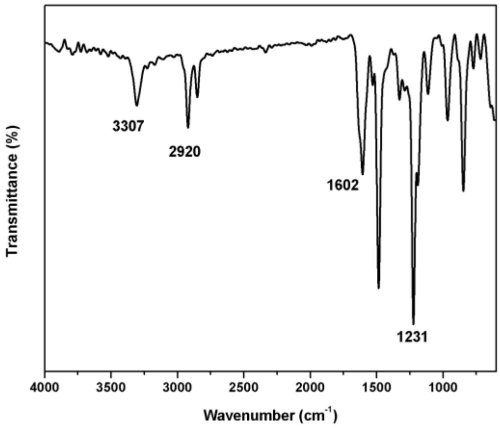


Figure 3.24 FT-IR spectrum of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide

^{1}H NMR spectrum (in DMSO-d_6) of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide is shown in **Figure 3.25.** In ^{1}H NMR spectrum, amide protons of acyl hydrazide group appeared as a broad singlet at 9.71 δ ppm while –NH_2 protons exhibited a broad signal over the range 4.0-5.0 δ ppm. The aromatic protons *ortho* to acyl hydrazide group appeared as multiplet in the range 7.81-7.85 δ ppm whereas rest of aromatic protons appeared as multiplet over the range 6.94-7.08 δ ppm. The benzylic –CH_2 exhibited a triplet at 2.53 δ ppm and methylene β to ring appeared as multiplet in the range 1.46-1.56 δ ppm. The rest of methylene and methyl group protons showed a multiplet in the range 1.13- 1.21 δ ppm and a triplet at 0.80 δ ppm, respectively.

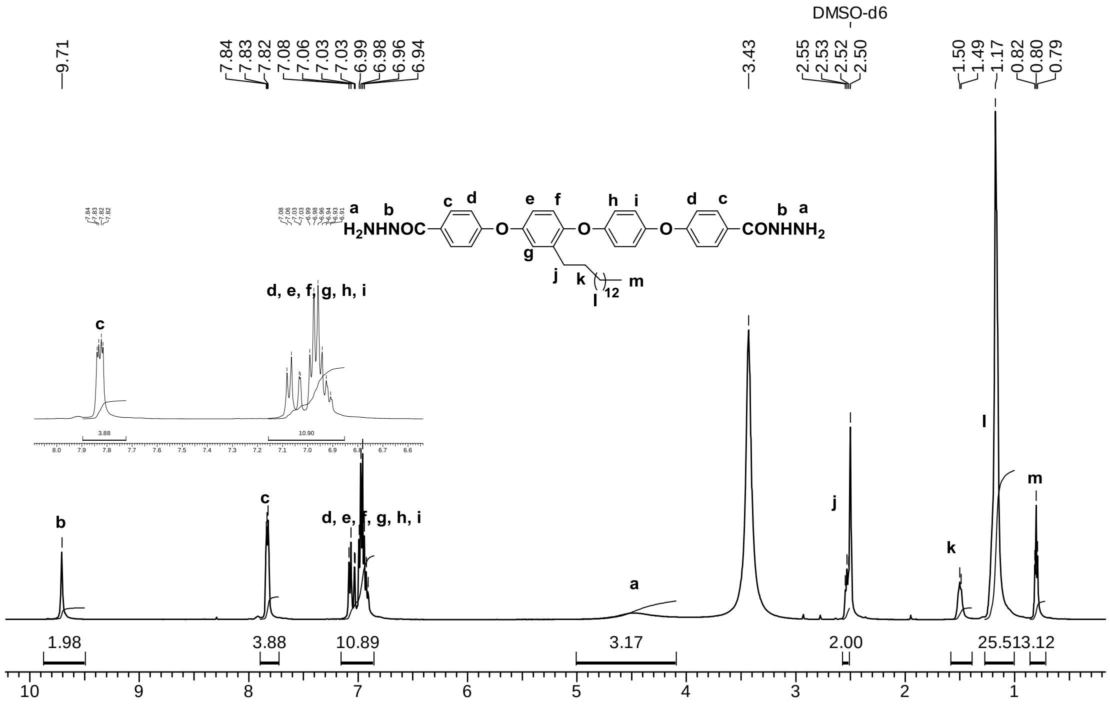


Figure 3.25 ^{1}H NMR spectrum (in DMSO-d_6) of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide

^{13}C NMR spectrum of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide along with spectral assignments is reproduced in **Figure 3.26.** The carbonyl carbon of acyl hydrazide groups showed peak at 165.57 δ ppm.

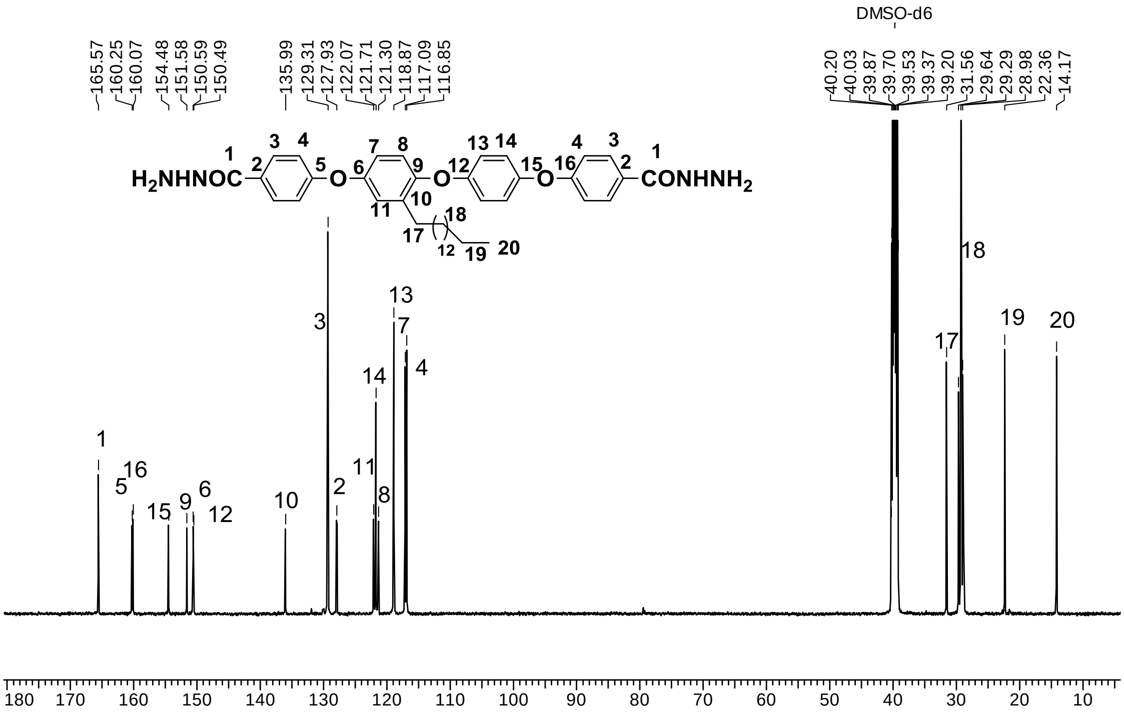
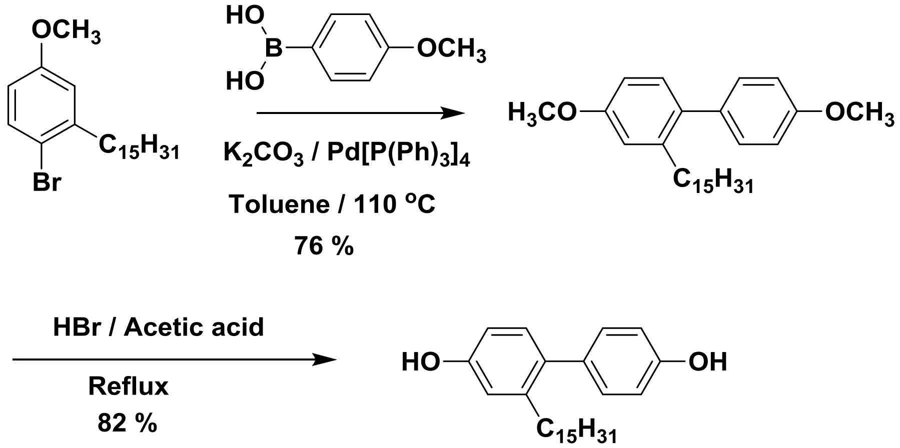


Figure 3.26 ^{13}**C NMR spectrum (in DMSO-d$_6$) of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy) benzohydrazide**

3.4.5 Synthesis of 3-pentadecyl biphenol:

Scheme 3.5 outlines the route followed for synthesis of 3-pentadecyl biphenol.



Scheme 3.5 Synthesis of 3-pentadecyl biphenol

The synthesis of 3-pentadecyl biphenol starting from 4-bromo 3-pentadecyl anisole involved two steps in which Suzuki–Miyaura coupling reaction is as the key step. Suzuki–Miyaura coupling is Pd-catalyzed reaction and one of the most efficient methods for the formation of C–C bonds.[26-28] Although several other methods (e.g. Kharash coupling, Negishi coupling, Stille coupling, Himaya coupling, Liebeskind–

Srogl coupling and Kumuda coupling) are available for C–C bonds formation, the Suzuki–Miyaura cross coupling reaction which produces biaryls has proven to be the most popular in recent times.[29] 4-Bromo 3-pentadecyl anisole was treated with 4-methoxy boronic acid and potassium carbonate in presence of catalytic amount of tetrakis(triphenylphosphine)palladium and toluene as a solvent. The deprotection of dimethoxy compound was carried out by HBr in acetic acid.[20, 30] The obtained 3-pentadecyl biphenol was purified using column chromatography and characterized by IR, ^{1}H NMR and ^{13}C NMR.

^{1}H NMR spectrum of 4, 4'-dimethoxy-2-pentadecyl-1,1'-biphenyl is represented in **Figure 3.27.** In the aromatic region, three protons *meta* to methoxy group appeared as a multiplet in range 7.05-7.16 δ ppm while four protons *ortho* to methoxy group appeared as a multiplet in the range 6.91-6.71 δ ppm. The protons of methoxy group exhibited two separate singlets at 3.80 and 3.81 δ ppm, it could be attributed to the non-symmetry in the structure. The protons of benzylic $–CH_2$ of pentadecyl chain exhibited a triplet at 2.50 δ ppm while protons of $–CH_2$ which is β to the aromatic ring appeared as multiplet in region 1.39-1.46 δ ppm. The other $–CH_2$ protons of the pentadecyl chain showed a multiplet in the range 1.13-1.24 δ ppm and terminal $–CH_3$ group protons appeared as a triplet at 0.84 δ ppm.

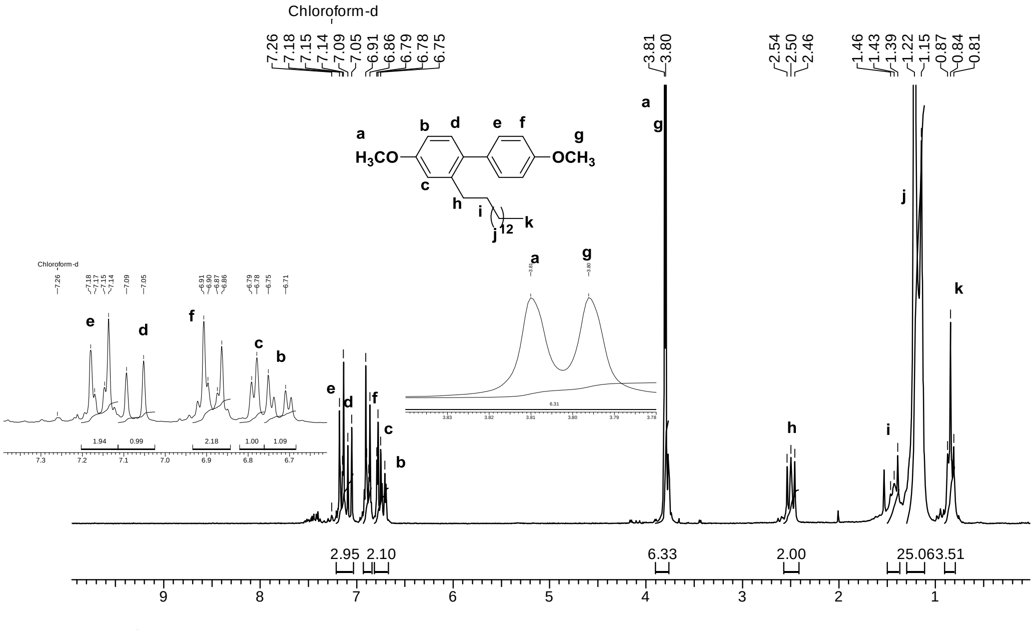


Figure 3.27 ^{1}H NMR spectrum (in $CDCl_3$) of 4, 4'-dimethoxy-2-pentadecyl-1,1'-biphenyl

^{13}C NMR spectrum of 4, 4'-dimethoxy-2-pentadecyl-1,1'-biphenyl along with assignments is reproduced in **Figure 3.28.** The assignments were also confirmed from DEPT spectrum.

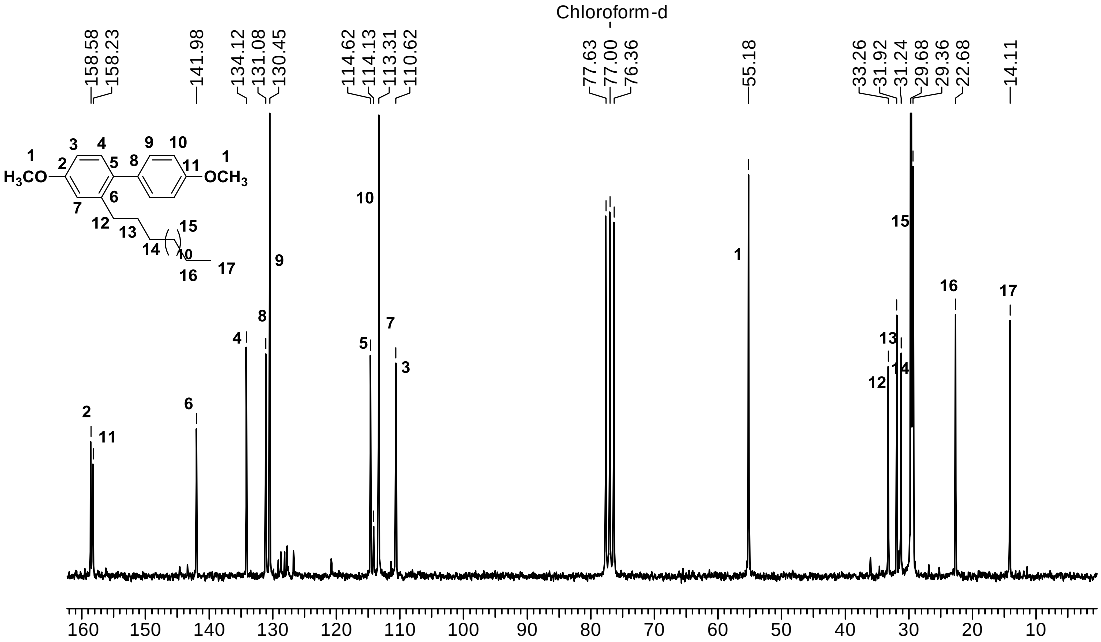


Figure 3.28 ^{13}C NMR spectrum (in CDCl$_3$) of 4, 4'-dimethoxy-2-pentadecyl-1,1'-biphenyl

FT-IR spectrum of 3-pentadecyl biphenol is shown in **Figure 3.29.** The broad absorption peak at 3281 cm^{-1} is due to -O-H bond stretching of the –OH group.

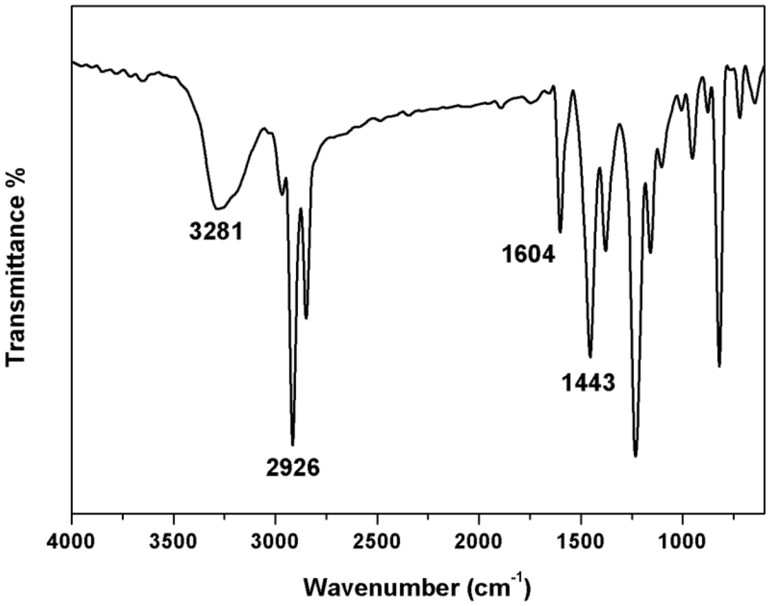


Figure 3.29 FT-IR spectrum of 3-pentadecyl biphenol

^{1}H NMR spectrum of 3-pentadecyl biphenol is depicted in **Figure 3.30**. The protons *meta* to –OH of aromatic ring without pentadecyl chain exhibited a doublet of triplet at 7.13 δ ppm while protons *ortho* to -OH of aromatic ring without pentadecyl chain exhibited doublet of triplet at 6.84 δ ppm. The doublets at 7.04 and 6.74 δ ppm are due to the protons *meta* and *ortho to* pentadecyl chain, respectively. The protons *para* to pentadecyl chain appeared as doublet of doublet at 6.67 δ ppm. The broad peak at 4.73 δ ppm is due to the phenolic hydroxy protons. The triplet at 2.50 δ ppm is assigned to benzylic $–CH_2$ of pentadecyl group, the methylene protons β to the aromatic ring appeared as a multiplet in the range 1.44-1.48 δ ppm and multiplet in the range 1.17-1.28 δ ppm could be assigned to the remaining $–CH_2$ protons of the pentadecyl chain. The terminal $–CH_3$ protons of pentadecyl chain showed a triplet at 0.88 δ ppm.

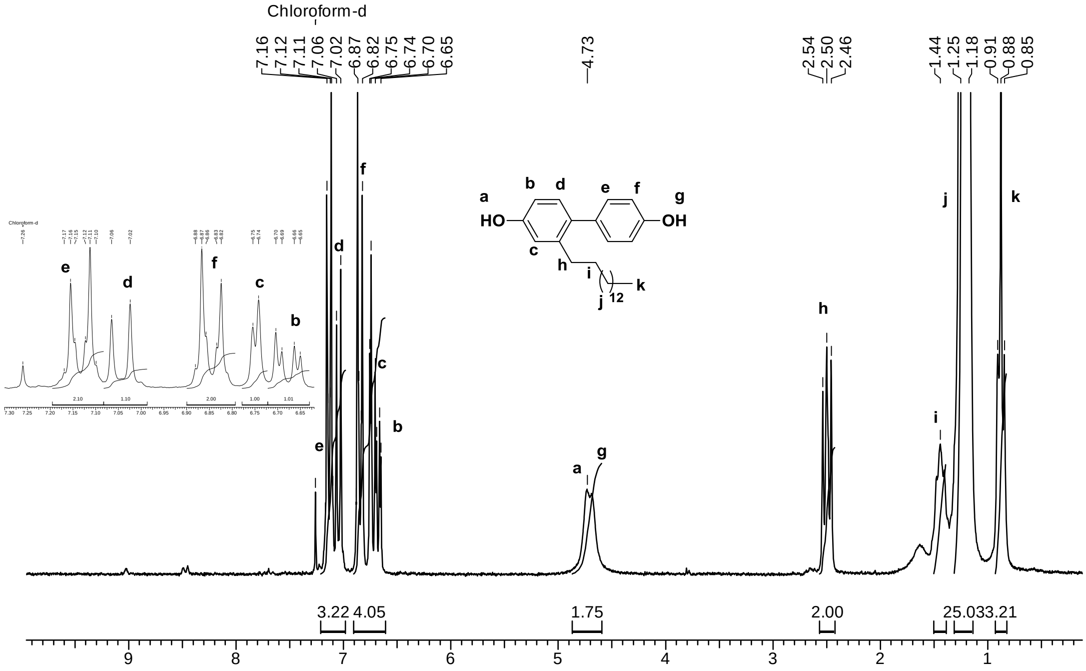


Figure 3.30 ^{1}H NMR spectrum (in $CDCl_3$) of 3-pentadecyl biphenol

^{13}C NMR spectrum of 3-pentadecyl biphenol along with assignments is represented in **Figure 3.31.** The assignments were also confirmed from DEPT spectrum.

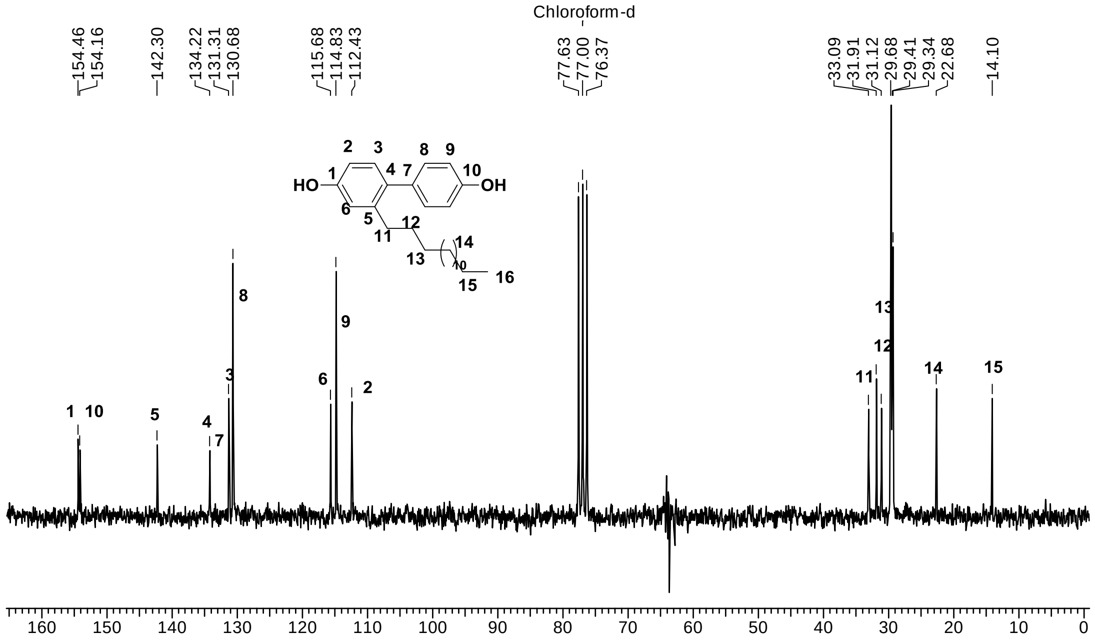
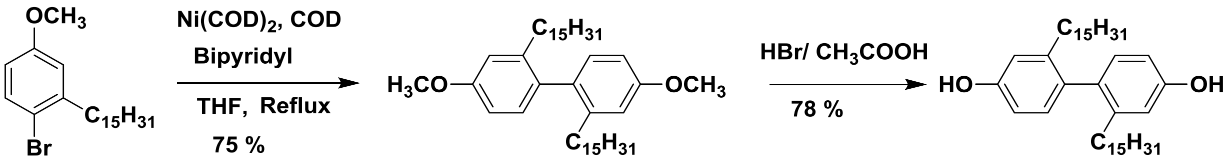


Figure 3.31 ^{13}C NMR spectrum (in $CDCl_3$) of 3-pentadecyl biphenol

3.4.6 Synthesis of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

A new fully bio-based biphenol viz., 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol was synthesized starting from 4-bromo-3-pentadecyl anisole following the route shown in **Scheme 3.6.**



Scheme 3.6 Synthesis of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

4,4'-Dimethoxy-2,2’-dipentadecyl-1,1'-biphenyl was synthesized by homocoupling of 4-bromo-3-pentadecyl anisole. The coupling was carried out in the presence of bis(1,5-cyclooctadiene)nickel [$Ni(COD)_2$], 1,5- cyclooctadiene (COD) and bipyridine in toluene. The reaction is known as Yamamoto coupling[29, 31] which is a carbon-carbon bond forming reaction of aryl halides *via* mediation of a transition metal catalyst, bis(cyclooctadiene)nickel(0). The product formed was purified by column chromatography.

^{1}H NMR spectrum of 4, 4'-dimethoxy-2,2’-dipentadecyl-1,1'-biphenyl is represented in **Figure 3.32.** The protons *meta* to methoxy group exhibited a doublet at 6.99 δ ppm, protons *ortho* to pentadecyl chain appeared as doublet at 6.81 δ ppm and protons *para* to pentadecyl chain appeared as doublet of doublet at 6.73. The protons of methoxy group appeared as a singlet at 3.84 δ ppm. The protons of benzylic $–CH_2$

group appeared as a multiplet in the region 2.18-2.42 δ ppm. The multiplicity may be because of different orientation of aryl rings. The $–CH_2$ group *β* to aromatic ring appeared as a multiplet in region 1.37-1.44 δ ppm. The remaining methylene group protons exhibited a multiplet over the range 1.14–1.26 δ ppm. The terminal $–CH_3$ group appeared as a triplet at 0.87 δ ppm.

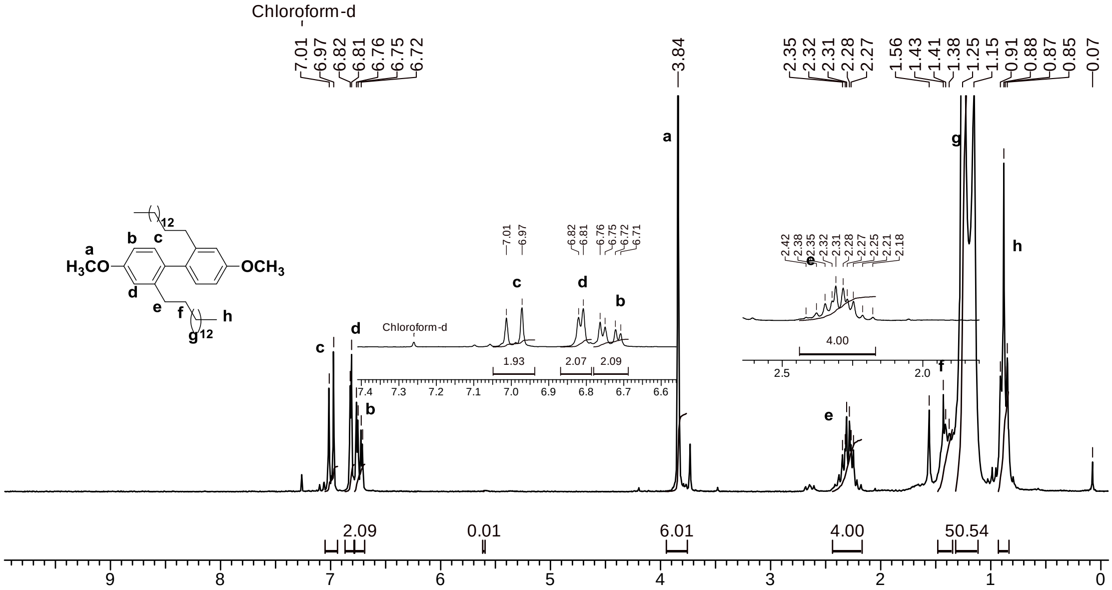


Figure 3.32 ^{1}H NMR spectrum (in $CDCl_3$) of 4,4'-dimethoxy-2,2'-dipentadecyl-1,1'-biphenyl

^{13}C NMR spectrum of 4,4'-dimethoxy-2,2'-dipentadecyl-1,1'-biphenyl along with assignments is reproduced in **Figure 3.33.**

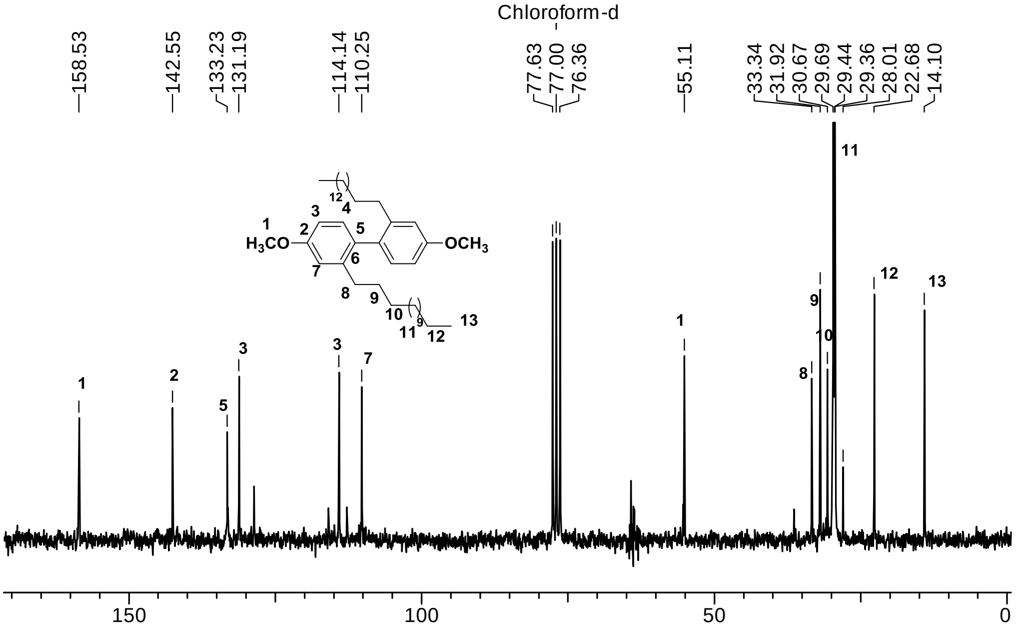


Figure 3.33 ^{13}C NMR spectrum (in $CDCl_3$) of 4,4'-dimethoxy-2,2'-dipentadecyl-1,1'-biphenyl

In next step, demethylation of 4,4'-dimethoxy-2,2'-dipentadecyl-1,1'-biphenyl using 48% hydrobromic acid and glacial acetic acid afforded the desired biphenol, 2, 2'-dipentadecyl-[1,1'-biphenyl]-4,4'-diol.[20, 30]

FT-IR spectrum of 2, 2'-dipentadecyl-[1,1'-biphenyl]-4,4'-diol is shown in **Figure 3.34.** Phenolic hydroxyl group band was observed at 3273 cm^{-1}.

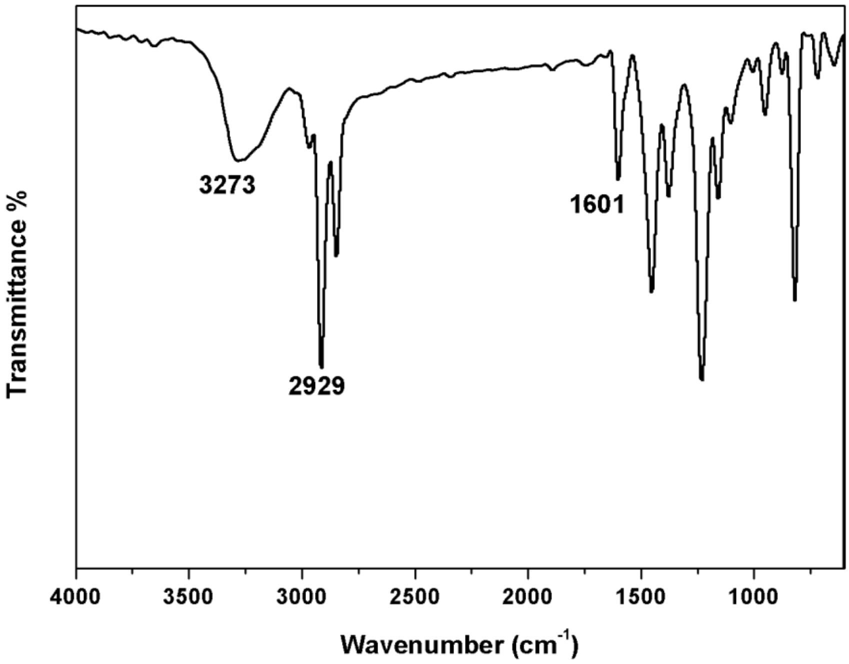


Figure 3.34 FT-IR spectrum of 2, 2'-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

^1H NMR spectrum of 2, 2'-dipentadecyl-[1,1'-biphenyl]-4,4'-diol is shown in **Figure 3.35.** The protons *meta* to hydroxyl groups exhibited a doublet at 6.93 δ ppm, protons *ortho* to pentadecyl chain exhibited a doublet at 6.72 δ ppm and protons *para* to pentadecyl chains appeared as a doublet of doublet at 6.65 δ ppm. The phenolic hydroxyl protons showed a broad singlet at 4.70 δ ppm. The multiplet in the region 2.19-2.33 δ ppm could be assigned to benzylic $–CH_2$ group. The benzylic $–CH_2$ groups are supposed to give a triplet but the $–CH_2$ groups of appeared as multiplet due to different conformations or some another electronic non equivalence in the structure. The $-CH_2$ group β to aromatic ring exhibited a multiplet in the region 1.36-1.40 δ ppm while rest of methylene groups of the pentadecyl chain appeared as multiplet in the region 1.27-1.33 δ ppm. The terminal $–CH_3$ group showed a triplet at 0.88 δ ppm.

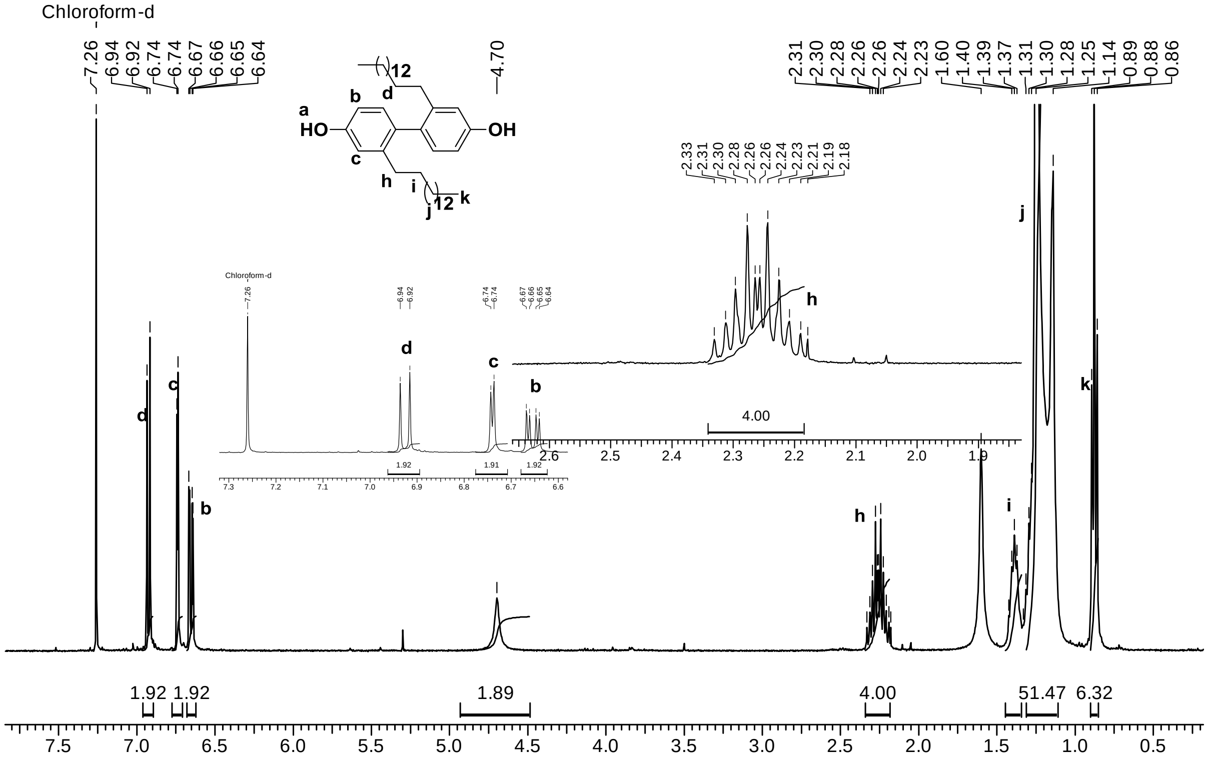


Figure 3.35 ^{1}H NMR spectrum (in CDCl$_3$) of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

^{13}C NMR spectrum of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol along with assignments of carbon atoms is shown in **Figure 3.36**

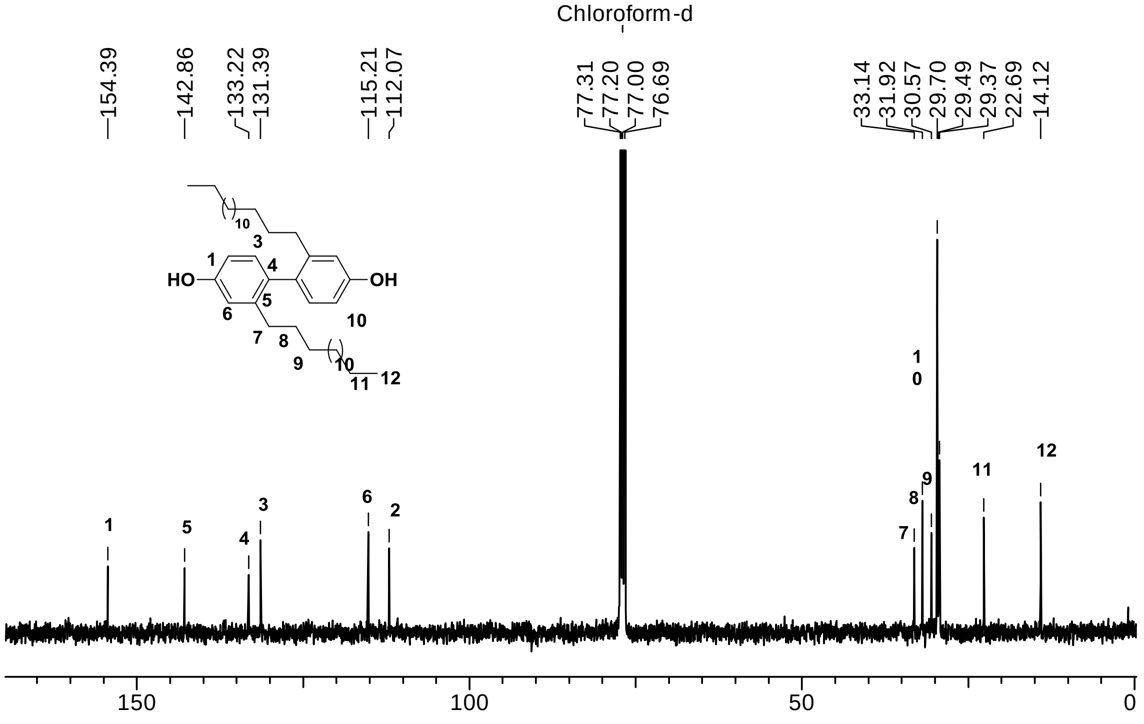
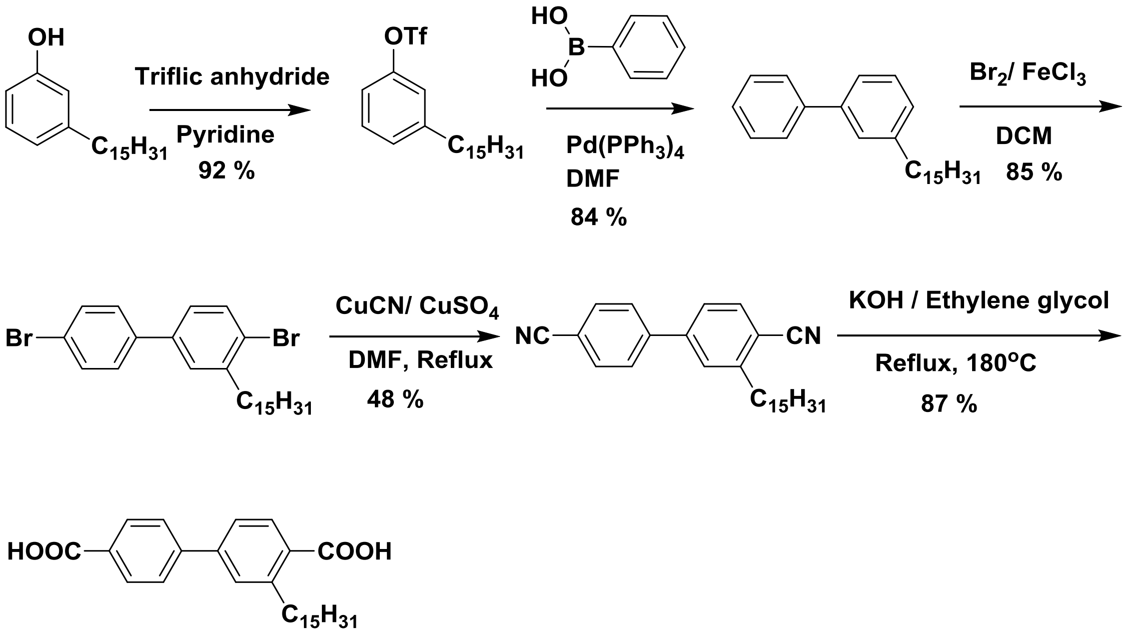


Figure 3.36 ^{13}C NMR spectrum (in CDCl$_3$) of 2, 2’-dipentadecyl-[1,1'-biphenyl]-4,4'-diol

3.4.7 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

3.4.7.1 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid

Scheme 3.7 outlines the route for synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxalic acid from 3-pentadecyl phenol.



Scheme 3.7 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid from 3-pentadecyl phenol

The synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid was carried out from 3-pentadecyl phenol using five steps. In the first step, 3-pentadecyl triflate was prepared from 3-pentadecyl phenol and trifluoromethanesulfonic anhydride in the presence of pyridine in dichloromethane as a solvent. Aryl triflates are well known as versatile intermediates for conversion of phenols into a wide range of aromatic compounds.[32, 33] The most common application of triflates is in organomatallic coupling reactions.[29] The formation of triflate was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

^{1}H NMR spectrum of 3-pentadecyl triflate is represented in **Figure 3.37**. The most downfield proton 'a' *ortho* to OTf appeared as a mutiplet in the region 7.33-7.39 δ ppm whereas proton *meta* to pentadecyl chain 'c' exhibited a doublet at 7.20 δ ppm. The multiplet in the region 7.07-7.11 could be attributed to the protons 'b' and 'd'. The benzylic methylene protons of the pentadecyl chain exhibited a triplet at 2.65 δ ppm. The protons of methylene group β to aromatic ring appeared as a multiplet in the region 1.50-1.65 δ ppm while remaining methylene protons of the pentadecyl chain appeared as mutiplet in the region 1.23-1.31 δ ppm. The terminal methyl group proton exhibited triplet at 0.89 δ ppm.

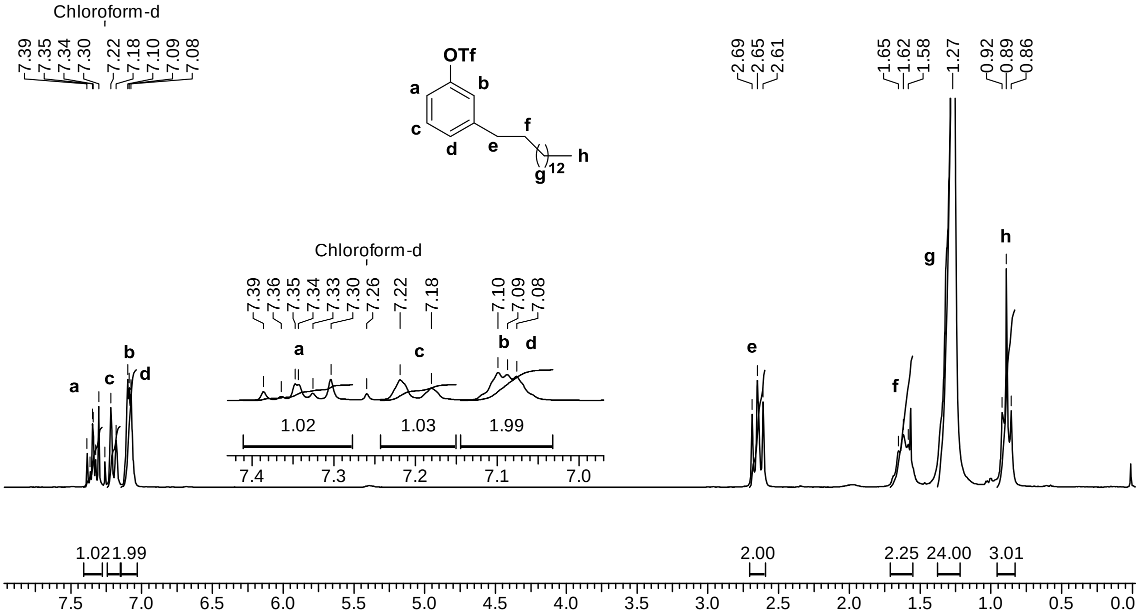


Figure 3.37 ^{1}H NMR spectrum (in $CDCl_3$) of 3-pentadecyl triflate

^{13}C NMR spectrum of 3-pentadecyl triflate along with assignments is presented in **Figure 3.38.** The assignments were also confirmed from DEPT spectrum.

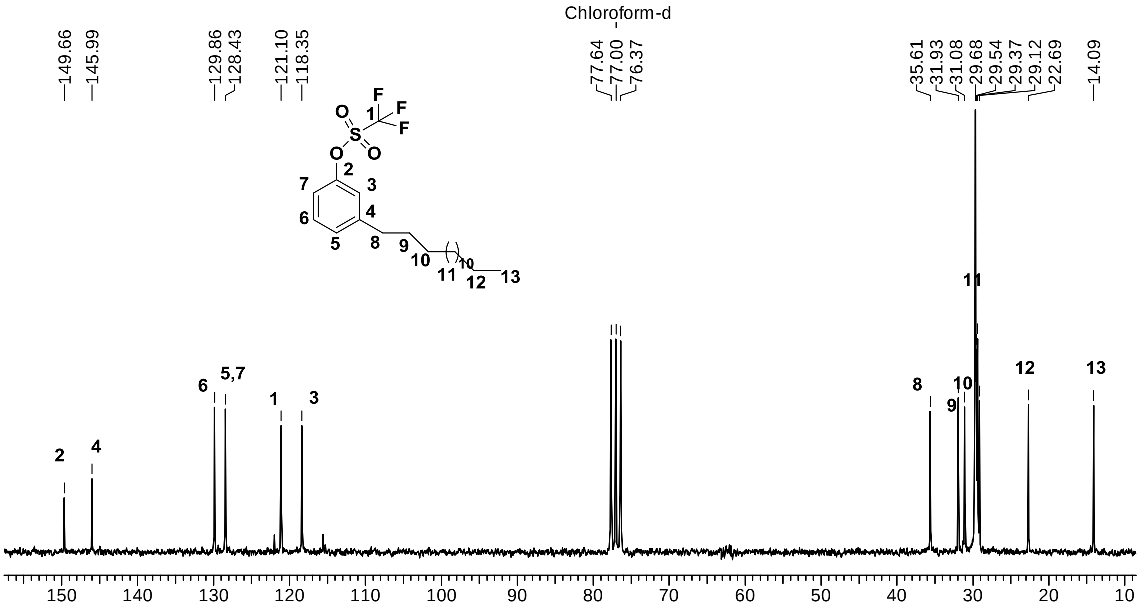


Figure 3.38 ^{13}C NMR spectrum (in $CDCl_3$) of 3-pentadecyl triflate

In the second step, 3-pentadecyl triflate was coupled with phenyl boronic acid in the presence of potassium carbonate and catalytic amount of tetrakis(triphenylphosphine)palladium using Suzuki coupling in toluene to obtain 3-pentadecyl biphenyl. 3-Pentadecyl biphenyl was purified by silica gel column chromatography and was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

^{1}H NMR spectrum of 3-pentadecyl biphenyl is reproduced in **Figure 3.39**. In ^{1}H NMR spectrum, the two doublets at 7.63 and 7.59 δ ppm could be attributed to the protons 'a' and 'f', respectively whereas the doublet at 7.19 δ ppm could be attributed to the proton 'e'. The rest of the aromatic protons (b, c, d, g) appeared as a mutiplet in the region 7.33-7.50 δ ppm. The benzylic $-CH_2$ group exhibited triplet at 2.69 δ ppm and $-CH_2$ group β to aromatic ring exhibited a mutiplet in the range 1.62-1.75 δ ppm. The remaining methylene protons and methyl group of the pentadecyl chain appeared as a multiplet in the range 1.21-1.35 δ ppm and triplet at 0.90, respectively.

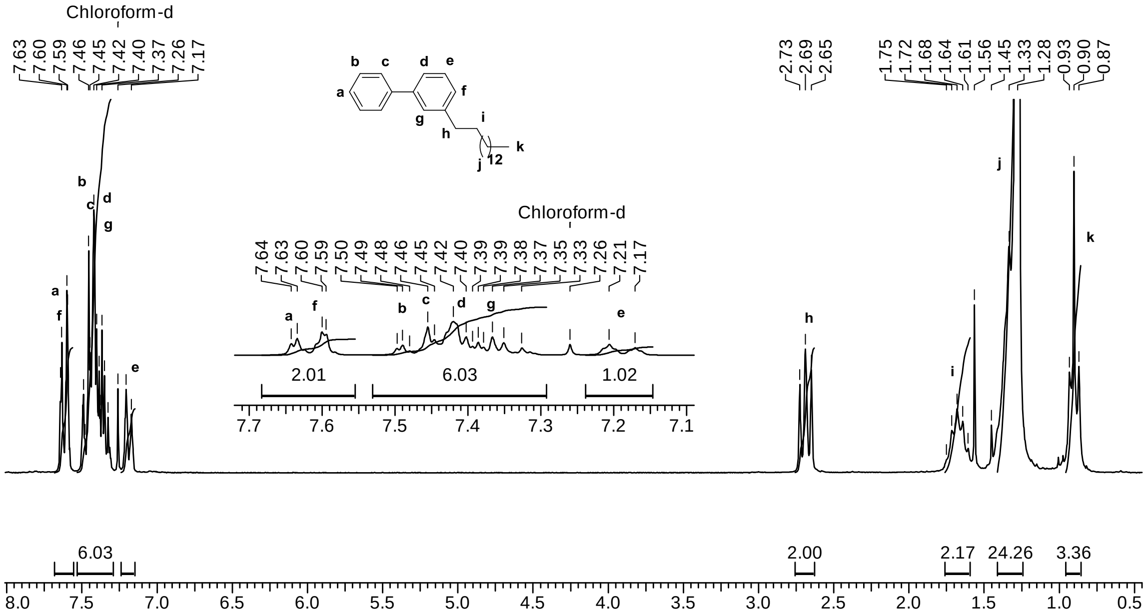


Figure 3.39 ^{1}H NMR spectrum (in $CDCl_3$) of 3-pentadecyl biphenyl

^{13}C NMR spectrum of 3-pentadecyl biphenyl along with assignments is shown in **Figure 3.40** and the assignments are in good agreement with the proposed structure.

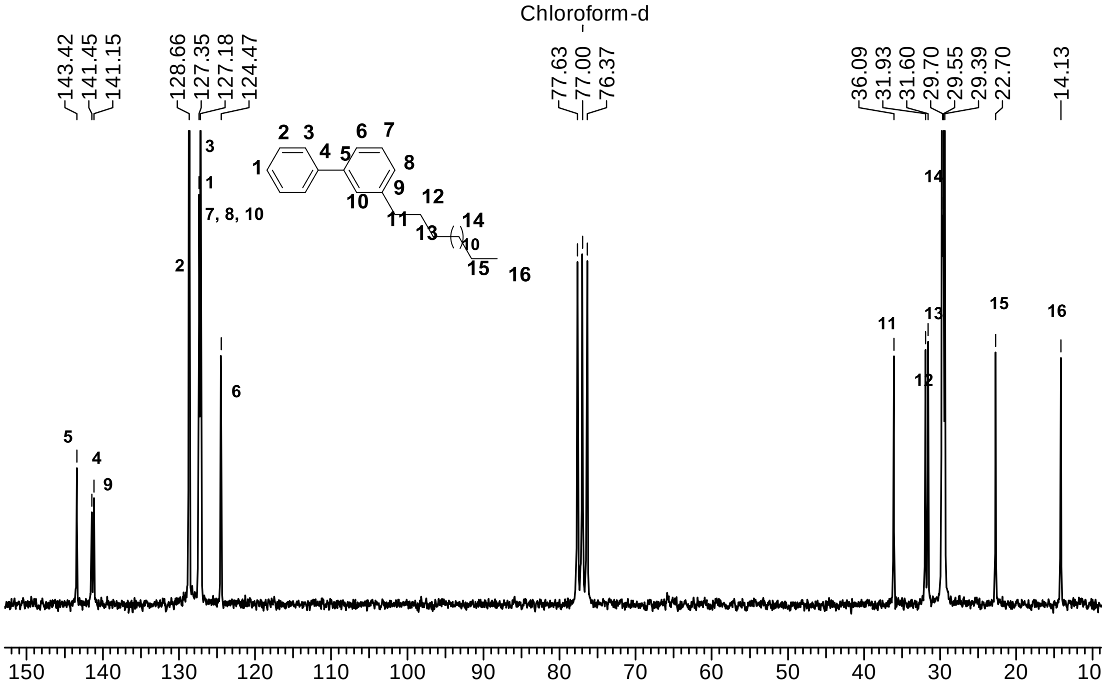


Figure 3.40 ^{13}C NMR spectrum (in CDCl$_3$) of 3-pentadecyl biphenyl

3-Pentadecyl biphenyl was selectively brominated at *para-para'* positions using bromine as brominating agent in the presence of ferric chloride and iodine as catalysts in dichloromethane.[34] The number of bromination procedures[35-37] with different brominating agents and catalyst are available but above mentioned method was found to be satisfactory for the bromination of 3-pentadecyl biphenyl with good selectivity. The product 4,4'-dibromo 3-pentadecyl biphenyl was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. In ^{1}H NMR spectrum of 4,4'-dibromo 3-pentadecyl biphenyl (**Figure 3.41**), three protons *ortho* to –Br exhibited multiplet in region 7.54-7.60 δ ppm. The multiplet in the range 7.37-7.44 δ ppm could be attributed to the protons *meta* to –Br (except 'e'). The most upfield aromatic proton 'e' exhibited a doublet of doublet at 7.21 δ ppm. The benzylic methylene protons of pentadecyl chain exhibited triplet at 2.77 δ ppm and protons of methylene group β to aromatic ring exhibited a mutiplet in the range 1.59-1.70 δ ppm. The rest of methylene protons appeared as a multiplet in the range 1.21-1.35 δ ppm. The terminal methyl group of the pentadecyl chain exhibited triplet at 0.90 δ ppm.

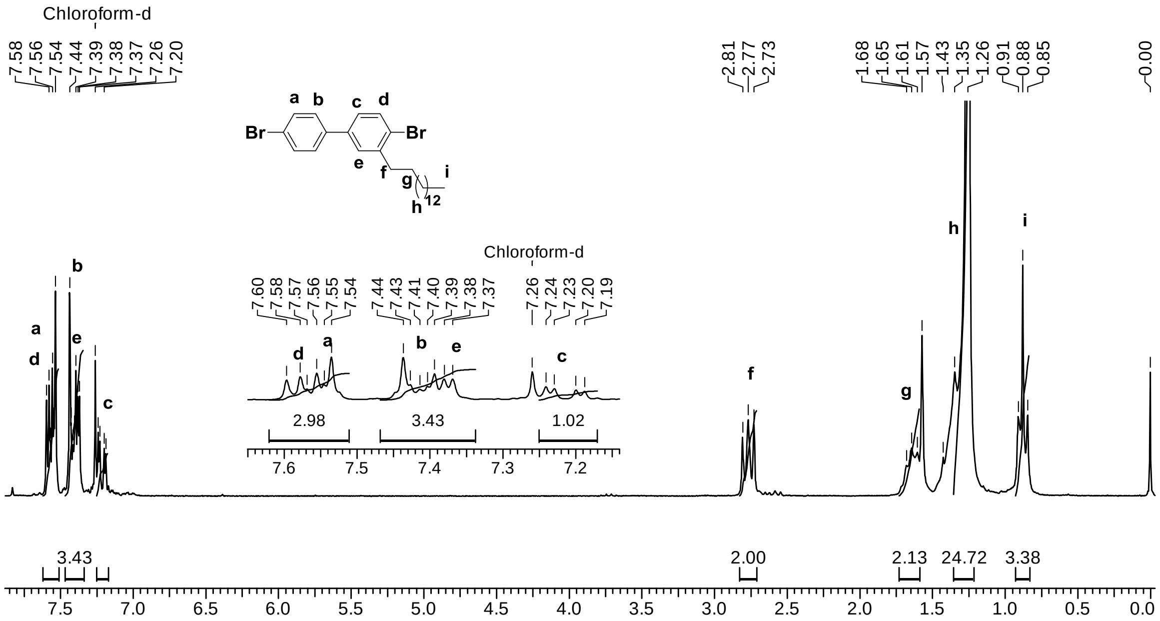


Figure 3.41 ^{1}H NMR spectrum (in CDCl$_3$) of 4,4'-dibromo 3-pentadecyl biphenyl

^{13}C NMR spectrum of 4,4'-dibromo 3-pentadecyl biphenyl along with assignments is shown in **Figure 3.42.**

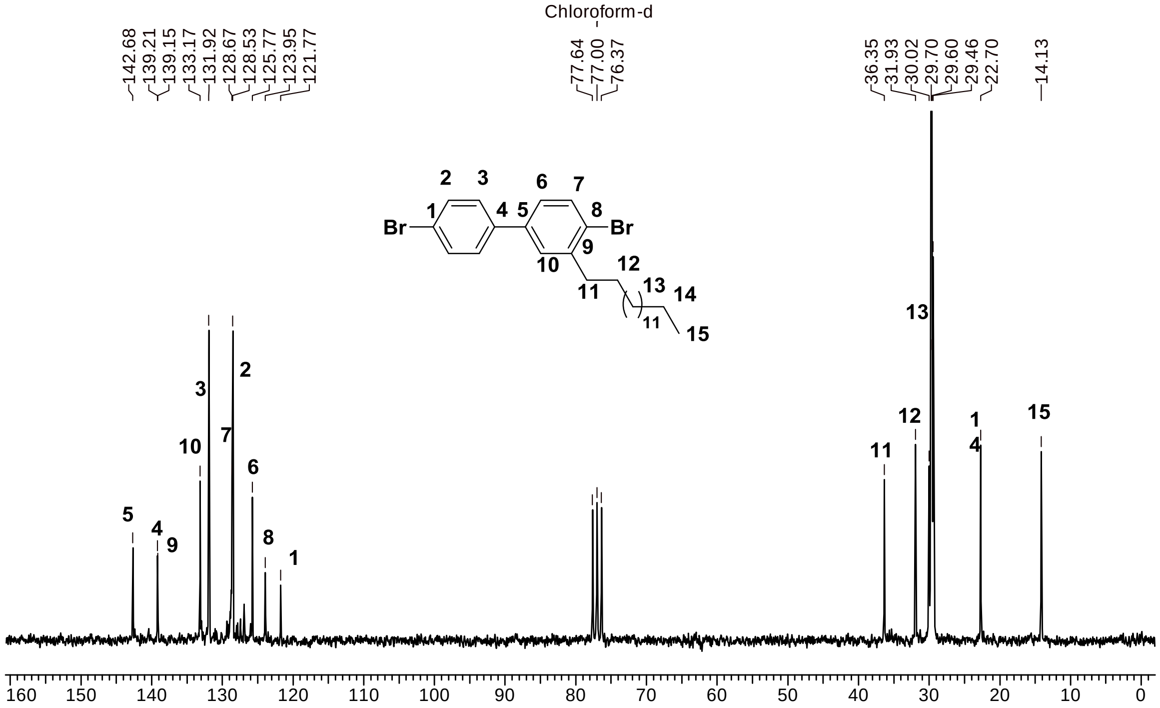


Figure 3.42 ^{13}C NMR spectrum (in CDCl$_3$) of 4,4'-dibromo 3-pentadecyl biphenyl

The most downfield carbons '5' and '4' appeared as two different signals, it could be attributed to non-symmetry in the structure. The carbon '5' appeared at 142.68 δ ppm whereas carbon '4' and carbon bearing pentadecyl chain exhibited two different but very close signals at and 139.21 and 139.15 δ ppm. The carbons *ortho* and *meta* to bromine of aromatic ring without pentadecyl chain appeared at 128.53 and 131.92 δ ppm, respectively. The peak at 133.15, 128.67 and 125.77 δ ppm could be assigned to carbons *ortho, meta* and *para* to pentadecyl chain, respectively. Carbons attached to bromine atom exhibited signals at 113.95 and 121.77 ppm. The carbons of pentadecyl chain appeared in the aliphatic region as shown in **Figure 3.42**.

The cyanation of 4,4'-dibromo 3-pentadecyl biphenyl was carried out using copper cyanide in the presence of copper sulfate as a catalyst in N, N-dimethyl formamide. This method of synthesis of aromatic nitriles is known as Rosenmund-von Braun reaction[38-40] and is the most practical and cost effective method as compared to the other cyanation methods.[41-50]

^{1}H NMR spectrum of 4, 4' dicyano 3-pentadecyl 1,1' biphenyl along with assignments is reproduced in **Figure 3.43.**

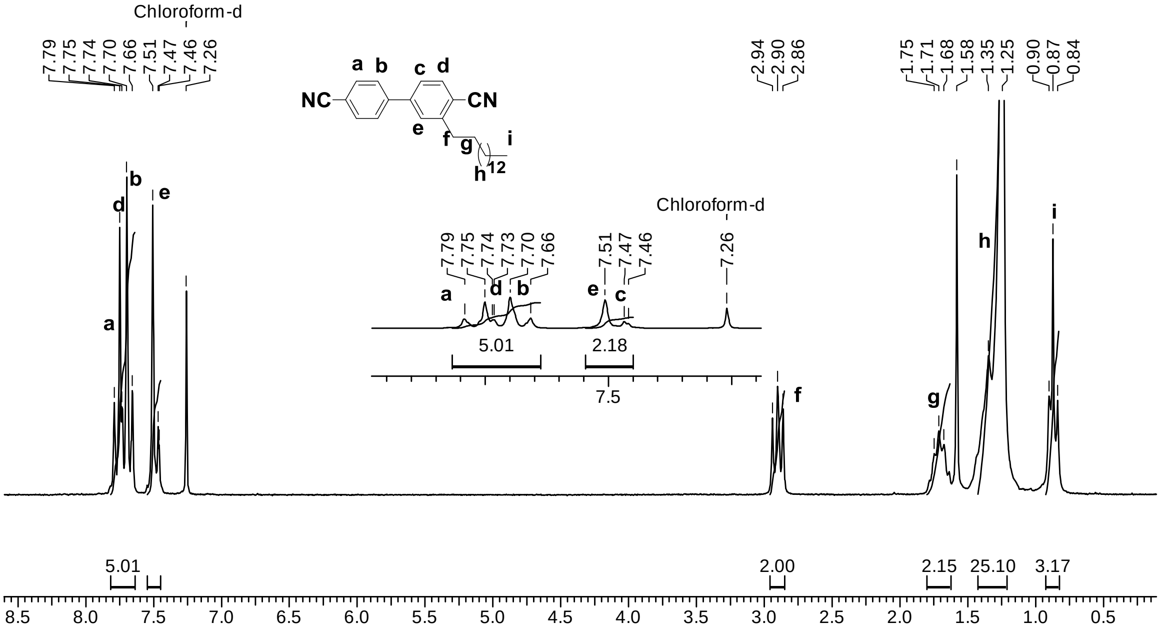


Figure 3.43 ^{1}H NMR spectrum (in CDCl$_3$) of 4, 4' dicyano 3-pentadecyl 1,1' biphenyl

The four protons of aromatic ring without pentadecyl chain and proton *ortho* to –CN of pentadecyl substituted ring appeared as a multiplet over the range 7.66-7.79 δ ppm. The protons *meta* to –CN group of aromatic ring without pentadecyl exhibited multiplet in range 6.45-6.52 δ ppm. The downfield shift in all aromatic protons as compared to precursor dibromo compound is due to electron withdrawing effect of –CN group. The benzylic protons of pentadecyl chain also get shifted to 2.90 δ ppm. The methylene protons β to aromatic ring exhibited multiplet in the range 1.66-1.76 δ ppm whereas the rest of methylene protons appeared as multiplet in the range 1.21-1.35 δ ppm. The terminal methyl group appeared as a triplet at 0.87 δ ppm.

^{13}C NMR spectrum of 4, 4’ dicyano 3-pentadecyl 1,1’ biphenyl along with assignments is shown in **Figure 3.44.** The peaks of the carbon of –CN groups appeared at 117.76 and 118.45 δ ppm which confirmed the formation of 4, 4’ dicyano 3-pentadecyl 1,1’ biphenyl.

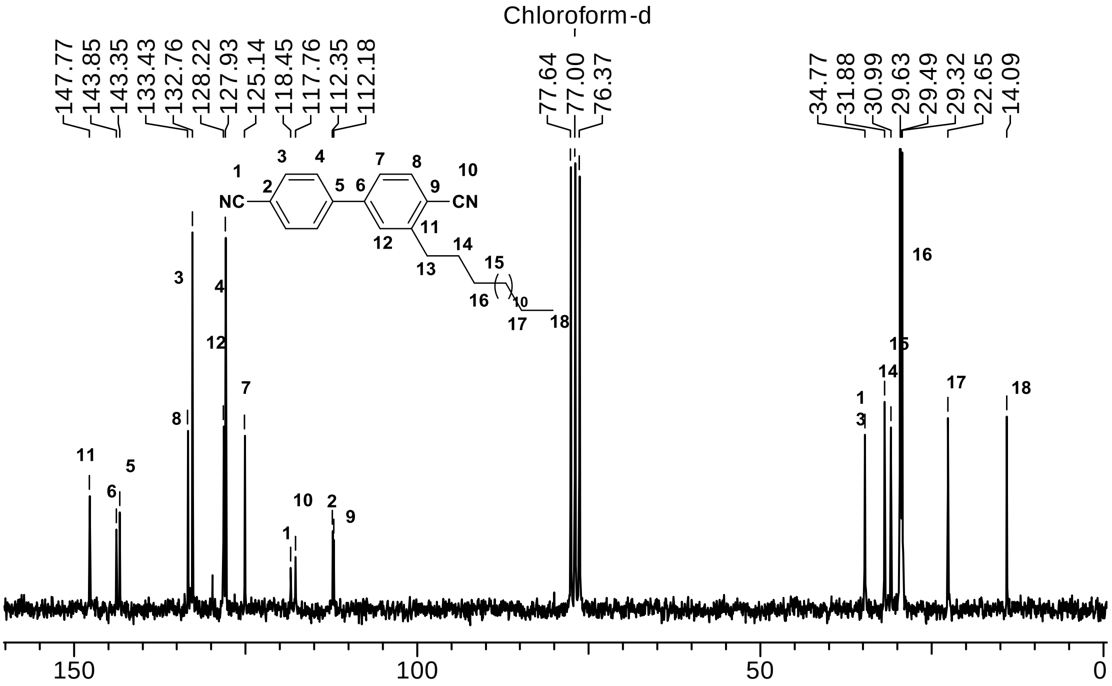


Figure 3.44 ^{13}C NMR spectrum (in CDCl$_3$) of 4, 4’ dicyano 3-pentadecyl 1,1’ biphenyl

The hydrolysis of 4, 4’ dicyano 3-pentadecyl 1,1’ biphenyl was carried out in ethylene glycol/water in the presence of potassium hydroxide to form 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid.[51, 52] The formation of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

FT-IR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid is shown in **Figure 3.45.** The broad absorption band in the region 3100-3600 cm^{-1} is a characteristic of –O-H stretching of –COOH group. The absorption bands at 1684 cm^{-1} is due to C=O stretching of carboxylic acid.

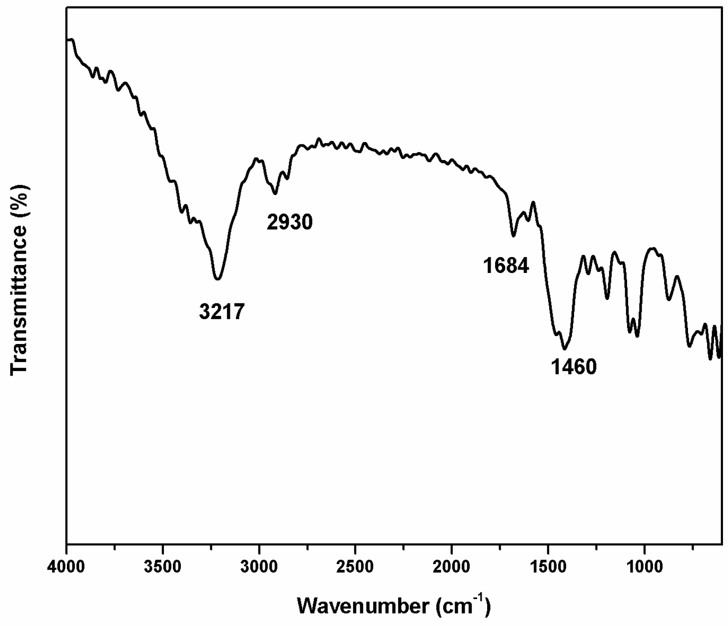


Figure 3.45 FT-IR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid

^{1}H NMR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid is depicted in **Figure 3.46.**

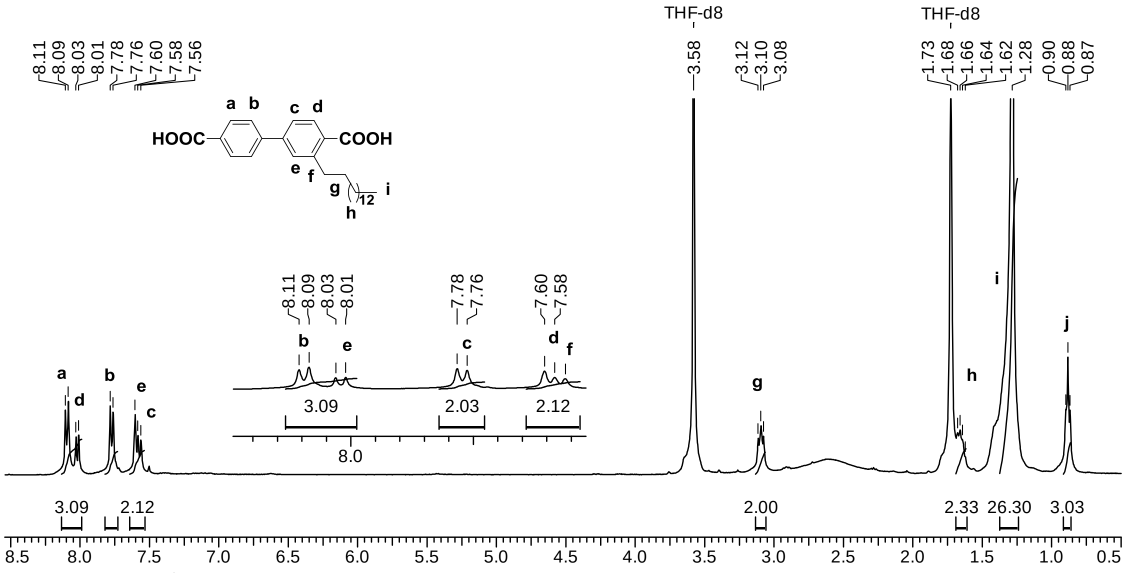


Figure 3.46 ^{1}H NMR spectrum (in THF-d_8) of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid

The protons *ortho* to carboxyl group of aromatic ring without pentadecyl chain appeared as a doublet at 8.10 δ ppm whereas proton *ortho* to carboxyl group on pentadecyl substituted aromatic ring exhibited a doublet at 8.02 δ ppm. The protons *meta* to carboxyl group of aromatic ring without pentadecyl chain exhibited a doublet at 7.77 δ ppm while that of pentadecyl substituted ring appeared as a multiplet in region 7.56-7.62 δ ppm. The benzylic methylene protons of pentadecyl chain exhibited a triplet at 3.10 δ ppm. The rest of $–CH_2$ groups exhibited a multiplet in the region 1.24-1.32 δ ppm and $–CH_3$ group showed a triplet at 0.88 δ ppm.

^{13}C NMR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid along with assignments is represented **Figure 3.47.**

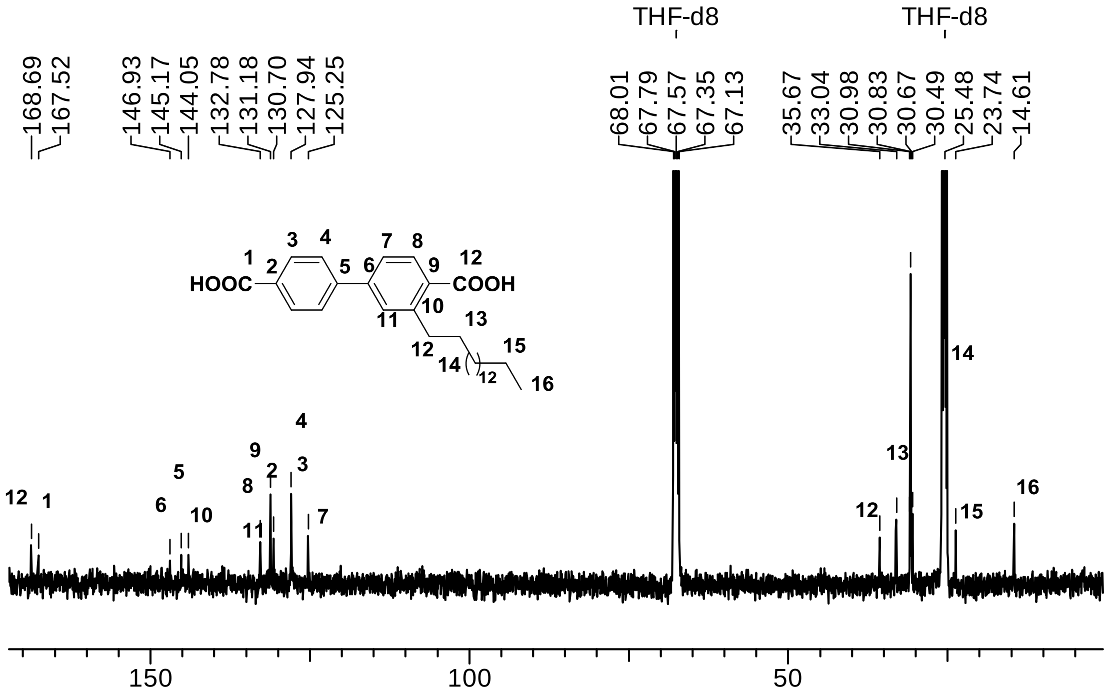
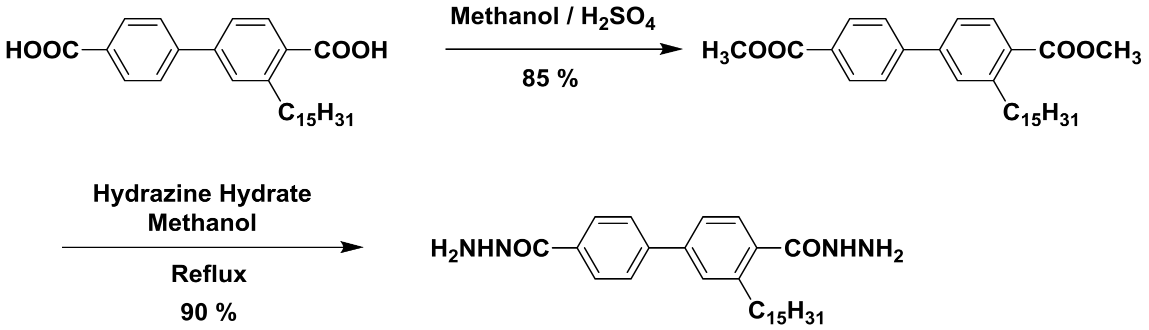


Figure 3.47 ^{13}C NMR spectrum (in THF-d_8) of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid

The carbonyl carbons of the carboxyl groups C_{12} and C_1 appeared at 168.69 and 167.52 δ ppm, respectively. The chemical shift values of other carbon atoms were in good agreement with the proposed structure of the diacid.

3.4.7.2 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

Scheme 3.8 depicts route for the synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide from 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxalic acid



Scheme 3.8 Synthesis of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide from 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxalic acid

The synthesis of dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate was carried out by esterification of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid using methanol in presence of concentrated sulfuric acid. The obtained diester was characterized by FT IR, ^{1}H NMR and ^{13}C NMR spectroscopy. FT-IR spectrum showed characteristic absorption band of ester carbonyl at 1721 cm^{-1}.

^{1}H NMR and ^{13}C NMR spectra of dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate with assignments are shown in **Figure 3.48** and **3.49**, respectively.

In ^{1}H NMR spectrum, protons *ortho* to ester carbonyl groups ‘b’ and ‘e’ appeared as doublets at 8.11 and 7.96 δ ppm, respectively. The protons *meta* to ester carbonyl of aromatic ring without pentadecyl chain ‘c’ exhibited a doublet at 7.68 δ ppm whereas protons ‘f’ and ‘d’ of pentadecyl-substituted aromatic ring exhibited a multiplet in the region at 7.46-7.50 δ ppm. The two methyl groups of ester exhibited two different singlets at 3.92 and 3.95 δ ppm which could be attributed to non-symmetrical structure. The benzylic –CH_2 appeared as a triplet at 3.02 δ ppm and rest of protons of the pentadecyl chain appeared in aliphatic region.

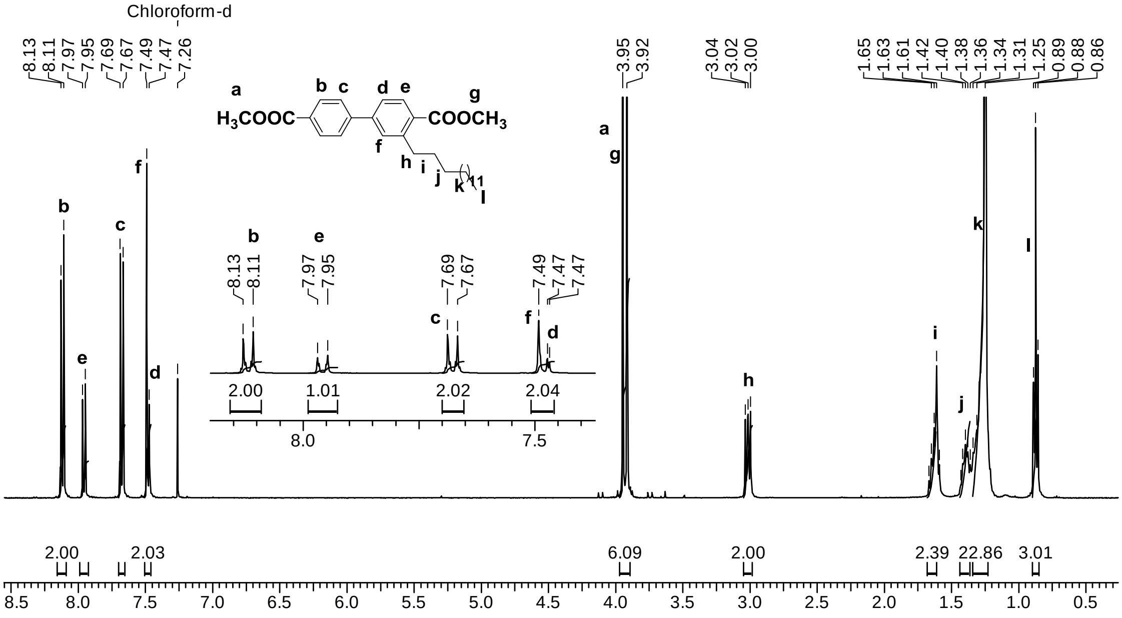


Figure 3.48 ^{1}H NMR spectrum (in $CDCl_3$) of dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate

In ^{13}C NMR spectrum, the carbonyl carbon showed two different peaks at 167.85 and 166.85 δ ppm. Similarly, methyl carbons of two ester groups exhibited two different peaks at 52.20 and 51.98 δ ppm. The assignments of other carbons are given in **Figure 3.49** and are in good agreement with proposed structure.

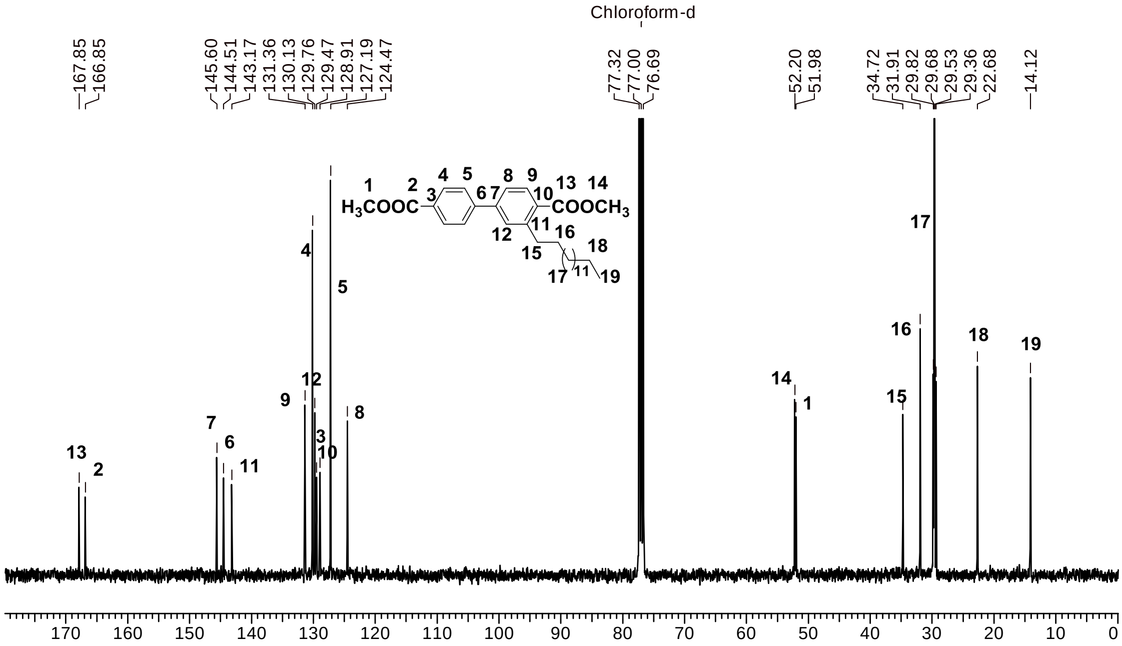


Figure 3.49 ^{13}C NMR spectrum (in CDCl$_3$) of dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate

In final step, dimethyl 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylate was refluxed with hydrazine hydrate in methanol to form 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide.[53, 54] 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide was characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopic methods.

Figure 3.50 depicts FT-IR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide. The broad absorption band at 3299 cm^{-1} is due to –N-H stretching of –NH$_2$ and –NH- group of –CONHNH$_2$ group. The absorption band at 1602 cm^{-1} corresponds to carbonyl stretching of acyl hydrazide.

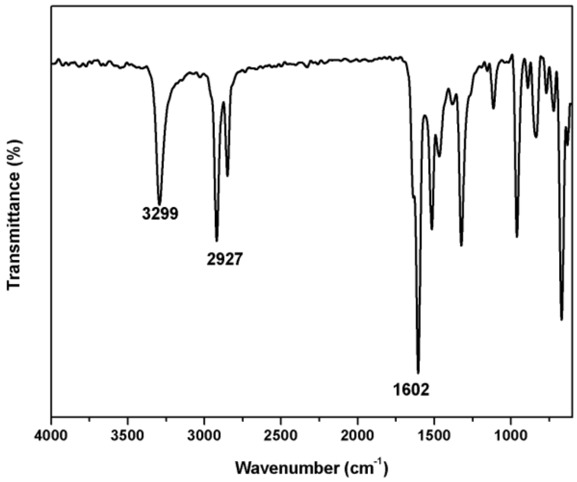


Figure 3.50 FT-IR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

^{1}H NMR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide is represented in **Figure 3.51**

The two –NH- protons of two acyl hydrazide groups exhibited two singlets at 8.98 and 8.67 δ ppm. The protons *ortho* and *meta* to acid hydrazide group of aromatic ring without pentadecyl chain appeared as doublets at 7.90 and 7.70 δ ppm, respectively while the protons of pentadecyl substituted aromatic ring exhibited a multiplet in the region 7.37- 7.55 δ ppm. The –NH_2 group protons of the acyl hydrazide groups showed a broad singlet at 4.27 δ ppm. The benzylic –CH_2 of pentadecyl chain appeared as a triplet at 2.86 δ ppm; whereas, rest of methylene group protons appeared as a multiplet in the range 1.62-1.70 δ ppm and a multiplet in region 1.25-1.33 δ ppm. The –CH_3 group appeared as a triplet at 0.89 δ ppm.

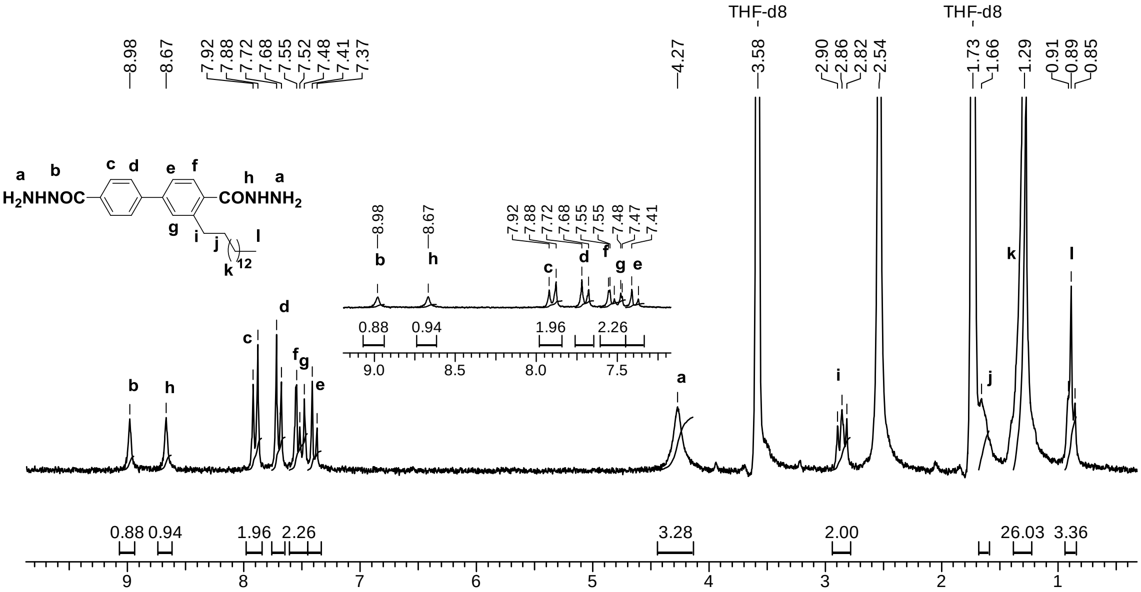


Figure 3.51 ^{1}H NMR spectrum (in THF-d_8) of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

^{13}C NMR spectrum of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide along with assignments is reproduced in **Figure 3.52.** In ^{13}C NMR spectrum, carbonyl carbons of the acyl hydrazide groups resonated at different frequencies giving rise to two peaks at 170.19 and 167.44 δ ppm.

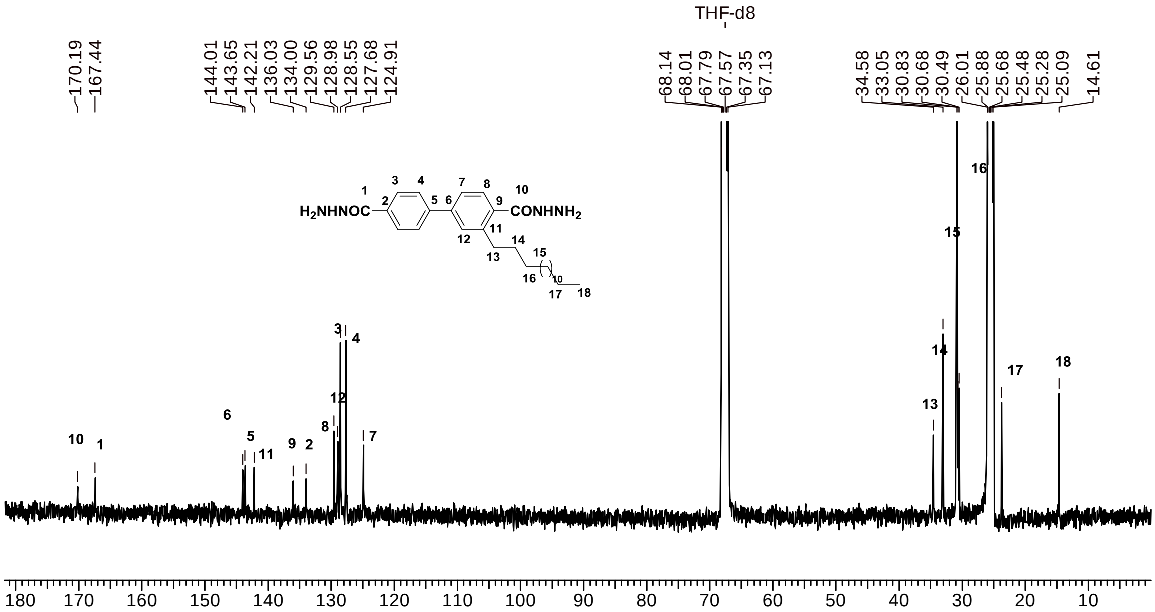


Figure 3.52 ^{13}C NMR spectrum (in THF-d$_8$) of 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

3.5 Conclusions

1. The utility of 3-pentadecyl phenol, which in turn was obtained from CNSL, as a promising renewable starting material for synthesis of various difunctional monomers such as dialdehyde, bisphenols, diamine, dihalide, dinitrile, diacids and diacylhydrazides was demonstrated. Ten new difunctional monomers viz;
    1. 4-(4-Formylphenoxy)-2-pentadecylbenzaldehyde
    2. 4-(4-Hydroxyphenoxy)-3-pentadecylphenol
    3. 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline
    4. 4-(4-(4-(4-Carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid
    5. 4-(4-(4-(4-(Hydrazinocarbonyl) phenoxy)- 2-pentadecyl phenoxy) phenoxy) benzohydrazide
    6. 3-Pentadecyl 4,4' biphenol
    7. 2, 2-Pentadecyl-[1,1'-biphenyl]-4,4'-diol
    8. 4,4’-Dibromo 3-pentadecyl biphenyl
    9. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid and
    10. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

    with different structural features such as pendent pentadecyl chain, flexible ether linkages or rigid biphenylene moiety were synthesized
2. The difunctional monomers represent valuable building-blocks for the synthesis of a host of high performance/ high temperature polymers.

References

1. C. W. Ulmer II, D. A. Smith, B. G. Sumpter and D. I. Noid, eds., *Computational and Theoretical Polymer Science*, 1998.
2. D. J. David and A. Misra, eds., *Relating Materials Properties to Structure with MATPROP Software Handbook and Software for Polymer Calculations and Materials Properties*, CRC Press, 2001.
3. P. M. Hergenrother, *High Perform. Polym.*, 2003, **15**, 3-45.
4. M.E.; Long and T. E. Rogers, eds., *Synthetic Methods in Step Growth Polymers*, John Wiley and Sons, New York, 2003.
5. A. P. Dove and M. A. R. Meier, *Macromol. Chem. Phys.*, 2014, **215**, 2135-2137.
6. R. Babu, K. O'Connor and R. Seeram, *Prog. Biomaterials*, 2013, **2**, 8.
7. M. N. Belgacem, A. Gandini and M. N. B. Gandini, in *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, 2008, pp. 39-66.
8. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, 2014, **5**, 3142-3162.
9. R. Auvergne, S. Caillol, G. David, B. Boutevin and J.-P. Pascault, *Chem. Rev.*, 2014, **114**, 1082-1115.
10. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals; Pergamon Press: New York*, 1989.
11. V. Madhusudhan, M. S. Ramaiah, N. B. Naidu and M. A. Sivasamban, *Ind. J. Technol.*, 1973, **11**, 347-350.
12. A. S. More, S. K. Pasale and P. P. Wadgaonkar, *Eur. Polym. J.*, 2010, **46**, 557-567.
13. S. K. Chowdhury, P. P. Wadgaonkar, T. L. Hoeks, S. K. Rajaraman, B. D. Sarwade and C. V. Avadhani, US 7569714 B2, 2009.
14. G. Evano, N. Blanchard and M. Toumi, *Chem. Rev.*, 2008, **108**, 3054-3131.
15. F. Monnier and M. Taillefer, *Angew. Chem. Int. Ed.*, 2009, **48**, 6954-6971.
16. A. S. More, A. S. Patil and P. P. Wadgaonkar, *Polym. Degrad. Stab.* , 2010, **95** 837-844.
17. R. Matmour, A. S. More, P. P. Wadgaonkar and Y. Gnanou, *J. Am. Chem. Soc.*, 2006, **128** 8158-8159.

18. L. F. Tietze, C. A. Vock, I. K. Krimmelbein and L. Nacke, *Synthesis*, 2009, **2009**, 2040-2060.
19. B. Andersh, D. L. Murphy and R. J. Olson, *Synth. Commun.*, 2000, **30**, 2091-2098.
20. M. V. Bhatt and S. U. Kulkarni, *Synthesis*, 1983, **1983**, 249-282.
21. K. Hwang and S. Park, *Synth. Commun.*, 1993, **23**, 2845-2849.
22. R. D. Shingte and P. P. Wadgaonkar, *US 6790993*, 2004.
23. S. Bapat, *Ph.D. Thesis submitted to University of Pune*, 2008.
24. R. D. Shingte, *Ph.D. Thesis submitted to University of Pune*, 2006.
25. A. S. More, S. K. Menon and P. P. Wadgaonkar, *J. Appl. Polym. Sci.*, 2012, **124**, 1281-1289.
26. A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147-168.
27. J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 9550-9561.
28. S. Kotha, K. Lahiri and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633-9695.
29. J. Hassan, M. Sevignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359-1470.
30. D. H. Wang, S. Z. D. Cheng and F. W. Harris, *Polymer*, 2008, **49**, 3020-3028.
31. R. Grisorio, P. Mastrorilli, G. Ciccarella, G. P. Suranna and C. F. Nobile, *Tet. Lett.*, 2008, **49**, 2078-2082.
32. H. Kotsuki, S. Kobayashi, H. Suenaga and H. Nishizawa, *Synthesis*, 1990, **1990**, 1145-1147.
33. A. R. Katritzky, J. Li, C. V. Stevens and D. J. Ager, *Org. Prep. Proced. Int.*, 1994, **26**, 439-444.
34. J. R. Desmurs and A. Nonn, US 4983781, 1991.
35. E. Berliner and J. C. Powers, *J. Am. Chem. Soc.*, 1961, **83**, 905-909.
36. A. Nonn, US 5107044, 1992.
37. A. Nonn, US 5015792, 1991.
38. K. W. Rosenmund and E. Struck, *Ber. Dtsch. Chem. Ges.*, 1919, **2**, 1749.
39. J. v. Braun and G. Manz, *Justus Liebigs Ann. Chem.*, 1931, **488**, 111-126.
40. D. T. Mowry, *Chem. Rev.*, 1948, **42**, 189-283.
41. G. P. Ellis and T. M. Romney-Alexander, *Chem. Rev.*, 1987, **87**, 779-794.
42. V. V. Grushin and H. Alper, *Chem. Rev.*, 1994, **94**, 1047-1062.
43. D. Wang, L. Kuang, Z. Li and K. Ding, *Synlett*, 2008, **2008**, 69-72.

44. D. M. Tschaen, R. Desmond, A. O. King, M. C. Fortin, B. Pipik, S. King and T. R. Verhoeven, *Synth. Commun.*, 1994, **24**, 887-890.
45. M. Sundermeier, A. Zapf and M. Beller, *Angew. Chem. Int. Ed.*, 2003, **42**, 1661-1664.
46. R. K. Arvela and N. E. Leadbeater, *J. Org. Chem.*, 2003, **68**, 9122-9125.
47. T. Schareina, A. Zapf and M. Beller, *Tet. Lett.*, 2005, **46**, 2585-2588.
48. H. J. Cristau, A. Ouali, J. F. Spindler and M. Taillefer, *Chem. Eur. J.*, 2005, **11**, 2483-2492.
49. J. Kim, H. J. Kim and S. Chang, *Angew. Chem. Int. Ed.*, 2012, **51**, 11948-11959.
50. D. Saha, L. Adak, M. Mukherjee and B. C. Ranu, *Org. Biomol. Chem.*, 2012, **10**, 952-957.
51. C. M. G. Henríquez, L. H. Tagle, C. A. Terraza, A. B. González, A. L. Cabrera and U. G. Volkmann, *J. Appl. Polym. Sci.*, 2011, **125**, 477-487.
52. A. S. More, S. K. Pasale and P. P. Wadgaonkar, *Eur. Polym. J.* , 2010, **46**, 557-567.
53. Y. Liu, X. Wu, C. He, Y. Jiao and C. Duan, *Chem. Commun.*, 2009, 7554-7556.
54. J. C. Chen, C. J. Chiang and Y. C. Liu, *Synth. Metals*, 2010, **160**, 1953-1961.

Chapter 4

Synthesis and Characterization of Polyesters Containing Ether Linkages and Pendent Pentadecyl Chains

4.1 Introduction

Among high performance polymers, aromatic polyesters are of great importance since they exhibit excellent thermal stability, mechanical properties, good chemical resistance and are excellent candidates for aviation, automobile and electrical industries.[1, 2] The poor solubilities in common organic solvents, coupled with high melting (T_m) and glass transition temperature (T_g) results in poor processability of aromatic polyesters [3, 4] which results from the presence of strong interchain interactions from symmetrical and polar groups. To surmount this, it is desirable to incorporate structural features in polyester backbone so as to obtain greater degree of solubility and improved processing characteristics without compromising their desirable characteristics.

Solubility / processability of polyesters may be improved by (i) introducing flexible linkages in the polymer backbone; (ii) introducing monomers with crank shaft or bent units along the backbone and (iii) the use of bulky side groups or flexible side chains.[5-21] These approaches work by forcing the chains apart and lend to the improved solubility and better processability.

Continuing with our efforts towards processable high performance polymers containing pendent pentadecyl chains,[22-30] we wish to report the interfacial polycondensation of HPPDP with terephthalic acid chloride (TPC), isophthalic acid chloride (IPC) and a mixture of TPC and IPC (50:50 mol %) to form a series of polyesters. Copolyesters were also prepared from varying composition of HPPDP and bisphenol-A (BPA) with TPC. The influence of pentadecyl chains on solubility, T_g and mechanical properties is discussed.

4.2. Experimental

4.2.1 Materials

4-(4-Hydroxyphenoxy)-3-pentadecylphenol (HPPDP) was prepared by procedure given in **Chapter 3**. Terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) (both received from Aldrich, USA) were purified by distillation under reduced pressure. 2, 2-Bis(4-hydroxyphenyl)propane (bisphenol-A, BPA) received from Aldrich, USA and sublimed before use. Benzyltriethylammonium chloride (BTEAC) was received from Aldrich, USA and was used as received. Dichloromethane, received from Rankem, India was dried over calcium hydride and distilled before use. The other solvents were of reagent grade quality and were purified before use according to the reported procedures.[39]

4.2.2 Measurements

Inherent viscosity (η_{inh}) of polymers was measured with 0.5 % (w/v) solution of polymer in chloroform or phenol- tetrachloroethane mixture (60:40, w/w) at 30 ± 0.1°C using an Ubbelhode suspended level viscometer.

η_{inh} was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

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

Molecular weights of (co)polyesters were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter.

FTIR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer.

NMR spectra were recorded on a Bruker NMR spectrometer at resonance frequency of 200 or 400 MHz for ^{1}H and 50 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

Solubility of (co) polyesters was determined at 3 wt. % concentration in various solvents at room temperature or on heating. For chloroform and tetrahydrofuran the temperature was 50 °C while that for dichloromethane it was 35 °C. For remaining solvents, the temperature used was 60 °C.

X-Ray diffractograms of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2°/min over a range of scattering angle from 5° to 40°. Dried polymer film or powder was used for X-ray measurements.

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

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10 °C/min in nitrogen atmosphere.

Dynamic mechanical analysis (DMA) of copolyesters as a function of temperature was determined on films cast from chloroform solution. The sample dimensions were 15 x 6.6 mm (length x width) and thickness between 0.10 and 0.15 mm. The measurements were carried out in a Rheometrics Scientific (model Mark IV)

(UK), using the tensile mode between 20 and 250 °C, at frequency of 1 Hz and heating rate of 10 °C/min under nitrogen atmosphere.

4.3 Synthesis of (co)polyesters

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

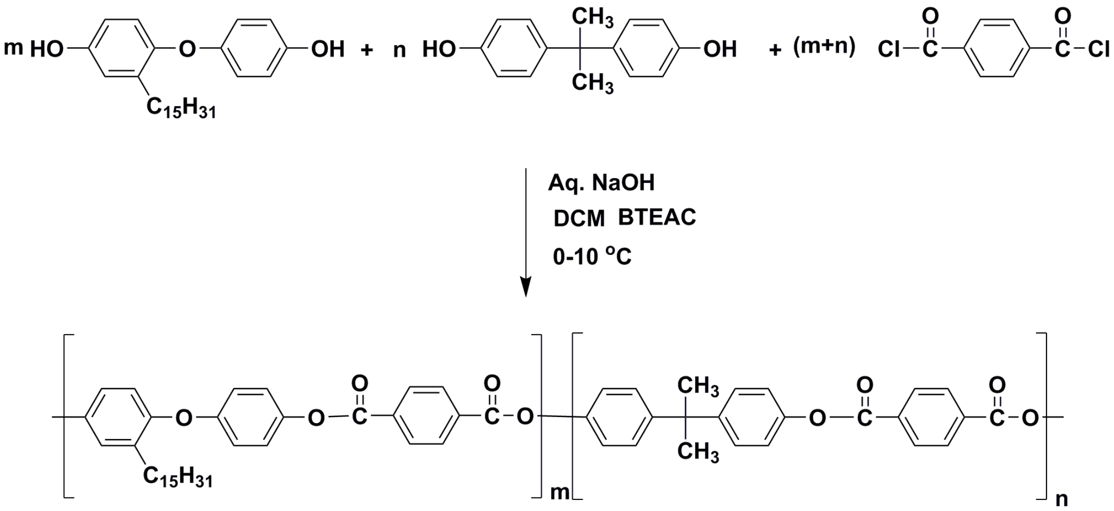
HPPDP (412 mg, 1 mmol) and 1M NaOH (1.95 mL) were taken into a 100 mL two-necked round bottom flask equipped with a high speed mechanical stirrer and an addition funnel and stirred for 10-15 minutes. BTEAC (30 mg) was added to the reaction mixture and the mixture was cooled to 10 °C. TPC (202 mg, 2 mmol) dissolved in dichloromethane (20 mL) was added in a single lot to the reaction mixture and the mixture was vigorously stirred at 2000 rpm for 1 h. The aqueous layer was decanted and organic layer was diluted with additional 15 mL of dichloromethane. The polymer solution was precipitated in excess of methanol, the precipitated polymer was washed several times with water and then with methanol and dried under reduced pressure for 48 h.

A similar procedure was followed for the synthesis of other (co)polyesters.

4.4 Results and Discussion

4.4.1 Synthesis of (co)polyesters

Scheme 4.1 illustrates synthesis of (co)polyesters based upon HPPDP. Polyesters and copolyesters were synthesized by interfacial polycondensation with a solution of diacid chloride in dichloromethane and aqueous solution of sodium salt of HPPDP or a mixture of sodium salts of both HPPDP and BPA using BTEAC as the phase transfer catalyst.



Scheme 4.1 Synthesis of (co)polyesters from HPPDP and BPA with TPC

Aromatic polyesters are generally difficult to process because of the rigid polymer backbone. Copolymerization is one of the most useful approaches for improving solubility and, in-turn, processability of polymers. Since BPA and TPC based polyester[31] is insoluble in common organic solvents such as chloroform and dichloromethane, it was of interest to study the effect of incorporation of HPPDP on the solubility properties of polyesters derived from BPA and TPC. Accordingly, TPC-based copolyesters were synthesized by varying composition of BPA and HPPDP. The results of polymerization reactions are summarized in **Table 4.1.** Inherent viscosity of (co) polyesters was in the range 0.70-1.21 dL/g. Results of GPC measurements for polyesters are presented in **Table 4.1**.

Table 4.1 Synthesis of (co)polyesters from HPPDP and BPA with aromatic diacid chlorides

Polymer	**Composition of Diols (mol%)**		**Composition of Diacid Chloride (mol%)**		**η_{inh} (dL/g)[a]**	**Molecular Weight**		**PDI (Mw/Mn)**
	HPPDP	**BPA**	**TPC**	**IPC**		**Mn ($x10^3$)**	**Mw($x10^3$)**	
PE-I	100	0	100	0	1.19	48.3	85.3	2.09
PE-II	100	0	0	100	0.74	24.4	55.0	2.25
PE-III	100	0	50	50	1.21	27.1	86.8	3.20
PE-IV	25	75	100	0	1.07	39.7	72.7	1.83
PE-V	15	85	100	0	0.72	19.1	49.3	2.50
PE-VI	10	90	100	0	0.70[b]	22.7	51.6	2.20
PE-VII	05	95	100	0	0.74[b]	16.0	23.1	1.44
PE-I	0	100	0	100	0.43[b]	-	-	-

a: η_{inh} was measured with 0.5% (w/v) solution of polyester in $CHCl_3$ at 30 ± 0.1°C.;

b: η_{inh} of polyester was measured with 0.5% (w/v) solution of polyester in phenol/tetrachloroethane (60/40,w/w) at 30 ± 0.1°C

Number average molecular weights (Mn) of polyesters were in the range 16,000-48,300 and polydispersity index was in the range 1.44-3.20. Inherent viscosity and GPC data indicated the formation of reasonably high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene as the standard.

Transparent, flexible and tough films of (co)polyesters could be cast from chloroform solution.

4.4.2 Structural characterization

(Co)polyesters were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. In the FTIR spectrum of polyester derived from HPPDP and IPC (**Figure 4.1)** ester carbonyl stretching and aromatic ether (Ar-O-Ar) stretching were observed at 1739 and 1220 cm^{-1}, respectively.

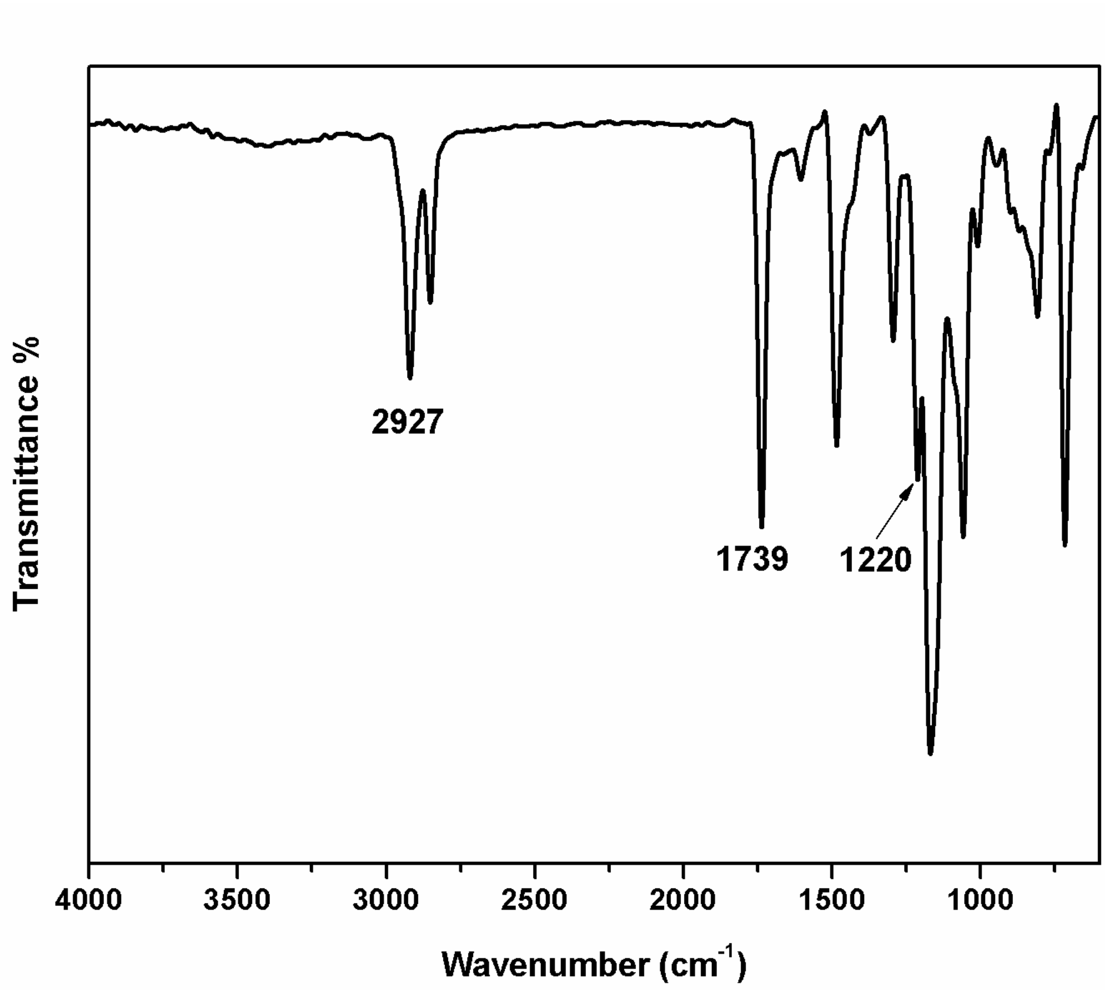


Figure 4.1 FT-IR spectrum of polyester (PE-II) derived from HPPDP and IPC

Figure 4.2 depicts ^{1}H NMR spectrum of polyester derived from HPPDP and TPC along with assignments. Terephthalic acid ring protons appeared as a singlet at δ = 8.35 ppm. The aromatic protons of HPPDP exhibited multiplet in the range 7.02-7.26 ppm. The benzylic methylene protons appeared as a triplet at δ = 2.67 ppm. The methylene protons in β-position to aromatic ring and remaining methylene protons exhibited broad peaks centered at 1.65 and 1.25 ppm, respectively. The terminal methyl group protons appeared as a triplet at 0.87 ppm.

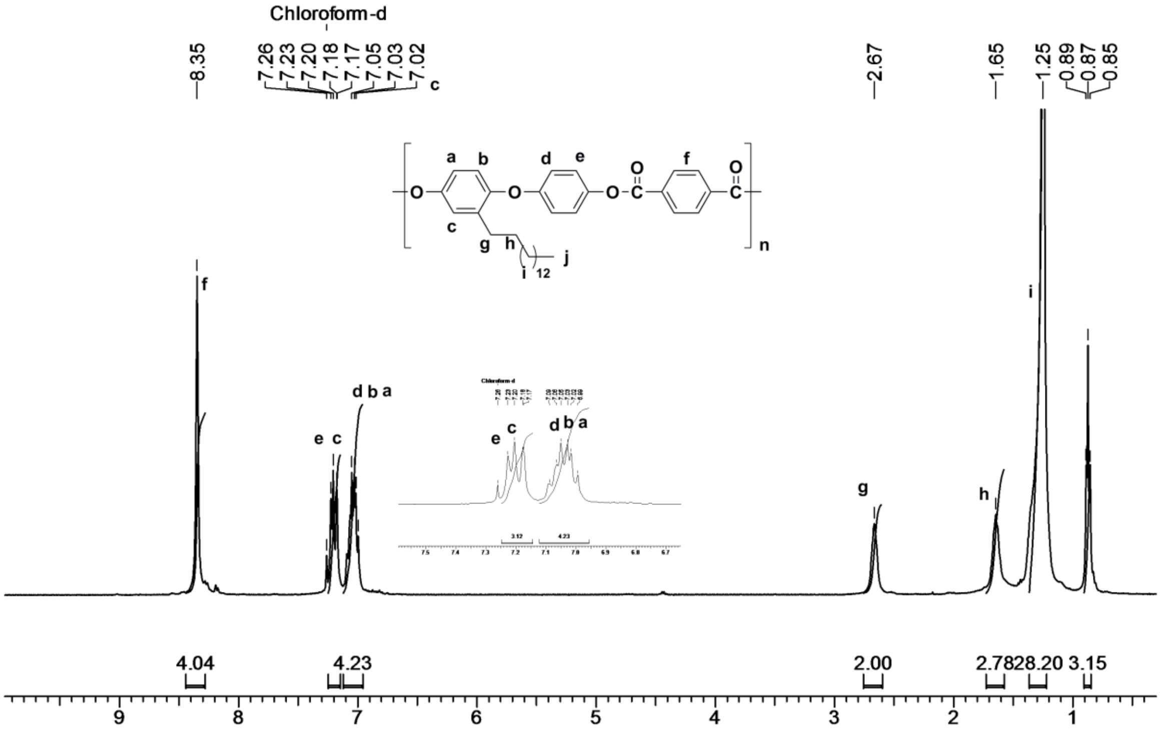


Figure 4.2 ^{1}H NMR spectrum (in CDCl$_3$) of polyester (PE-I) derived from HPPDP and TPC

^{13}C NMR spectrum of polyester (PE-I) derived from HPPDP and TPC along with assignments is reproduced in **Figure 4.3.** The appearance of peak at 164.45 δ ppm corresponds to carbonyl carbon of ester group.

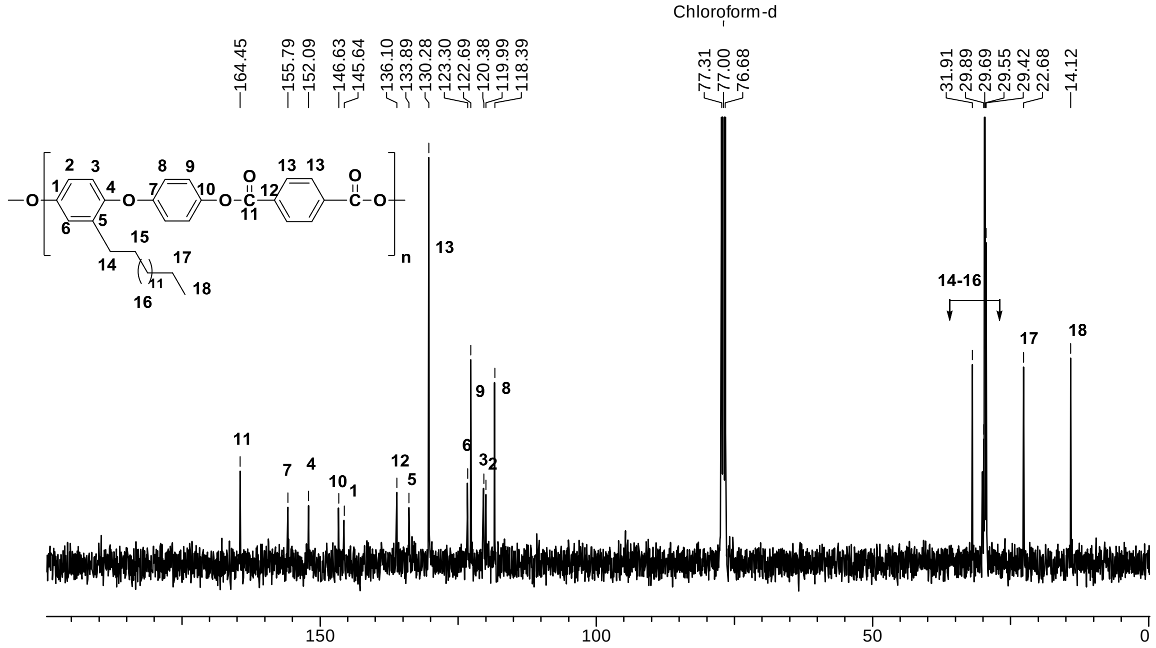


Figure 4.3 ^{13}C NMR spectrum (in CDCl$_3$) of polyester (PE-I) derived from HPPDP and TPC

^{1}H NMR spectrum of polyester (PE-II) derived from HPPDP and IPC is represented in **Figure 4.4.** The protons of isophthalic acid moiety viz. f, g and h appeared as a singlet at 9.05 δ ppm, a doublet at 8.48 δ ppm and a triplet at 7.70 δ ppm, respectively. The aromatic protons of HPPDP moiety appeared as a multiplet in the range 7.0-7.23 δ ppm. The benzylic methylene protons exhibited a triplet at δ = 2.66 ppm. The protons of methylene group β to aromatic ring exhibited a multiplet in the range 1.59-1.65 δ ppm while rest of methylene groups appeared as a multiplet in the range 1.22-1.35 δ ppm. The terminal methyl group exhibited a triplet at 0.86 ppm.

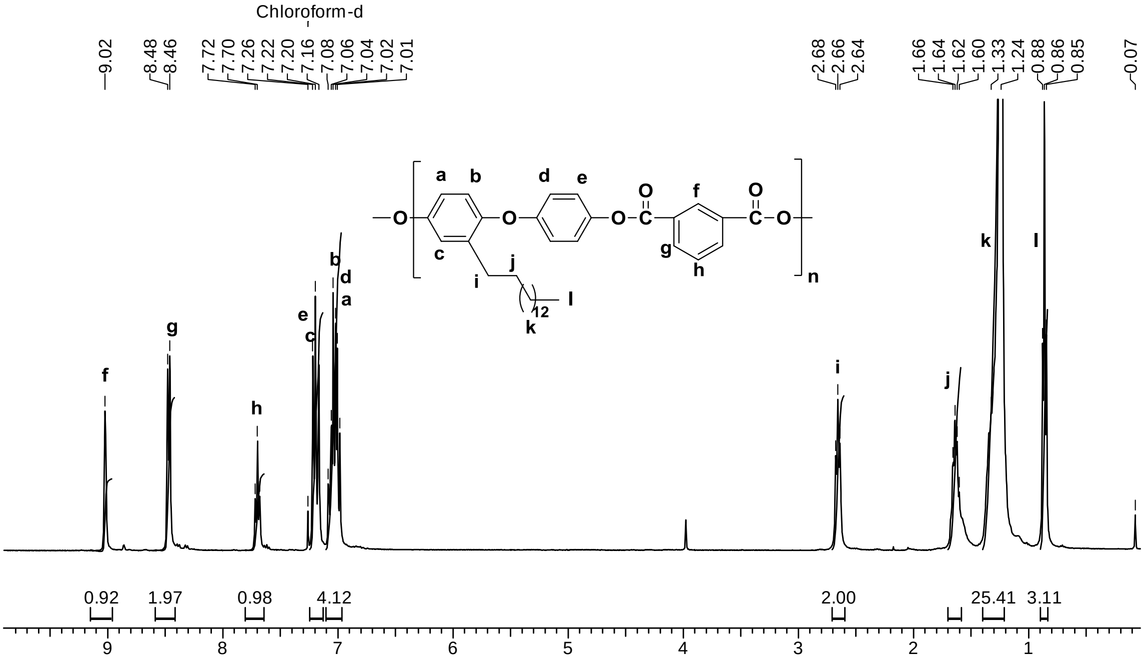


Figure 4.4 ^{1}H NMR spectrum (in $CDCl_3$) of polyester (PE-II) derived from HPPDP and IPC

Figure 4.5 depicts ^{13}C NMR spectrum of polyester (PE-II) derived from HPPDP and IPC. The ester carbonyl carbon appeared at 164.50 δ ppm and other spectral assignments are in good agreement with the proposed structure.

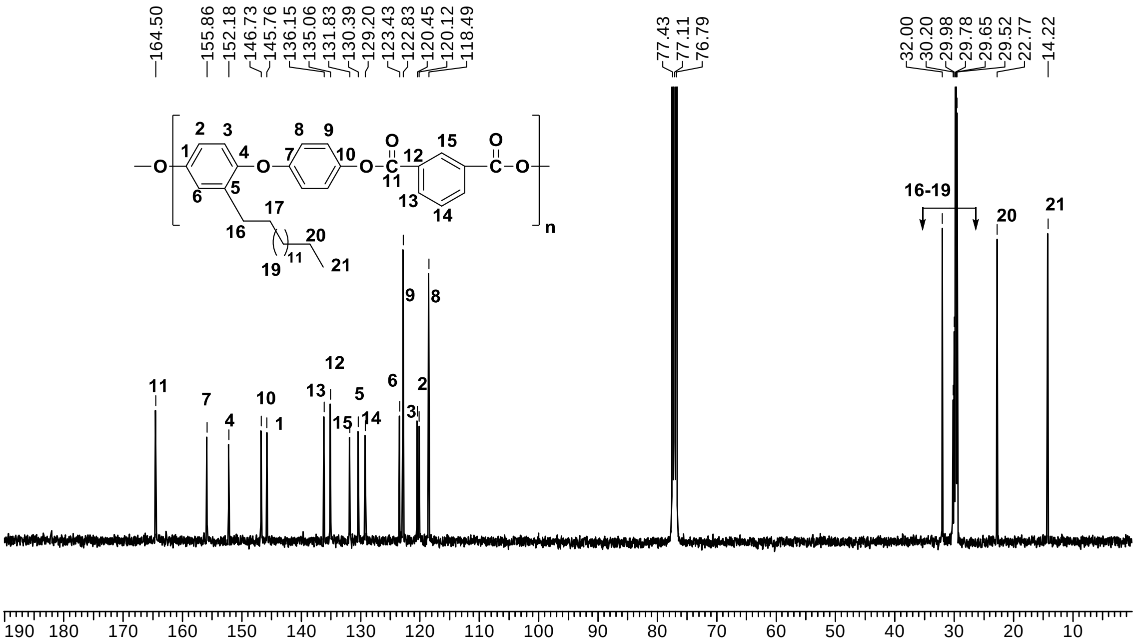


Figure 4.5 ^{13}C NMR spectrum (in CDCl$_3$) of polyester (PE-II) derived from HPPDP and IPC

^{1}H NMR spectroscopy was used to determine the composition of copolyesters. To calculate the composition, the integrated intensity of terephthalic acid ring protons was compared with that of benzylic methylene protons of pentadecyl chain which appeared as a triplet at 2.66 ppm. (**Figure 4.6**) The integrated intensity ratio of these peaks was used to determine the molar percentage incorporation of HPPDP. As shown in **Table 4.2,** there is an excellent agreement between the observed incorporation of HPPDP and the amount taken for polymerization.

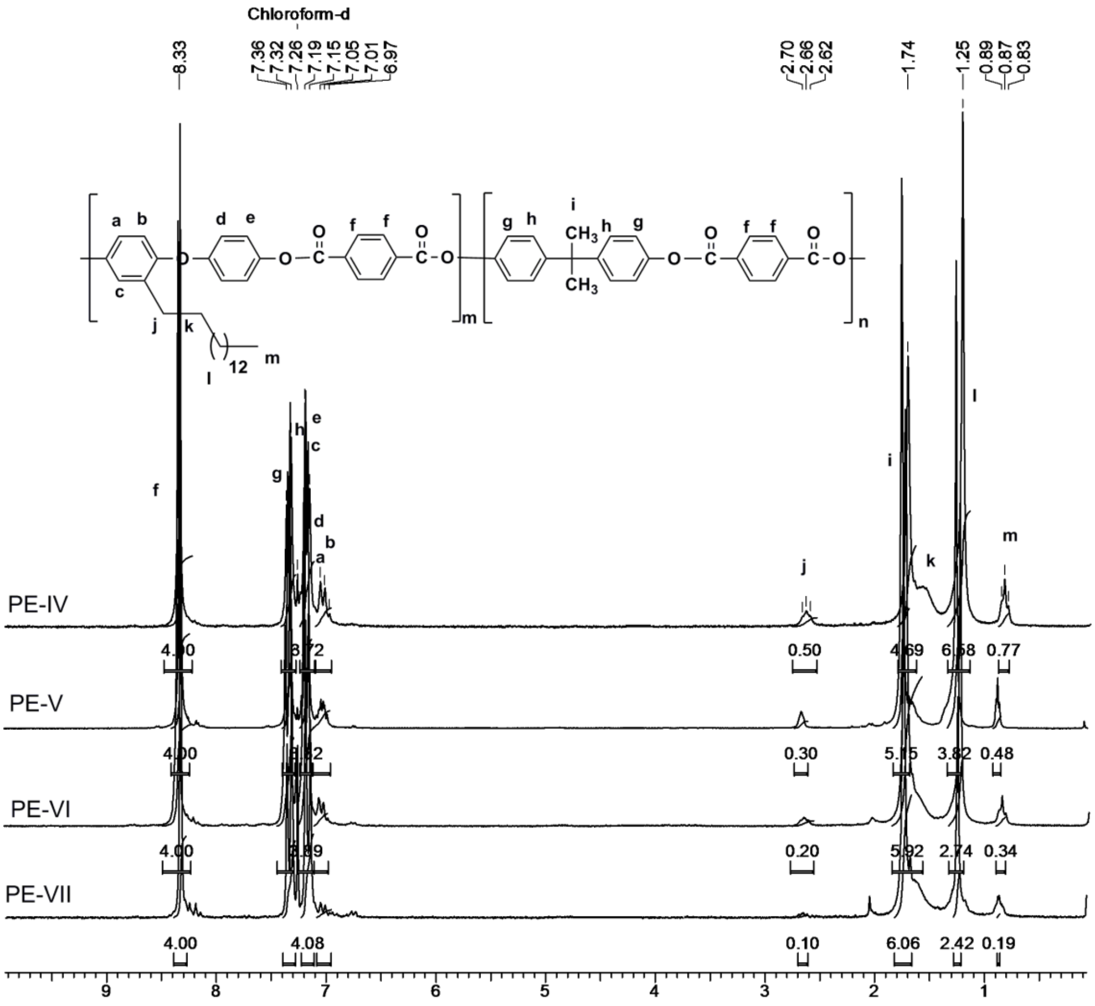


Figure 4.6 ^{1}H NMR spectra (in $CDCl_3$) of copolyesters derived from various proportions of HPPDP and BPA with TPC (PE-IV to VII)

Table 4.2 Copolyester composition from ^{1}H NMR spectra

Copolyester	Feed HPPDP, mol%	Observed HPPDP, mol%
PE-IV	**25**	**25**
PE-V	**15**	**15**
PE-VI	**10**	**10**
PE-VII	**05**	**05**

4.4.3 Solubility measurements

The solubility of (co)polyesters was tested in different organic solvents at 3 wt% concentration. The solubility data is summarized in **Table 4.3**.

Table 4.3 Solubility data of (co)polyesters containing pendent pentadecyl chains and that of reference polyester based on BPA-TPC

(Co) polyester	**Composition of diol, (mol%)**		**Diacid Chloride (mol%)**		**Chloroform**	**Dichloromethane**	**Tetrahydrofuran**	**DMF**	**DMAc**	**DMSO**	***m*-Cresol**	**Pyridine**
	HPPDP	**BPA**	**TPC**	**IPC**								
PE-I	100	0	100	0	++	++	++	+0	+0	+0	++	++
PE-II	100	0	0	100	++	++	++	+0	+0	+0	++	++
PE-III	100	0	50	50	++	++	++	+0	+0	+0	++	++
PE-IV	25	75	100	0	++	++	+0	--	--	--	++	+-
PE-V	15	85	100	0	++	++	+0	--	--	--	++	+0
PE-VI	10	90	100	0	+-	+-	+0	--	--	--	++	+0
PE-VII	05	95	100	0	+0	+0	--	--	--	--	++	--
PE-VIII	0	100	100	0	--	--	--	--	--	--	--	--

++ : soluble at room temperature; +- : soluble on heating; +0 : partially soluble on heating; -- : insoluble on heating; (Heating temperatures for different solvents are mentioned in the experimental section).

Polyesters obtained from HPPDP and aromatic diacid chlorides were soluble in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, *m*-cresol and pyridine and were also found to be soluble upon heating in aprotic polar solvents such as DMAc and N,N dimethylformamide (DMF). It is to be noted that reference polyesters based on 4, 4'-oxybisphenol with TPC and BPA with TPC (PE-VIII) are reported to be insoluble in common organic solvents such as chloroform and dichloromethane.[31, 32]

The solubility tests of copolyesters indicated that even at 15 mol% incorporation of HPPDP, the solubility of copolyesters in common organic solvents was improved significantly. This improvement in solubility indicates that the incorporation of pendent pentadecyl chains in polyester backbone disturbs the dense chain packing of polymer chains which facilitates penetration of the solvent molecules.

4.4.4 X-Ray diffraction studies

To investigate the effect of pendent pentadecyl chain on the crystallinity of polyesters, X-ray diffractograms of HPPDP-based (co)polyesters along with that of polyester derived from BPA and TPC (PE-VIII) were studied (**Figure 4.7)**.

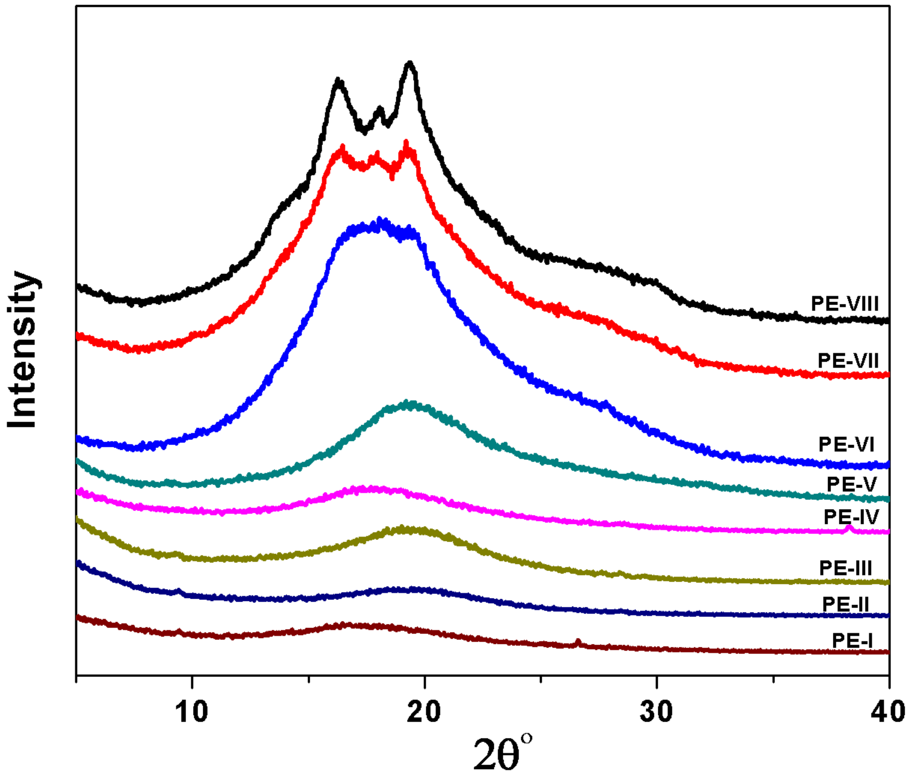


Figure 4.7 X-Ray diffractograms of (co) polyesters containing pendent pentadecyl chain along with that of BPA-TPC polyester

XRD patterns for polyesters derived from HPPDP and aromatic diacid chlorides (PE-I, PE-II and PE-III) exhibited amorphous nature which could be mainly because of the presence of pentadecyl chains which hinders the packing of polymer chains. The amorphous nature was also reflected in their improved solubility. X-Ray diffractograms of polyester derived from BPA and TPC (PE-VIII) showed partially crystalline nature as depicted in **Figure 4.7.**[31] Copolyesters synthesized with varying molar percentage incorporation of HPPDP showed decrease in crystallinity with increase in percentage of HPPDP. This could be attributed to presence of pendent pentadecyl chains which cause disruption of chain regularity and packing.

4.4.5 Thermal properties

The thermal behavior of (co)polyesters was analyzed using TGA at a heating rate of 10 °C min^{-1} under nitrogen. Thermogravimetric analysis (TG) curves of (co)polyester are shown in **Figure 4.8**. The temperatures at 10% weight loss (T_{10}) of (co)polyesters were determined and the values are given in **Table 4.4**.

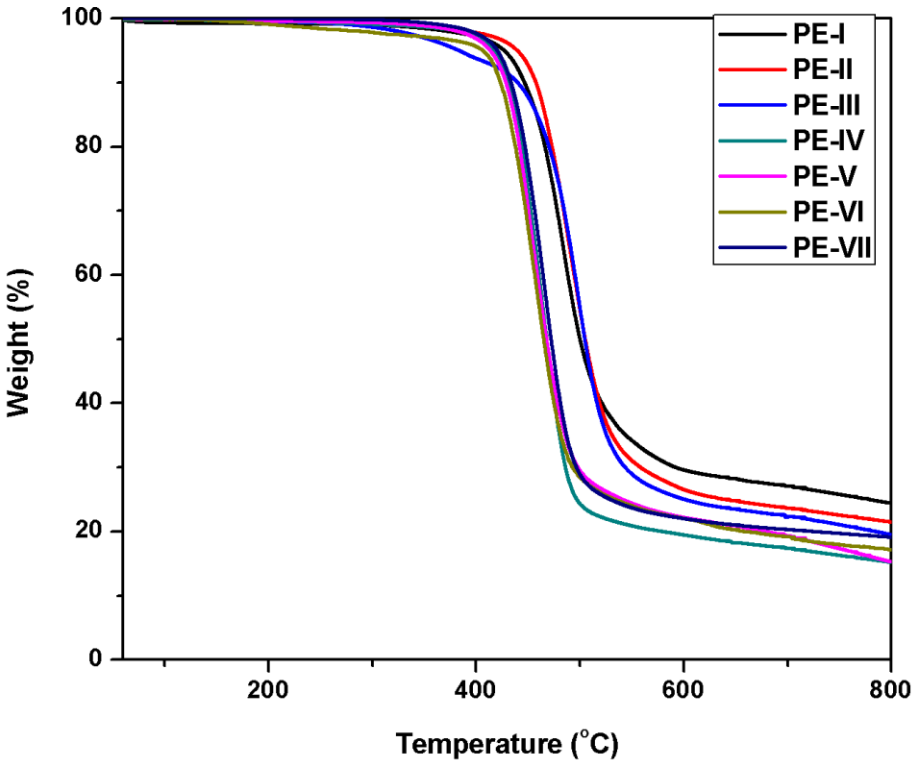


Figure 4.8 TG curves of (co)polyesters derived from HPPDP and BPA with aromatic diacid chlorides

T_{10} values for polyesters derived from HPPDP and aromatic diacid chlorides were in the range 425–435 °C indicating their good thermal stability. T_{10} values for copolyesters derived from HPPDP and BPA with TPC were in the range 440–455 °C. A comparison of T_{10} values of (co)polyesters containing pendent pentadecyl chains with reported T_{10} value of polyester based on BPA and TPC (T_{10} =495 °C),[31] indicated a decrease in the thermal stability due to the presence of thermally labile aliphatic pentadecyl chain.

Table 4.4 Thermal properties of (co)polyesters

Polymer	Composition of Diols (mol%)		Diacid Chloride (mol%)		T_{10} (°C)	Char Yield at 800 °C (%)	T_g (°C)
	HPPDP	BPA	TPC	IPC			
PE-I	100	0	100	0	430	19	47
PE-II	100	0	0	100	425	15	29
PE-III	100	0	50	50	435	18	37
PE-IV	25	75	100	0	440	16	147
PE-V	15	85	100	0	455	22	160
PE-VI	10	90	100	0	450	24	168
PE-VII	05	95	100	0	445	25	202
PE-VIII	0	100	100	0	495	29	210

Differential scanning calorimetry (DSC) was used for determination of glass transition (T_g) temperatures of (co)polyesters. T_g values were calculated from second heating cycle of polyester samples at heating rate of 10 °C/min. DSC curves for (co)polyesters are represented in **Figure 4.9 and 4.10.** T_g values are given in **Table 4.4.**

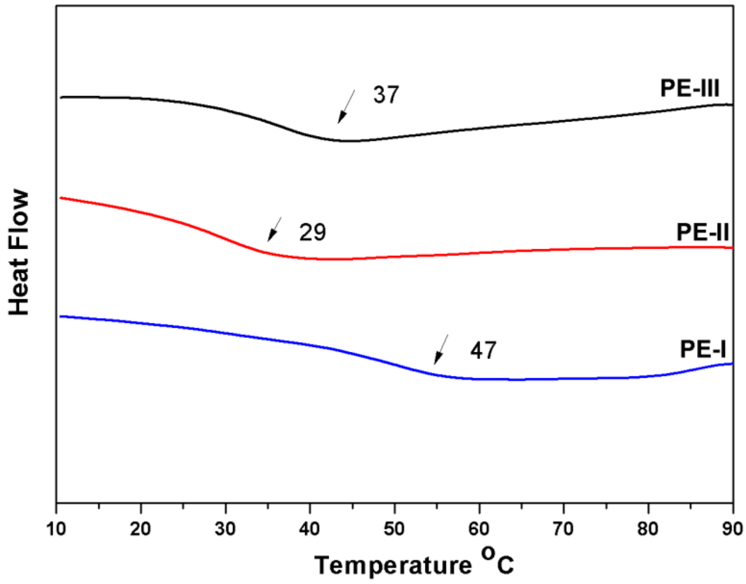


Figure 4.9 DSC curves of (co)polyesters derived from HPPDP and aromatic diacid chlorides

T_g values of polyester PE-I, PE-II, PE-III were found to be 47, 29 and 37 °C, respectively. A comparison of these values with softening temperature of polyester based on 4, 4’-oxybisphenol (softening range: 240-260 °C) [32] indicated that there is appreciable decrease in T_g of polyesters due to incorporation of pendent pentadecyl chains. The flexible pentadecyl chains could act as packing disruptive groups resulting into reduction in T_g of polyesters.

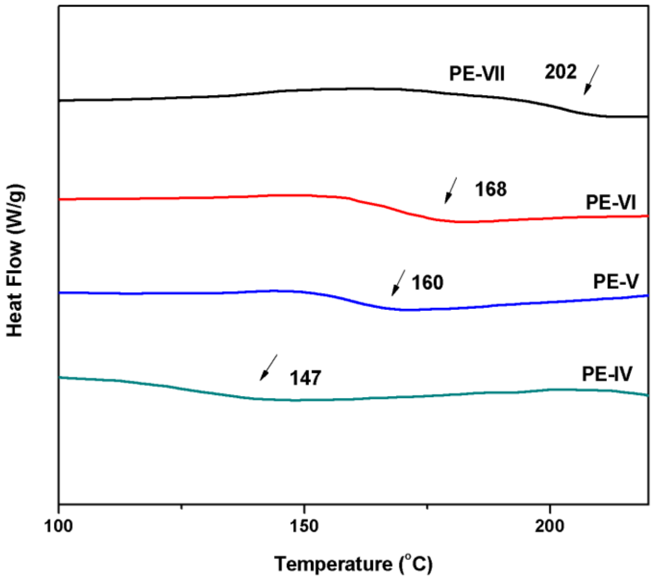


Figure 4.10 DSC curves of copolyesters derived from HPPDP and BPA with aromatic diacid chlorides

Copolyesters (PE-IV to VII) derived from a mixture of HPPDP and BPA with TPC exhibited T_g values in the range 147-202 °C. The data clearly indicated that T_g values of copolyesters decrease with the increase in HPPDP content. This could be attributed to the presence of pentadecyl chains which could act as packing disruptive groups and resulting into increase in the chain mobility and consequently decrease in T_g of copolyesters. Importantly, these (co)polyesters have a wide processing window as there is a large difference between T_g values (27-202 °C) and T_{10} values (425-455 °C).

4.4.6 Dynamic mechanical properties

Dynamic mechanical behavior of two selected copolyesters (PE-IV and PE-V) containing pendent pentadecyl chains was studied by DMA. **Figure 4.11** presents DMA curves (storage modulus E’, loss modulus E’’ and damping factor tan δ as a function of temperature) of polyester PE-IV. The storage modulus and Tα values of PE-IV and PE-V are included in **Table 4.5**. DMA data showed that the storage modulus E’ of copolyesters is of the order of 10^9 Pa. The values of storage modulus for PE-IV and PE-V at 35 °C are 0.8 x 10^9 and 1.2 x 10^9 Pa, respectively which indicated that storage modulus decreased with higher content of pentadecyl chains in the polyesters. Similar results were observed when pentadecyl chain was incorporated in cyanate ester resins.[33]

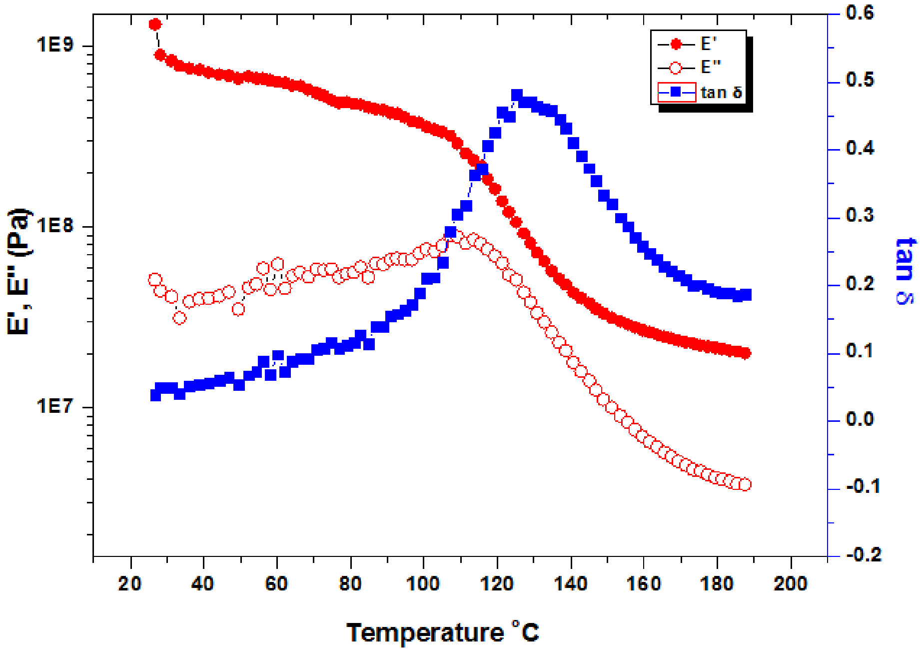


Figure 4.11 DMA curves of copolyester PE-IV

It can also be seen that the temperature at which the onset of glass to rubber transition occurs decreased as incorporation of HPPDP in copolyesters increased. This behavior is due to increase in content of pendent pentadecyl chains which act as packing disruptive group in copolyesters. This behavior is more clearly seen from tan δ curves. Copolyesters showed a well-defined maximum for α-transition (T_α) which appeared at 133 and 155 °C, respectively for PE-IV and PE-V. Thus, the maximum in tan δ for copolyesters deceased as concentration of HPPDP in copolyesters increased.

Table 4.5 Dynamic mechanical properties of selected copolyesters (PE-IV and V)

Polyester	Composition of Diol, mol%		Composition of TPC, mol%	T_g (°C)	E’(Pa)
	BPA	HPPDP			
PE-IV	75	25	100	133	0.75 x 10^9
PE-V	85	15	100	155	1.2 x 10^9

4.5 Conclusions

1. A series of polyesters containing ether linkages in the main chain and pendent pentadecyl chains was synthesized from HPPDP and aromatic diacid chlorides by phase-transfer catalysed interfacial polycondensation. A series of copolyesters was synthesized from a mixture of HPPDP and BPA with terephthalic acid chloride.
2. (Co)polyesters with inherent viscosities in the range 0.70-1.21 dL/g were obtained. (Co)polyesters were soluble in chloroform, dichloromethane, pyridine and *m*-cresol at room temperature. Tough, transparent and flexible films could be cast from solutions of (co)polyesters in chloroform.
3. X-Ray diffractograms showed that polyesters containing pendent pentadecyl chains were amorphous in nature.
4. T_{10} values for (co)polyesters were in the range 425-455 °C indicating their good thermal stability. A drop in T_g values (27-202 °C) and storage modulus (E') of (co)polyesters was observed due to the presence of flexible pentadecyl chains which act as packing disruptive groups.

References

1. P. E. Cassidy, *Thermally Stable Polymers, New York: Dekker,*, 1980.
2. M. Arroyo, in *Handbook of Thermoplastics*, ed. O. Olabisi, Marcel Dekker Inc., New York, 1997, pp. 599-608.
3. S. V. Vinogradova, V. A. Vasnev and P. M. Valetskii, *Russ. Chem. Rev.*, 1994, **63**, 833.
4. D.-J. Liaw, B.-Y. Liaw, J.-J. Hsu and Y.-C. Cheng, *J. Polym. Sci. Part A: Polym. Chem.*, 2000, **38**, 4451-4456.
5. S.-H. Hsiao and H.-W. Chiang, *E. Polym. J.*, 2004, **40**, 1691-1697.
6. M. D. Joshi, A. Sarkar, O. S. Yemul, P. P. Wadgaonkar, S. V. Lonikar and N. N. Maldar, *J. Appl. Polym. Sci.*, 1997, **64**, 1329-1335.
7. S. S. Vibhute, M. D. Joshi, P. P. Wadgaonkar, A. S. Patil and N. N. Maldar, *J. Polym. Sci. Part A: Polym. Chem.*, 1997, **35**, 3227-3234.
8. Y.-T. Chern, *Macromolecules*, 1995, **28**, 5561-5566.
9. Y.-T. Chern and C.-M. Huang, *Polymer*, 1998, **39**, 2325-2329.
10. S. H. Hsiao and J. H. Chiou, *Polym. J.*, 2001, **33**, 95-101.
11. S.-H. Hsiao and H.-Y. Chang, *J. Polym. Res.*, 1995, **2**, 99-108.
12. S. Watanabe, A. Kobayashi, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 1994, **32**, 909-915.
13. S. Watanabe, H. Murayama, M. Murata, Y. Masuda, M. Tanabe and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 2229-2235.
14. H.-J. Jeong, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 1991, **29**, 1293-1299.
15. B. Tamami, H. Yeganeh and G. Kohmareh, *Eur. Polym. J.*, 2004, **40**, 1651.
16. R. D. Shingte, *Thesis submitted to University of Pune, Pune, India.*, 2006.
17. D. H. Wang, S. Z. D. Cheng and F. W. Harris, *Polymer*, 2008, **49**, 3020-3028.
18. P. N. Honkhambe, M. V. Biyani, N. S. Bhairamadgi, P. P. Wadgaonkar and M. M. Salunkhe, *J. Appl. Polym. Sci.*, 2010, **117**, 2545-2552.
19. P. N. Honkhambe, N. S. Bhairamadgi, M. V. Biyani, P. P. Wadgaonkar and M. M. Salunkhe, *Eur. Polym. J.*, 2010, **46**, 709-718.
20. O. Kreye, S. Oelmann and M. A. R. Meier, *Macromol. Chem. Phys.*, 2014, **214**, 1452-1464.
21. C. H. R. M. Wilsens, B. A. J. Noordover and S. Rastogi, *Polymer*, 2014, **55**, 2432-2439.

22. A. S. More, P. V. Naik, K. P. Kumbhar and P. P. Wadgaonkar, *Polym. Int.*, 2010, **59**, 1408-1414.
23. A. S. More, S. K. Pasale, P. N. Honkhambe and P. P. Wadgaonkar, *J. App. Polym. Sci.*, **121**, 3689-3695.
24. A. S. More, S. K. Pasale and P. P. Wadgaonkar, *Eur. Polym. J.* , 2010, **46**, 557-567.
25. N. V. Sadavarte, C. V. Avadhani, P. V. Naik and P. P. Wadgaonkar, *Eur. Polym. J.*, 2010 **46**, 1307-1315.
26. N. V. Sadavarte, M. R. Halhalli, C. V. Avadhani and P. P. Wadgaonkar, *Eur. Polym. J.*, 2009 **45** 582-589
27. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, 2014, **5**, 3142-3162.
28. N. V. Sadavarte, S. S. Patil, C. V. Avadhani and P. P. Wadgaonkar, *High Perform. Polym.*, 2013, **25**, 735-743.
29. A. S. More, P. S. Sane, A. S. Patil and P. P. Wadgaonkar, *Polym. Degrad. Stab.*, 2010, **95**, 1727-1735.
30. N. V. Sadavarte, C. V. Avadhani and P. P. Wadgaonkar, *High Perform. Polym.*, 2011, **23**, 494-505.
31. P. Liu, L. Zeng, G. Ye and J. Xu, *J. Polym. Res.*, 2013, **20**, 1-9.
32. W. Podkoscielny and D. Wdowicka, *J. Appl. Polym. Sci.*, 1991, **43**, 2213-2217.
33. A. D. Kulkarni, B. V. Tawade and P. P. Wadgaonkar, *High Perform. Polym.*, 2014, **25**, 278-286.

Chapter 5

Synthesis and Characterization of Polyimides Containing Multiple Ether Linkages and Pendent Pentadecyl Chains

5.1 Introduction

Aromatic polyimides are an important class of high performance/ high temperature polymers and are recognized for their excellent thermo-mechanical and electrical properties. They have wide applications in automobile, aerospace, electronic packaging, fuel cells, gas separation, adhesives, etc.[1-6] In spite of their excellent properties, many polyimides tend to be insoluble in most of the organic solvents and have high softening temperatures because of rigid backbone as well as strong interchain interactions due to charge transfer complex formation which poses problems during processing.[7-9] Therefore, several approaches have been utilized to improve their melt and/or solution processability without losing their advantageous properties.[10] The three common approaches involved structural modifications resulting into tailoring of properties and these are i) introduction of hinge atoms, flexible or kinked linkages in the polymer backbone,[11-19] ii) introduction of bulky substituent or flexible pendent group[20-24] and iii) disruption of symmetry and regularity through copolymerization.[25] Thus, a number of attempts have been made towards design and synthesis of new diamines and dianhydrides containing flexiblizing groups either in the main structure or as pendent group, bulky groups, cardo, spiro or multicyclic structures, and molecular asymmetry for producing a variety of polyimides with improved solubility and processabilty.[26-32]

The approach concerning synthesis of monomers containing flexible ether linkages is of particular interest because it provides lower internal energy of rotation and also disrupts the linear progression in the polymer backbone. Thus, the introduction of multiple ether linkages resulted into polyimides with enhanced melt processability, low dielectric constants and good optical transparency. Alternatively, organo-soluble polyimides with pendent long-chain alkyl groups have been reported.[33-42] The introduction of pendent alkyl chains onto rigid backbone of polyimide causes reduced coplanarity of aromatic rings and disrupts orientation of macromolecular chains, thus causing a drop in T_g. Also pendent alkyl group acts as an additional handle for interaction with the solvent which results in improvement in solubility of the rigid polyimides.

In the last few years, our research group has been focusing on the synthesis of processable polyimides derived from monomers based on CNSL.[12, 43, 44] In line with these studies, in the present work we would like to study the effect of incorporation of pendent pentadecyl chain along with multiple ether linkages on the processing characteristics of polyimides. The flexibilizing ether moieties are expected to impart melt processing characteristics to polyimides and so is the effect of pentadecyl chains. Towards this end, we utilized a new aromatic diamine namely 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline (APDPPA) for synthesis of polyetherimides by polycondensation with 3,3’,4,4’-oxydiphthalic anhydride (ODPA), 4,4’-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA) and 3,3’,4,4’-biphenyl tetracarboxylic dianhydride (BPDA) by one-step high temperature solution method. Polyetherimides were characterized by inherent viscosity measurements, FTIR, ^{1}H NMR, ^{13}C NMR spectroscopy, gel permeation chromatography, solubility tests, wide angle X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and UV-Vis spectroscopy. The effect of multiple ether linkages and pendent pentadecyl chains on thermal and solubility characteristics has been evaluated.

5.2 Experimental

5.2.1 Materials

4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline (APDPPA) was synthesized as described in **Chapter 3**. The dianhydrides 3,3’,4,4’-oxydiphthalic anhydride (ODPA), 4,4’-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA) and 3,3’,4,4’-biphenyl tetracarboxylic dianhydride (BPDA), all received from Aldrich, USA were sublimed before use. Isoquinoline and calcium chloride were received from Rankem, Mumbai, India and were used as received. Dichloromethane and *m*-cresol, both from S. D. Fine Chem., India were dried and distilled according to the reported procedures.[45]

5.2.2 Measurements

Inherent viscosity (η_{inh}) of polyetherimides was determined using an Ubbelhode suspended level viscometer at a concentration of 0.5 % (w/v) solution of polymer in chloroform at 30±0.1°C.

η_{inh} was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

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

Molecular weights of polyetherimides were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5Å to 50 Å), Detector - RI, room temperature.

Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter.

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

^{1}H NMR spectra of polyetherimides were recorded on Bruker 500 MHz spectrometer at resonance frequency of 500 MHz using $CDCl_3$ as a solvent.

The solubility of polyetherimides was determined at 3 % concentration (w/v) in various solvents at room temperature or on heating.

X-Ray diffraction patterns of polyetherimides were obtained on a Rigaku MicroMax-007HF X-ray diffractometer operating at 40 kV and 30 mA. Dried polymer films or powder samples were exposed to the X-ray beam for 3 minutes and the scattering pattern was imaged by Rigaku R-AXIS IV++ area detector. The 2D pattern was converted to 1D pattern by Rigaku 2DP software.

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

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10 °C / minute in nitrogen atmosphere.

UV-Visible spectra of polyetherimide solutions in chloroform were recorded with Perkin-Elmer Lambda 950 UV/Vis Spectrometer in transmittance mode.

5.3 Synthesis of polyimides

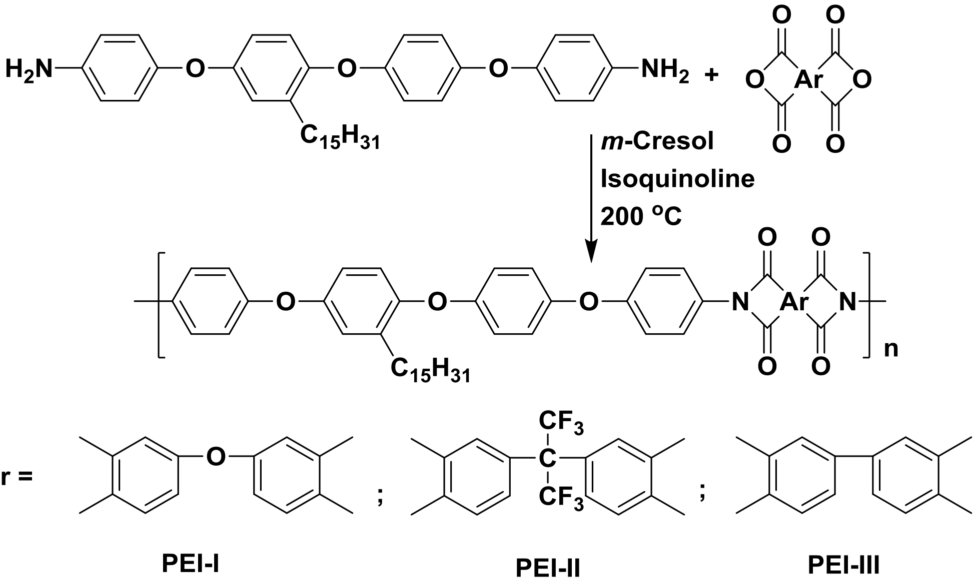
Polyetherimides were synthesized by one-step high temperature solution polycondensation in *m*-cresol. A representative procedure for the synthesis of polyimides is described below:

Into a 25 mL three-necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a calcium chloride guard tube were added APDPPA (0.594 g, 1 mmol) and freshly distilled *m*-cresol (7 mL). To the homogeneous solution, ODPA (0.310 g, 1 mmol) was added in portions at room temperature. The reaction mixture was stirred for 3 h at room temperature. The temperature was then raised to 200 °C and the reaction mixture was stirred for 6 h at that temperature. The polymerization reaction was performed under gentle stream of nitrogen so that water formed during imidization was continuously flown away by the nitrogen stream. The reaction mixture was cooled to room temperature and was poured into excess methanol. The precipitated polymer was washed with methanol to remove *m*-cresol, the polymer was dissolved into chloroform, reprecipitated into methanol, filtered and was dried at 80 °C for 24 h under reduced pressure.

5.4 Results and Discussion

5.4.1 Synthesis of polyetherimides

Three new polyetherimides were synthesized by one-step high temperature solution polycondensation of APDPPA with three aromatic dianhydrides namely, 3,3’,4,4’-oxydiphthalic anhydride (ODPA), 4,4’-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA) and 3,3’,4,4’-biphenyl tetracarboxylic dianhydride (BPDA) in *m*-cresol in the presence of isoquinoline as a catalyst (**Scheme 5.1**). Results of polymerization reactions are summarized in **Table 5.1.**



Scheme 5.1 Synthesis of polyetherimides from APDPPA and aromatic dianhydrides

Table 5.1 Synthesis of polyetherimides from APDPPA and aromatic dianhydrides

Polyetherimide	**Diamine**	**Dianhydride**	**η_{inh} (dL/g)[a]**	**GPC data[b]**		
				M_n	**M_w**	**PDI**
PEI-I	APDPPA	ODPA	0.70	24,500	48,500	2.0
PEI-II	APDPPA	6-FDA	0.67	29,700	67,900	2.2
PEI-III	APDPPA	BPDA	0.66	17,100	48,700	2.9

a: η_{inh} was measured with 0.5% (w/v) solution of polyetherimides in chloroform at 30 ± 0.1°C

b: GPC in chloroform, calibration standard: polystyrene

Polyetherimides were obtained in almost quantitative and η_{inh} values were in the range 0.66-0.70 dL/g. The results of GPC measurements of polyetherimides in chloroform are presented in **Table 5.1**. The number average molecular weights (Mn) were in the range 17,100 to 29,700 with polydispersity index (Mw/Mn) in the range 2.0-2.9. η_{inh} Values and GPC data indicated the formation of reasonably high molecular weight polymers. However, the molecular weight values provided by GPC are not to be considered absolute as the GPC was calibrated using polystyrene standards. Tough, transparent, and flexible films of polyetherimides could be cast from their chloroform solutions.

5.4.2 Structural characterization

The formation of polyetherimides was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

A representative FT-IR spectrum of polyetherimide (PEI-III) based on APDPPA and BPDA is reproduced in **Figure 5.1.**

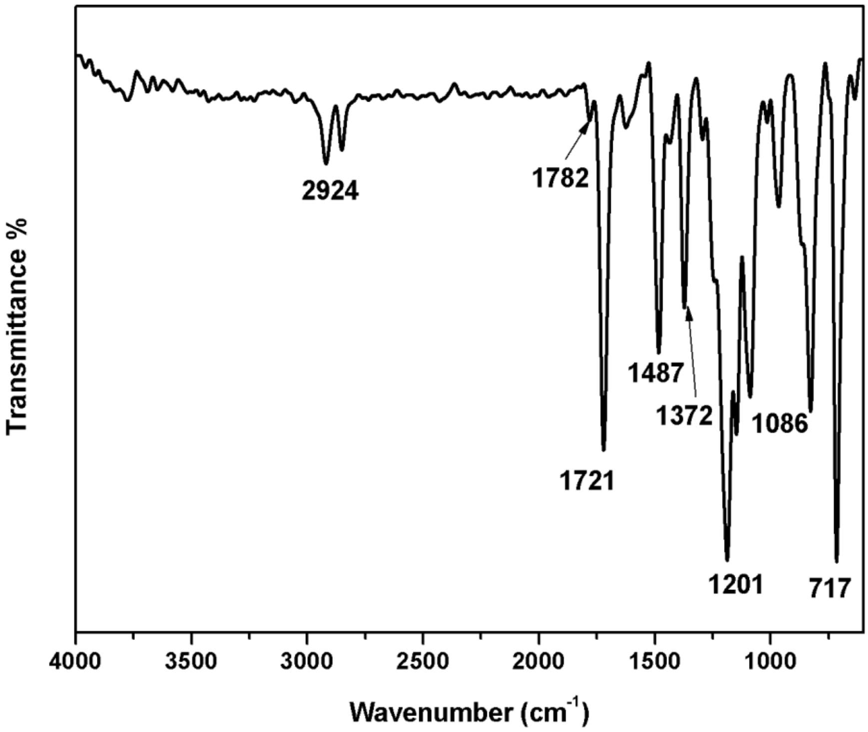


Figure 5.1 FT-IR spectrum of polyetherimide (PEI-III) derived from APDPPA and BPDA

FT-IR spectrum of PEI-III showed the characteristic absorptions of imide ring at 1782 cm^{-1} (asymmetric stretching of the carbonyl) and 1721 cm^{-1} (symmetric stretching of carbonyl) and C-N bond stretching at 1372 cm^{-1} as well as bending at 717 cm^{-1}. The absorption band at 1086 cm^{-1} is due to the imide ring deformation. In addition, absorption band at 1201 cm^{-1} attributed to aromatic ether (Ar-O-Ar) stretching was also observed.

^{1}H NMR spectrum of polyetherimide (PEI-I) derived from APDPPA and ODPA is reproduced in **Figure 5.2.**

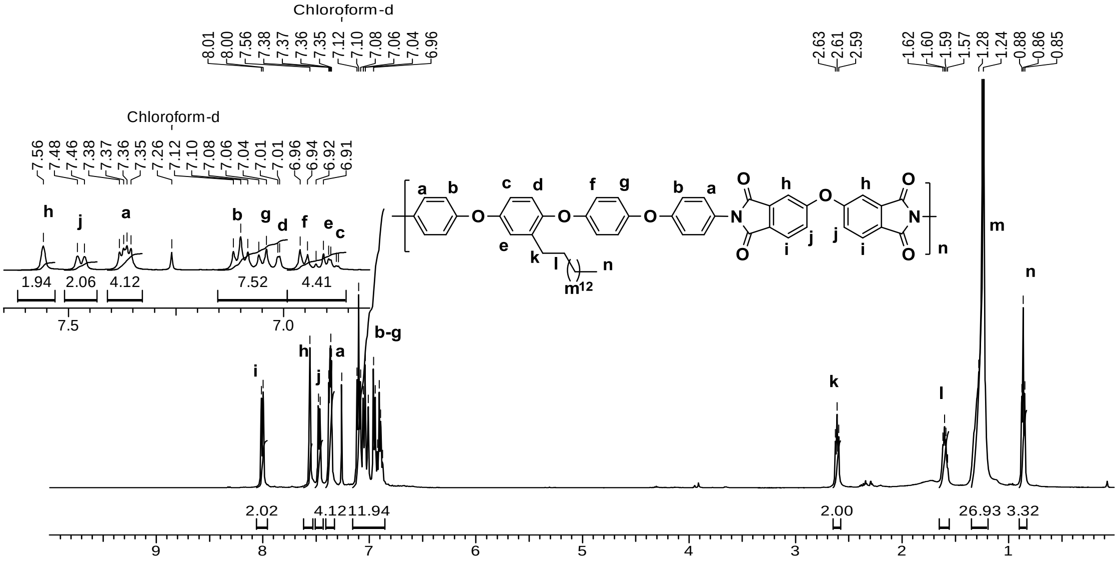


Figure 5.2 ^{1}H NMR spectrum (in $CDCl_3$) of polyetherimide (PEI-I) derived from APDPPA and ODPA

In ^{1}H NMR spectrum, proton *meta* to ethereal oxygen of ODPA moiety exhibited a doublet at 8.0 δ ppm. The remaining protons of ODPA, h and j, appeared as a singlet 7.56 δ ppm and a doublet at 7.47 δ ppm, respectively. Further, four protons *ortho* to imide nitrogen appeared as four signals in the range 7.34-7.39 δ ppm. The remaining 11 aromatic protons exhibited a multiplet in the range 6.90-7.12 δ ppm. The benzylic methylene protons appeared as a triplet at 2.61 δ ppm while other methylene protons appeared in the range 1.24-1.28 δ ppm. The terminal methyl protons appeared as a triplet at 0.86 δ ppm.

^{1}H NMR spectrum of polyetherimide (PEI-II) derived from APDPPA and 6FDA along with assignments is represented in **Figure 5.3.** In ^{1}H NMR spectrum, protons *meta* to the bridged carbon atom of dianhydride moiety appeared as a doublet at 8.03 δ ppm whereas protons h and j which are *ortho* to the bridged carbon atom exhibited a singlet at 7.94 δ ppm and a doublet at 7.87 δ ppm, respectively. The protons *ortho* to the nitrogen atom exhibited four signals in the region 7.34-7.37 δ ppm while remaining protons of diamine moiety appeared as a multiplet in the range 6.89-7.12 δ ppm. The protons of the pentadecyl chain appeared in the aliphatic region.

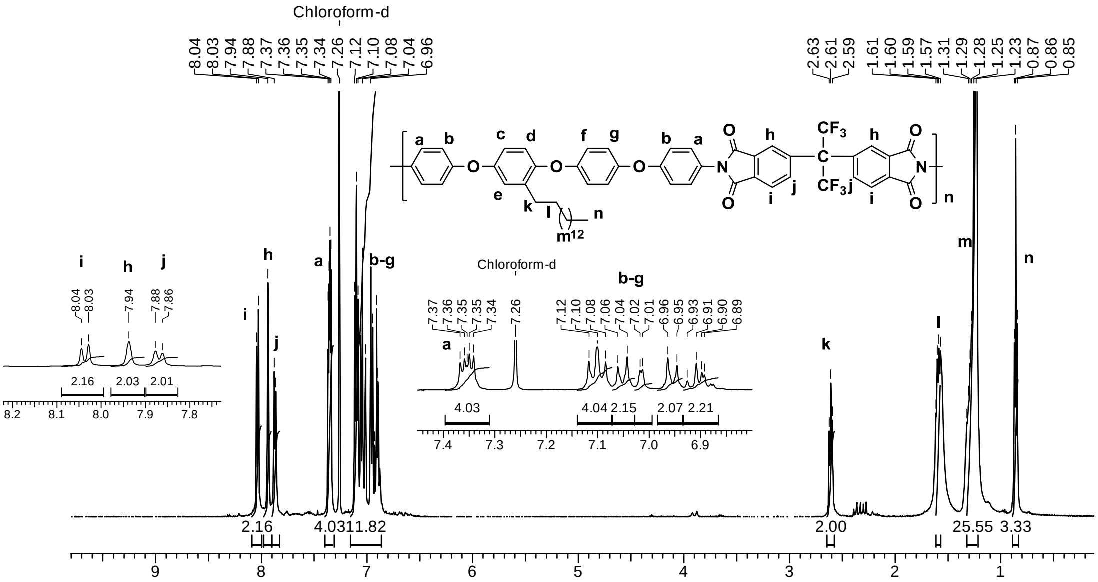


Figure 5.3 ^{1}H NMR spectrum (in $CDCl_3$) of polyetherimide (PEI-II) derived from APDPPA and 6FDA

^{1}H NMR spectrum of polyetherimide (PEI-III) derived from APDPPA and BPDA is shown in **Figure 5.4.**

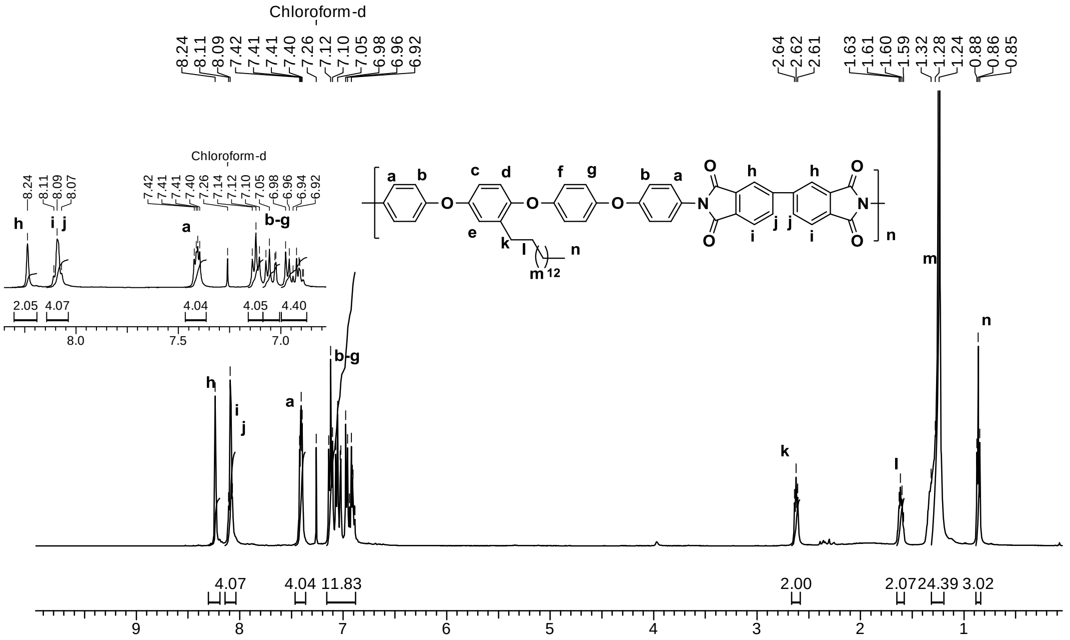


Figure 5.4 ^{1}H NMR spectrum (in $CDCl_3$) of polyetherimide (PEI-III) derived from APDPPA and BPDA

The protons h flanked by carbonyl and aromatic ring appeared as a doublet at 8.24 δ ppm whereas protons i and j exhibited a multiplet in the region 8.07-8.11 δ ppm. The four aromatic protons *ortho* to nitrogen of diamine moiety displayed four signals in the range δ 7.39-7.43 ppm. The rest of the aromatic protons of diamine exhibited multiplet in the range δ 6.92-7.12 ppm. The protons of the pentadecyl chain appeared at respective position in aliphatic region as assigned in **Figure 5.4.**

The protons *ortho* to imide nitrogen exhibited four signals which is in fact expected to show doublet only. The appearance of the multiplet could be due to the constitutional isomerism resulting from the non-symmetrical structure of diamine. Constitutional isomerism is experienced when polymers possess the same overall composition but different order of atoms or groups of atoms.[43, 46-50] It was observed and investigated for the fist-time by Pino and coworkers.[46] Their study showed that for appearance of constitutional isomerism in a polycodensate, there should at least one non-symmetric monomer used in its synthesis. Further, they have investigated the influence of constitutional isomerism on their thermal properties and crystallinity. In their work, they have systematically explained factors affecting regularity in the polycondensation such as kinetics of the reaction, ratio of the rate constant of the groups.

In the polyetherimides, the feasible 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.[51, 52] In ^{1}H NMR spectrum of polyetherimides, theoretically one would expect three doublets corresponding to protons *ortho* to imide nitrogen, if constitutional isomers were present. However, on close scrutiny of 400 MHz NMR spectra of polyetherimides the protons *ortho* to nitrogen displayed four signals only; it could be due to overlapping of the expected three doublets. The overlapping of the signals might have happened because of small differences in their δ values.

The possible structural orientations of polyetherimides are depicted in **Figure 5.5**.

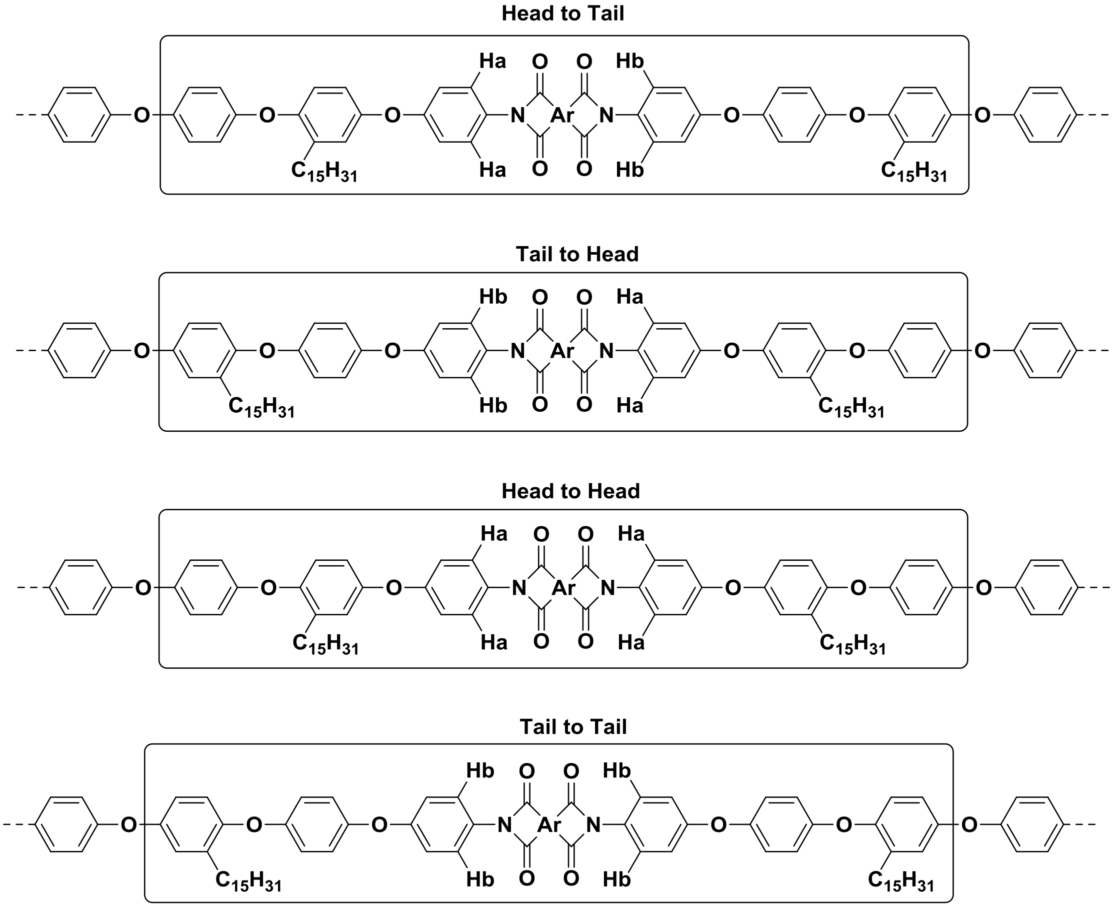


Figure 5.5 Plausible sequences in polyetherimides derived from APDPPA and aromatic dianhydrides

5.4.3 Solubility measurements

The solubility tests of polyetherimides were carried out at 3 % w/v in organic solvents at room temperature or at 50 °C. The solubility data is collected in **Table 5.2**. The literature reveals that polyimides generally show poor solubility in common organic solvents. Interestingly, polyetherimides (PEI-I, PEI-II, PEI-III) showed excellent solubility in solvents such as chloroform, dichloromethane, tetrahydrofuran, DMF, DMAc, NMP, pyridine, m-cresol and DMSO. It is worth mentioning that solubility behavior of polyetherimides is better than that of 4, 4’-oxydianiline (ODA) or 4,4'-((oxybis(4,1-phenylene))bis(oxy))dianiline (OBPBODA) based polyimides which are reported to be insoluble in common organic solvents such as chloroform and dichloromethane.[53] The improved solubility of these polyetherimides could be attributed to the combined effect of presence of multiple ether linkages, packing disruptive pendent pentadecyl chains and constitutional isomerism. These features are responsible for decrease in packing density and intermolecular interactions between polymer chains.

Table 5.2 Solubility of polyetherimides

Polymer	Dianhydride	Chloroform	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO	Acetone	n-Hexane	Toluene
PEI-I	ODPA	++	++	++	++	++	++	++	++	++	--	--	--
PEI-II	6-FDA	++	++	++	++	++	++	++	++	++	--	--	+-
PEI-III	BPDA	++	++	++	++	++	++	++	++	++	--	--	--

++ : soluble at room temperature; +- : soluble on heating; -- : insoluble on heating at 60 °C

5.4.4 X-Ray diffraction studies

The crystallinity of polyetherimides was determined by wide-angle-X-ray diffraction (WAXD) studies. X-Ray diffractograms of polyetherimides derived from APDPPA and aromatic dianhydrides are reproduced in **Figure 5.6.**

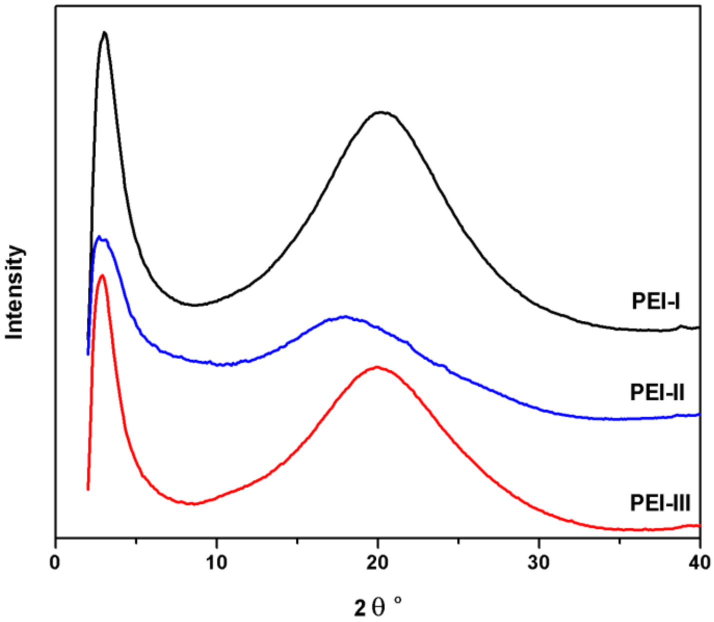


Figure 5.6 X-Ray diffractograms of polyetherimides derived from APDPPA and aromatic dianhydrides

A broad halo at about 2θ ≈ 20° was observed which indicated the amorphous nature of polymers. The amorphous nature of polyetherimides could be attributed to the presence of pendent pentadecyl chains and multiple ether linkages in the backbone. These structural features minimize the interchain interactions and restrict close packing of polymer chains, resulting in amorphous nature of polyetherimides. The amorphous nature endows polyetherimides with good solubility. However, polyetherimides derived from 4,4'-((oxybis(4,1-phenylene))bis(oxy))dianiline (OBPBODA) were found to be semicrystalline in nature[53] (e.g. polyetherimide derived from OBPBODA-ODPA showed both T_g = 204 °C and T_m = 332 °C).[54] Additionally, polyetherimides exhibited reflections in the small-angle region at 2θ ≈ 3°. This observation is reasonable because the presence of pentadecyl chain leads to the formation of layered structures. It is well known that polymers with flexible long chains strongly tend to form layered crystalline structure in the solid state.[17, 43, 44, 55-58]

5.4.5 Thermal properties

Thermal stability of polyetherimides was investigated by thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C / minute in nitrogen atmosphere **(Figure 5.7)**.

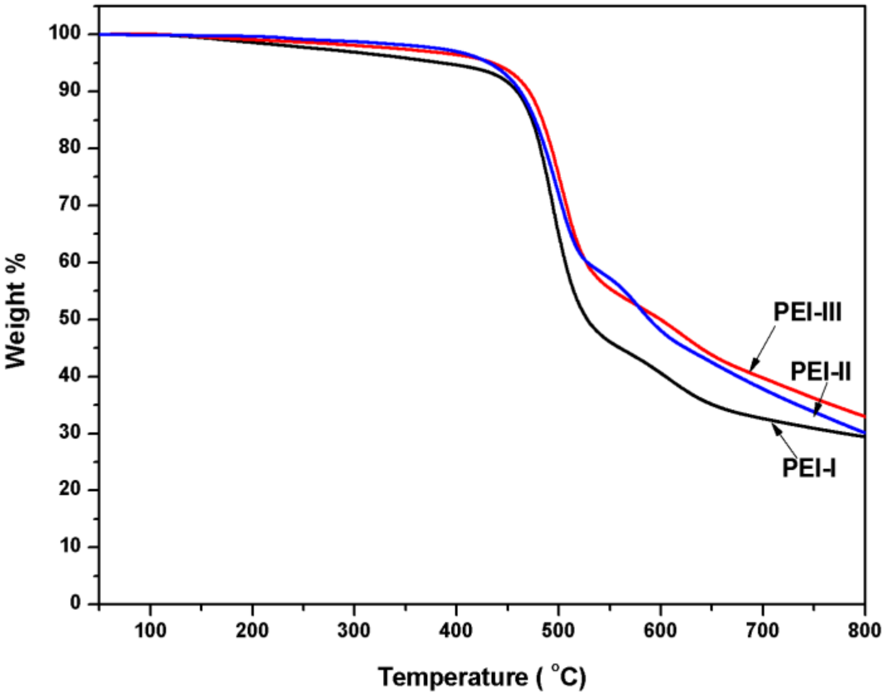
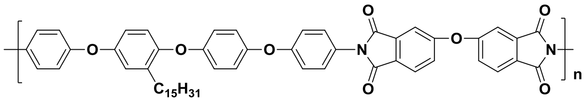
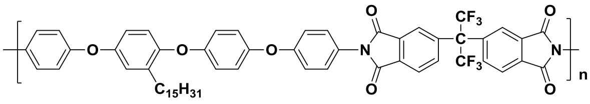
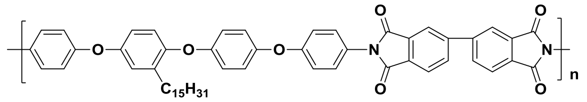


Figure 5.7 TG curves of polyetherimides derived from APDPPA and aromatic dianhydrides

The decomposition temperature at 10% weight loss (T_{10}) and char yields at 800 °C were calculated from original thermograms and the data is presented in **Table 5.3**. The T_{10} value of polymer is an important criterion for evaluation of thermal stability and the values are in the range 460-470 °C indicating their good thermal stability. The char yields / weight residues left at 800 °C were in the range 29-33 %.

Table 5.3 Thermal and optical properties of polyetherimides derived from APDPPA and aromatic dianhydrides

Polymer	Polyetherimide	T_{10} (°C)	Weight residue at 800 °C (%)	T_g (°C)	λ_o (nm)
PEI-I		460	29	113	242
PEI-II		470	33	122	240
PEI-III		460	30	131	251

Glass transition temperatures (T_g) of polyetherimides were evaluated by means differential scanning calorimetry (DSC) at a heating rate of 10 °C / min in nitrogen atmosphere and T_g values are listed in **Table 5.3**. DSC curves of polyetherimides obtained from second heating scans are represented in **Figure 5.8.** The T_g values of PEI-I, PEI-II and PEI-III were 113, 122 and 131 °C, respectively. The PEI-III has highest T_g (131 °C) as it is derived from BPDA which has rigid biphenyl moiety. Conversely, lowest T_g of PEI-I in the series could be attributed to incorporation of additional flexible ether linkages present in ODPA. The PEIs derived from APDPPA exhibited lower T_gs than that of corresponding polyimides derived from 4, 4’-oxydianiline (ODA) (T_g of polyimide derived from 4,4’-oxydianiline and ODPA is 242 °C).[54] The T_g of PEI-I (113 °C) is much lower than that of reference polyimide based on 4,4'-((oxybis(4,1-phenylene))bis(oxy))dianiline (OBPBODA) and ODPA (204 °C).[54] The drop in T_g could be attributed to decrease in chain packing due to packing disruptive effect of pentadecyl chains. Thus, the combined influence of both pentadecyl chain and multiple ether linkages causes decrease the interchain interactions and disturb close packing of polymer chains, resulting in polyetherimides with lower T_g.

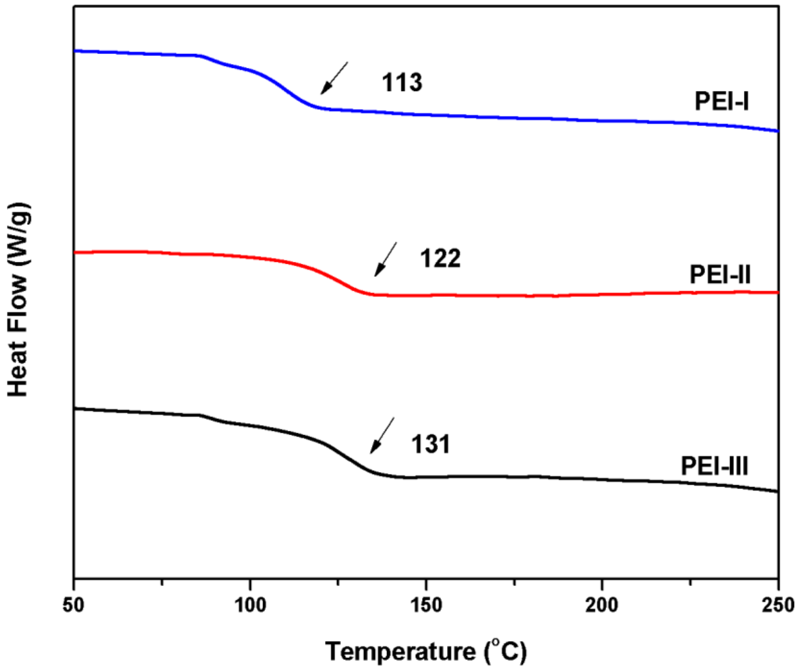


Figure 5.8 DSC curves of polyetherimides derived from APDPPA and aromatic dianhydrides

5.4.6 Optical properties

The optical properties of polyetherimides were analyzed by UV-Visible spectroscopy (**Figure 5.9)** and cut off wavelength (absorption edge, λo) values are given in **Table 5.3**.

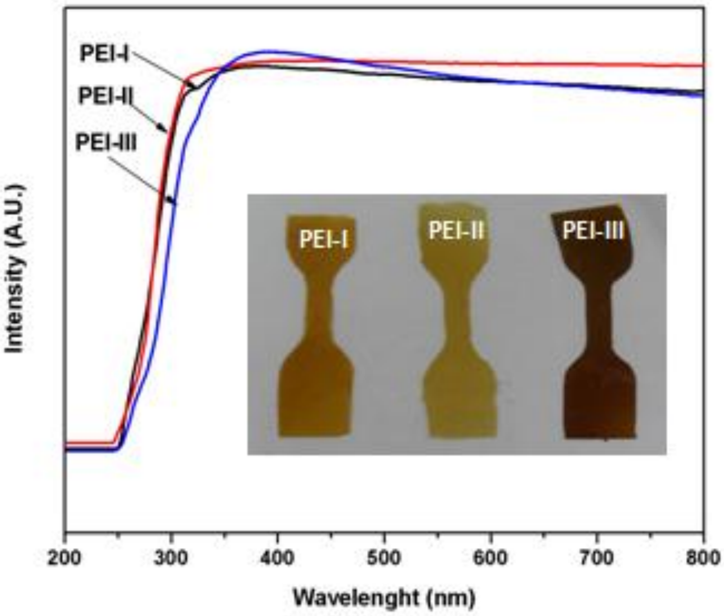


Figure 5.9 UV-Visible absorption spectra of polyetherimides derived from APDPPA and aromatic dianhydrides in $CHCl_3$ solution

The cut-off wavelength (λo) observed in UV-Visible absorption spectra is the measure of the colour intensity of polyimides. Polyetherimides exhibited shorter λo in the range 241-251 nm. Normally, polyimides show strong absorption in UV-visible spectra due to highly conjugated aromatic structures and formation of intermolecular charge-transfer complex (CTC). Most conventional polyimides have dark amber to brown coloration due to charge-transfer complex (CTC) formation which in turn is associated with electronic characteristics of monomer used in the polyimide synthesis. The colour of polyimides changes from deep to pale depending on the type of dianhydride used: BPDA > ODPA > 6-FDA, when diamine monomer is the same. The lower λo of PEI-I (242 nm) compared to that of PEI-III (251 nm) could be attributed to the presence of ether-oxygen which functions as a separator linkage and enhances chain mobility, thereby, causing reduction in CTC formation. The lowest λ_o of 240 nm of PEI-II which is based on 6-FDA is because of bulky and electron withdrawing hexafluoroisopropylidene groups which reduce the CTC formation between alternating electron donor (diamine) and electron acceptor (dianhydride) moieties.

5.5 Conclusions

1. A series of new polyetherimides containing pendent pentadecyl chains and multiple ether linkages was synthesized from 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline and commercially available aromatic dianhydrides.
2. Reasonably high molecular weight polyetherimides were formed as indicated by their inherent viscosity measurements, which were in the range 0.66-0.70 dL/g.
3. Polyetherimides showed good solubilities in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, DMF, DMAc, NMP, pyridine, *m*-cresol and DMSO.
4. Polyetherimides could be cast into tough, transparent and flexible films from chloroform solutions.
5. X-Ray diffraction analysis showed that the polyetherimides were amorphous and a reflection in small angle region indicated layered packing of pentadecyl chains.
6. DSC study demonstrated lowering of glass transition temperatures (T_g) which were in the range 113-131 °C.
7. T_{10} values of polyetherimides were in the range 460-470 °C indicating their good thermal stability.
8. The incorporation of pendent pentadecyl chains and flexible ether linkages increased gap between T_g and T_{10} of polyetherimides offering them a wider processing window and thus, the opportunities for melt processability.

References

1. K. L. Mittal, ed., *Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications*, VSP Brill, Leiden, 2009.
2. D. M. Stoakley, A. K. Stclair and C. I. Croall, *J. Appl. Polym. Sci.*, 1994, **51**, 1479-1483.
3. M. Ding, *Prog. Polym. Sci.*, 2007, **32**, 623-668.
4. H. R. Kricheldorf, J. de Abajo and J. G. de la Campa, in *Progress in Polyimide Chemistry I*, Springer Berlin Heidelberg, 1999, pp. 23-59.
5. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, eds., *Polyimides*, Blackie & Son Ltd., Glasgow and London, 1990.
6. D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai and C.-S. Ha, *Prog. Polym. Sci.*, 2012, **37**, 907-974.
7. T. L. St. Clair, in *Polyimides*, eds. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, Chapman and Hall, New York, 1990.
8. J. Salley, C. Frank, T. Miwa and R. Roginski, in *Advances in Polyimide Science and Technology*, ed. C. K. Feger, M.; Htoo, M.S., Technomic Publishing Co., Lancater, PA, 1993.
9. Y. Imai, *React. Funct. Polym.*, 1996, **30**, 3-15.
10. A. Ghosh, S. K. Sen, S. Banerjee and B. Voit, *RSC Adv.*, 2012, **2**, 5900-5926.
11. S. Mehdipour-Ataei and H. Heidari, *J. Appl. Polym. Sci.*, 2004, **91**, 22-26.
12. N. V. Sadavarte, M. R. Halhalli, C. V. Avadhani and P. P. Wadgaonkar, *Eur. Polym. J.*, 2009, **45,** 582-589
13. C. Hamciuc, E. Hamciuc, I. Sava, I. Diaconu and M. Bruma, *High Perform. Polym.*, 2000, **12**, 265-276.
14. E. Hamciuc, M. Bruma, B. Schulz and T. Kopnick, *High Perform. Polym.*, 2003, **15**, 347-359.
15. I. Bacosca, E. Hamciuc, M. Bruma and I. Ronova, *J. Iran. Chem. Soc.*, 2012, **9**, 901-910.
16. I. Sava, S. Chisca, M. Bruma and G. Lisa, *Polym. Bull.*, 2010, **65**, 363-375.
17. D. H. Wang, Z. Shen, M. Guo, S. Z. D. Cheng and F. W. Harris, *Macromolecules*, 2007, **40**, 889-900.
18. C. S. Wang and T. S. Leu, *Polymer*, 2000, **41**, 3581-3591.
19. L. Wang, P. Chang and C.-L. Cheng, *J. Appl. Polym. Sci.*, 2006, **100**, 4672-4678.

20. A. Ghosh and S. Banerjee, *High Perform. Polym.*, 2009, **21**, 173-186.
21. E. M. Maya, A. E. Lozano, J. de Abajo and J. G. de la Campa, *Polym. Degrad. Stab.*, 2007, **92**, 2294-2299.
22. S. Mehdipour-Ataei and Y. Nazari, *J. Appl. Polym. Sci.*, 2012, **124**, 2891-2901.
23. M. Ghaemy and M. Barghamadi, *J. Appl. Polym. Sci.*, 2009, **112**, 815-821.
24. C. Wang, X. Zhao, G. Li and J. Jiang, *Polym. Degrad. Stab.*, 2009, **94**, 1746-1753.
25. F. W. Harris and L. H. Lanier, in *Structure-Solubility Relationships in Polymers*, eds. F. W. Harris and R. B. Seymour, Academic Press, New York, 1997.
26. D. J. Liaw, B. Y. Liaw and C. W. Yu, *Polymer*, 2001, **42**, 5175-5179.
27. D.-J. Liaw and B.-Y. Liaw, *Polym J*, 1999, **31**, 1270-1273.
28. D.-J. Liaw, B.-Y. Liaw, L.-J. Li, B. Sillion, R. Mercier, R. Thiria and H. Sekiguchi, *Chem. Mater.*, 1998, **10**, 734-739.
29. R. R. Pal, P. S. Patil, R. T. Dere, M. M. Salunkhe, N. N. Maldar and P. P. Wadgaonkar, *J. Appl. Polym. Sci.*, 2005, **97**, 1377-1384.
30. F. Akutsu, G. Saito, M. Miyamoto, Y. Kasashima, M. Inoki and K. Naruchi, *Macromol. Chem. Phys.*, 1996, **197**, 2239-2245.
31. H. Zhao, G. Chen, Y. Zhou, X. Li and X. Fang, *J. Appl. Polym. Sci.*, 2015, **132**, DOI: 10.1002/app.42317.
32. I. S. Chung and S. Y. Kim, *Macromolecules*, 2000, **33**, 3190-3193.
33. Y. Tsuda, K. Kanegae and S. Yasukouchi, *Polym. J.*, 2000, **32**, 941-947.
34. Y. Tsuda, T. Kawauchi, N. Hiyoshi and S. Mataka, *Polym. J.*, 2000, **32**, 594-601.
35. Y. Tsuda, M. Kojima, T. Matsuda and J. M. Oh, *Polym. J*, 2008, **40**, 354-366.
36. Y. Tsuda, M. Kojima and J. M. Oh, *Polym. J*, 2006, **38**, 1043-1054.
37. Y. Tsuda, J. M. Oh and R. Kuwahara, *Int. J. Mol.Sci.*, 2009, **10**, 5031-5053.
38. A. Sarkar, *Ph. D. Dissertation, University of Pune, Pune, India,*, 2005.
39. J. K. Lee, S. J. Lee, J. C. Jung, W.-C. Zin, T. Chang and M. Ree, *Polym. Adv. Technol.*, 2006, **17**, 444-452.
40. K. H. Lee and J. C. Jung, *Polym. Bull.*, 1998, **40**, 407-414.
41. S. J. Lee, J. C. Jung, S. W. Lee and M. Ree, *J. Polym. Sci. Part A: Polym. Chem.*, 2004, **42**, 3130-3142.

42. Y. J. Lee, J. G. Choi, I.-k. Song, J. M. Oh and M. H. Yi, *Polymer*, 2006, **47**, 1555-1562.
43. N. V. Sadavarte, C. V. Avadhani, P. V. Naik and P. P. Wadgaonkar, *Eur. Polym. J.*, 2010 **46**, 1307-1315.
44. A. S. More, A. S. Patil and P. P. Wadgaonkar, *Polym. Degrad. Stab.*, 2010, **95,** 837-844.
45. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals; Pergamon Press: New York*, 1989.
46. P. Pino, G. P. Lorenzi, U. W. Suter, P. G. Casartelli, A. Steinmann, F. J. Bonner and J. A. Quiroga, *Macromolecules*, 1978, **11**, 624-626.
47. F. T. Gentile and U. W. Suter, *Die Makromol. Chem.*, 1991, **192**, 663-671.
48. R. R. Pal, P. S. Patil, M. M. Salunkhe, N. N. Maldar and P. P. Wadgaonkar, *Eur. Polym. J.*, 2009, **45**, 953-959.
49. A. S. More, P. S. Sane, A. S. Patil and P. P. Wadgaonkar, *Polym. Degrad. Stab.* , 2010, **95**, 1727-1735.
50. N. V. Sadavarte, C. V. Avadhani and P. P. Wadgaonkar, *High Perform. Polym.*, 2011, **23**, 494-505.
51. P. Thiruvasagam, *J. Polym. Res.*, 2012, **19**, 1-9.
52. P. Thiruvasagam, *Des. Monomers and Polym.*, 2014, **17**, 166-175.
53. T. J. Dingemans, E. Mendes, J. J. Hinkley, E. S. Weiser and T. L. StClair, *Macromolecules*, 2008, **41**, 2474-2483.
54. S. Tamai, A. Yamaguchi and M. Ohta, *Polymer*, 1996, **37**, 3683-3692.
55. R. Duran, M. Ballauff, M. Wenzel and G. Wegner, *Macromolecules*, 1988, **21**, 2897-2899.
56. A. Sarkar, A. S. More, P. P. Wadgaonkar, G. Jic Shin and J. Chul Jung, *J. Appl. Polym. Sci.*, 2007, **105**, 1793-1801.
57. D. Kim and J. Jung, *Polym. Bull.*, 2003, **50**, 311-318.
58. Y. S. Kim and J. C. Jung, *J. Polym. Sci. Part A: Polym. Chem.*, 2002, **40**, 1764-1774.

Chapter 6

Synthesis and Characterization of Polyhydrazides and Poly(1,3,4-oxadiazole)s Containing Multiple Ether Linkages and Pendent Pentadecyl Chains

6.1 Introduction

Polyhydrazides are interesting polymeric materials because they have wide applications as fibers and membranes due to their excellent dyeability, improved elasticity and fair absorption characteristics. Furthermore, polyhydrazides serve as precursors to poly(1,3,4-oxadiazole)s and polytriazoles. Poly(1,3,4-oxadiazole)s are an useful class of high performance polymers which find wide applications as polymer light emitting diodes (PLEDs) and other polymer electronic devices by virtue of their opto-electronic properties.[1-19]

Regrettably, poly(1,3,4-oxadiazole)s exhibit poor organosolubility and/or brittleness which causes the difficulties in their processing. There are various approaches utilized for improving the solubility and decreasing the glass transition temperature (T_g) resulting into processable poly(1,3,4-oxadiazole)s. These include: i) incorporation of flexible linkages into the polymer backbone and ii) introduction of bulky pendent group or flexible long chains onto the polymer backbone. A survey of literature revealed that incorporation of long flexible side chains and flexible ether linkages are more effective to improve processability of poly(1,3,4-oxadiazole)s.[20-39] These structural features are responsible for reducing interchain interactions and decreasing internal energy of rotation leading to lowering of thermal transition temperatures (T_g and T_m).

We report herein the synthesis of a series of polyhydrazides and poly(1,3,4-oxadiazole)s containing multiple ether linkages and pendent pentadecyl chains. Polyhydrazides were obtained by polycondensation of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide and aromatic diacid chlorides which on cyclodehydration afforded poly(1,3,4-oxadiazole)s. Polyhydrazides and poly(1,3,4-oxadiazole)s were characterized by inherent viscosity measurements, FTIR, NMR spectroscopy, solubility measurements, wide angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Poly(1,3,4-oxadiazole)s were also characterized by gel permeation chromatoghaphy (GPC), UV-Visible spectroscopy (UV), photoluminescence (PL) and cyclic voltammetry analysis (CV).

6.2 Experimental

6.2.1 Materials

4-(4-(4-(4-(Hydrazinocarbonyl) phenoxy)-2-pentadecylphenoxy) phenoxy) benzohydrazide (HPPDPB) was synthesized as described in **Chapter 3**. Terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) (both, received from Aldrich, USA), were purified by distillation under reduced pressure before use. Anhydrous lithium chloride, received from Aldrich, USA, was dried at 180 °C for 8 h under reduced pressure. N,N-Dimethylacetamide (DMAc), received from Merck, India, was dried over calcium hydride and distilled under reduced pressure. Phosphorus oxychloride ($POCl_3$) (Spectrochem, Mumbai, India) was distilled under reduced pressure. All solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[40]

6.2.2 Measurements

Inherent viscosities (η_{inh}) of polyhydrazides and poly(1,3,4-oxadiazole)s was measured with 0.5 % (w/v) solution of polymer in N,N-dimethylacetamide and chloroform, respectively at $30 \pm 0.1^{o}C$ using an Ubbelhode suspended level viscometer.

η_{inh} was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

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

Molecular weights of poly(1,3,4-oxadiazole)s were measured on ThermoFinnigan make gel permeation chromatography (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5 Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter.

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

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

The solubility of poly(1,3,4-oxadiazole)s was determined at 3 wt.% concentration in various solvents at room temperature or on heating.

X-Ray diffraction patterns of polymers were obtained on a Rigaku MicroMax-007HF X-ray diffractometer operating at 40 kV and 30 mA. Dried polymer films or powder samples were exposed to the X-ray beam for 3 minutes and the scattering pattern was imaged by Rigaku R-AXIS IV++ area detector. The 2D pattern was converted to 1D pattern by Rigaku 2DP software.

Thermogravimetric analysis was performed on Perkin-Elmer STA 6000 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 10 °C / minute in nitrogen atmosphere.

UV-Visible absorption measurements were carried out on Perkin Elmer spectrophotometer while photoluminescence was recorded on Cary Eclipse VARIAN Fluorescence Spectrophotometer in chloroform solutions (~10^{-5} mol/L)

6.3 Synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s

6.3.1 Synthesis of polyhydrazides

A representative procedure for the synthesis of polyhydrazides is described below:

Into a 50 mL two necked round bottom flask equipped with a calcium chloride guard tube, a nitrogen inlet and a magnetic stirring bar were placed HPPDPB (500 mg, 0.735 mmol) and N,N-dimethylacetamide (10 mL) containing LiCl (500 mg). The reaction mixture was cooled to 0 °C. Terephthalic acid chloride (149 mg, 0.735 mmol) was added to the reaction mixture. The reaction was carried out at 0 °C for 2 h and then at room temperature under stirring for 12 h. At the end of the reaction time, the viscous solution formed was poured into aqueous methanol and the precipitated polymer was filtered and washed several times with water and then with methanol. The polymer was dried at 60 °C under reduced pressure.

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

6.3.2 Synthesis of poly(1,3,4-oxadiazole)s

A representative procedure for the synthesis of poly(1,3,4-oxadiazole)s is described below:

Into a 50 mL two necked round bottom flask equipped with a reflux condenser, a nitrogen inlet and a magnetic stirring bar were placed polyhydrazide (derived from HPPDPB) (400 mg) and $POCl_3$ (20 mL). The reaction mixture was refluxed for 12 h under nitrogen atmosphere. The clear solution was slowly poured into aqueous methanol. The precipitated polymer was filtered, washed several times with water and then with methanol. Finally, the polymer was dried under reduced pressure at 50 °C for 3 h.

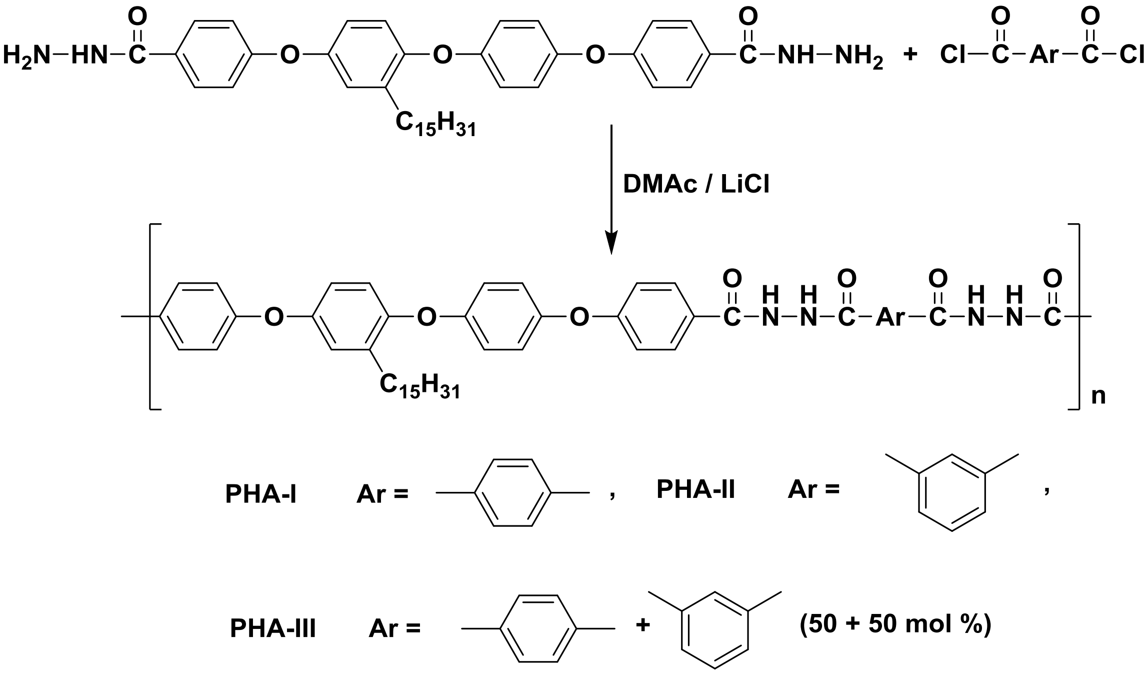
A similar procedure was followed for the synthesis of other poly(1,3,4-oxadiazole)s.

6.4 Results and Discussion

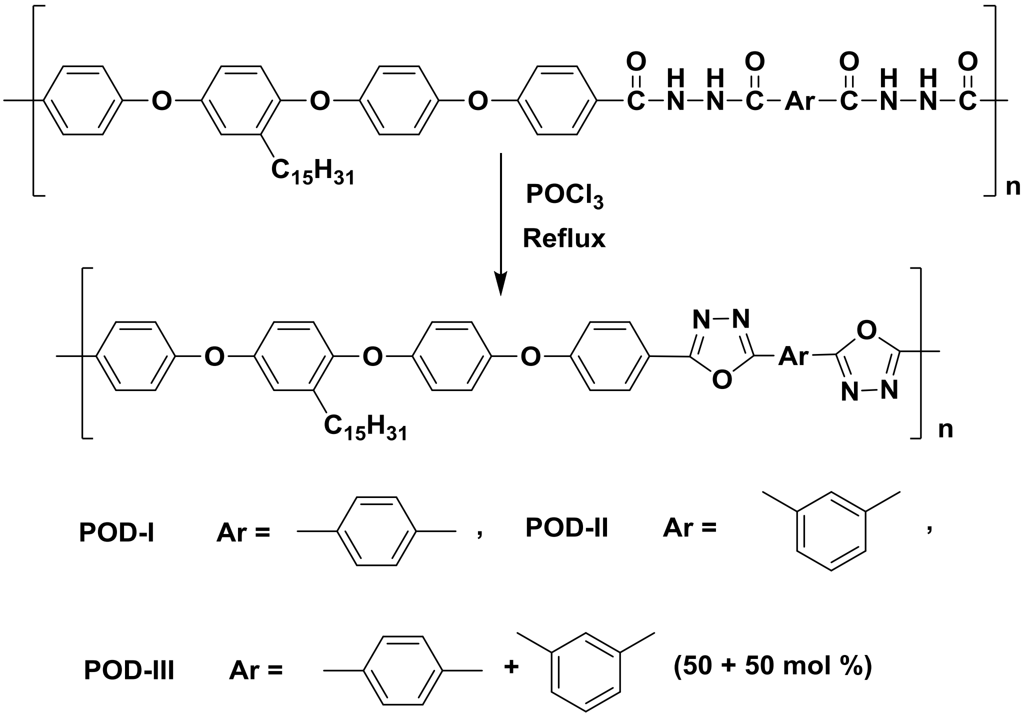
6.4.1 Synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s

In the literature, there are reports on high temperature polycondensations for polyhydrazide synthesis,[41, 42] but low temperature solution polycondensation in DMAc/ LiCl is the widely utilized method for synthesis of polyhydrazides.[43-49]

Scheme 6.1 illustrates synthesis of polyhydrazides from HPPDPB and aromatic diacid chlorides while **scheme 6.2** depicts synthesis of poly(1,3,4-oxadiazole)s by cyclodehydration of polyhydrazides using $POCl_3$.[51]



Scheme 6.1 Synthesis of polyhydrazides from HPPDPB and aromatic diacid chlorides



Scheme 6.2 Synthesis of poly(1,3,4-oxadiazole)s by cyclization of polyhydrazide

Inherent viscosities of polyhydrazides measured in DMAc were in the range 0.65-0.72 dL/g **(Table 6.1)** indicating formation of reasonably high molecular weight polymers. Inherent viscosities of poly(1,3,4-oxadiazole)s measured in chloroform were found to be in the range 0.54-0.62 dL/g. The reduction in inherent viscosity while conversion of polyhydrazide to poly(1,3,4-oxadiazole) could be attributed the different solvent used for inherent viscosity measurements and/or compactness in the chain structure of poly(1,3,4-oxadiazole)s as compared to parent polyhydrazides. Poly(1,3,4-oxadiazole)s could be cast into tough, transparent and flexible films from chloroform solutions. The GPC measurements of poly(1,3,4-oxadiazole)s in chloroform showed the molecular weights in the range 17,900-23,600 indicating the formation of reasonably high molecular weight polymers. But, GPC molecular weight values should not be considered as absolute as the polystyrene standards were used for calibration of GPC.

Table 6.1 Synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s from HPPDPB and aromatic diacid chlorides

Polymer	Diacylhydrazide	Diacid Chloride, mol%		η_{inh} (dL/g)
		TPC	IPC	
PHA-I	HPPDPB	100	0	0.72[a]
PHA-II	HPPDPB	0	100	0.69[a]
PHA-III	HPPDPB	50	50	0.65[a]
POD-I	HPPDPB	100	0	0.56[b]
POD-II	HPPDPB	0	100	0.54[b]
POD-III	HPPDPB	50	50	0.62[b]

a: η_{inh} was measured with 0.5% (w/v) solution of polyhydrazide in N,N-dimethyl acetamide at 30 ± 0.1°C.;

b: η_{inh} was measured with 0.5 % (w/v) solution of poly(1,3,4-oxadiazole) in chloroform at 30 ± 0.1 °C

6.4.2 Structural characterization

The formation of polyhydrazides and poly(1,3,4-oxadiazole)s was confirmed by FT-IR and NMR spectroscopy.

A representative FT-IR spectra of polyhydrazide (PHA-I) and poly(1,3,4-oxadiazole) (POD-I) derived from HPPDPB and TPC are shown in **Figure 6.1 and 6.2,** respectively.

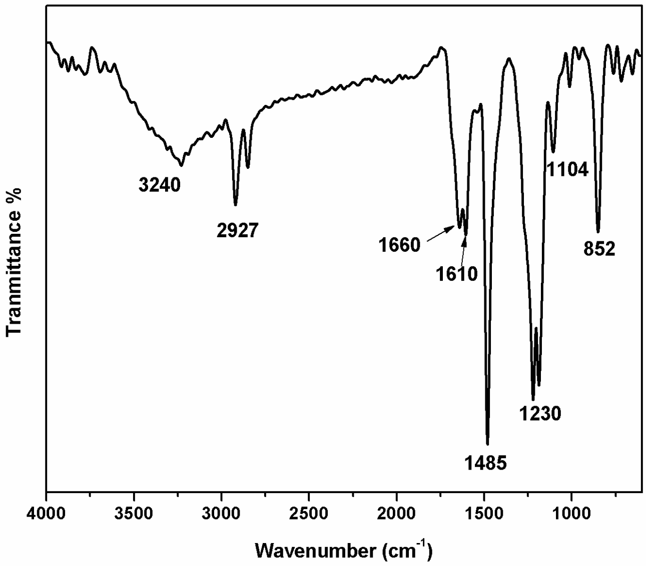


Figure 6.1 FT-IR spectrum of polyhydrazide (PHA-I) derived from HPPDPB and TPC

The conversion of PHA-I to POD-I could be confirmed from disappearance of carbonyl stretching at 1660 cm^{-1} and N-H stretching in the region 3100-3600 cm^{-1} after cyclodehydration. The absorption bands at 1230 and 1225 cm^{-1} due to Ar-O-Ar stretching were observed in PHA-I and POD-I, respectively. The characteristic bands of 1,3,4-oxadiazole ring are observed at 1071 (=C-O-C=) and 1617 (-C=N-), confirming the formation of poly(1,3,4-oxadiazole)s.

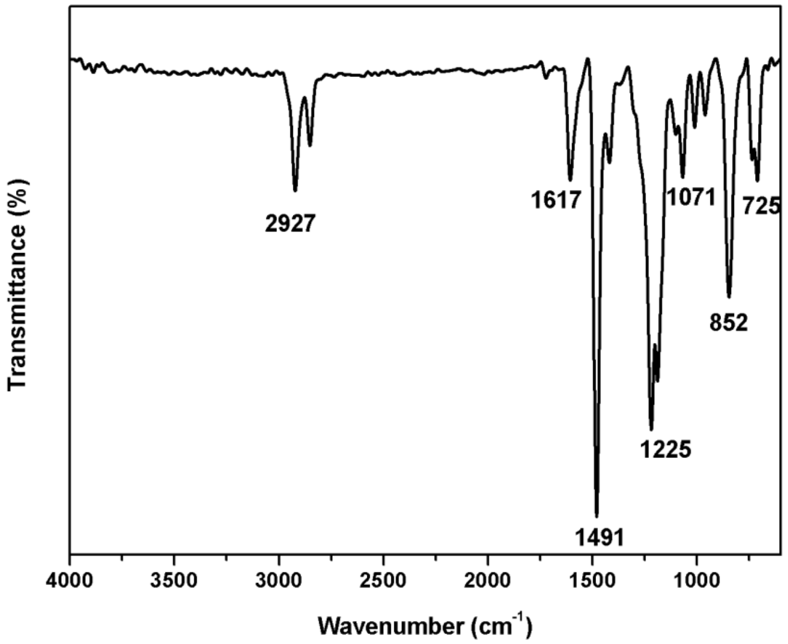


Figure 6.2 FT-IR spectrum of poly (1,3,4-oxadiazole) (POD-I) derived from HPPDPB and TPC

^{1}H NMR spectrum of polyhydrazide (PHA-I) derived from HPPDPB and TPC is represented in **Figure 6.3.** The hydrazide protons 'g' and 'h' flanked by two carbonyl groups (-CO-NH-NH-CO-) exhibited two distinct singlets at 10.52 and 10.66 δ ppm, respectively. The hydrazide proton attached to carbonyl group of TPC moiety experienced downfield shift as compared to that attached to carbonyl group of HPPBP moiety. The four TPC ring protons 'i' and four protons 'a' *ortho* to carbonyl appeared as a multiplet in the range 7.94-8.02 δ ppm. The remaining aromatic protons exhibited a multiplet in the range 7.0-7.17 δ ppm. The protons of benzylic –CH_2 exhibited a triplet at 2.58 δ ppm. The protons of methylene group β to aromatic ring appeared as a mutiplet in the range 1.51-1.59 δ ppm. The protons of remaining methylene groups exhibited a multiplet over the range 1.12-1.24 δ ppm. The protons of terminal –CH_3 group of the pentadecyl chain displayed a triplet at 0.83 δ ppm.

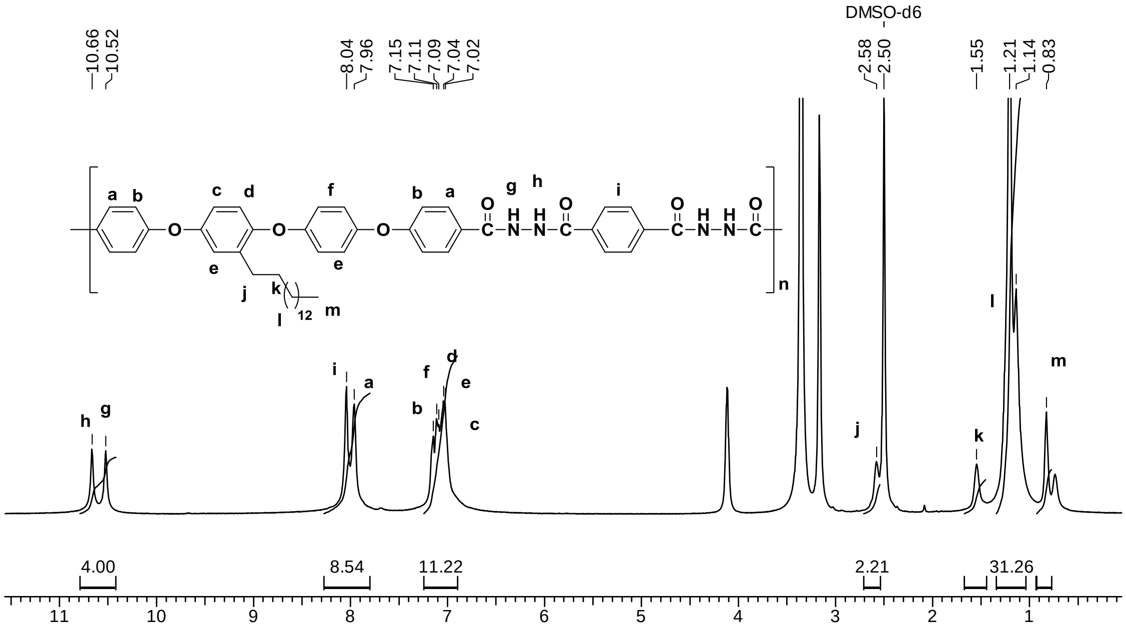


Figure 6.3 ^{1}H NMR spectrum (in DMSO-d$_6$) of polyhydrazide (PHA-I) derived from HPPDPB and TPC

^{1}H NMR spectrum of polyhydrazide (PHA-II) derived from HPPDPB and isophthaloyl chloride is depicted in **Figure 6.4.**

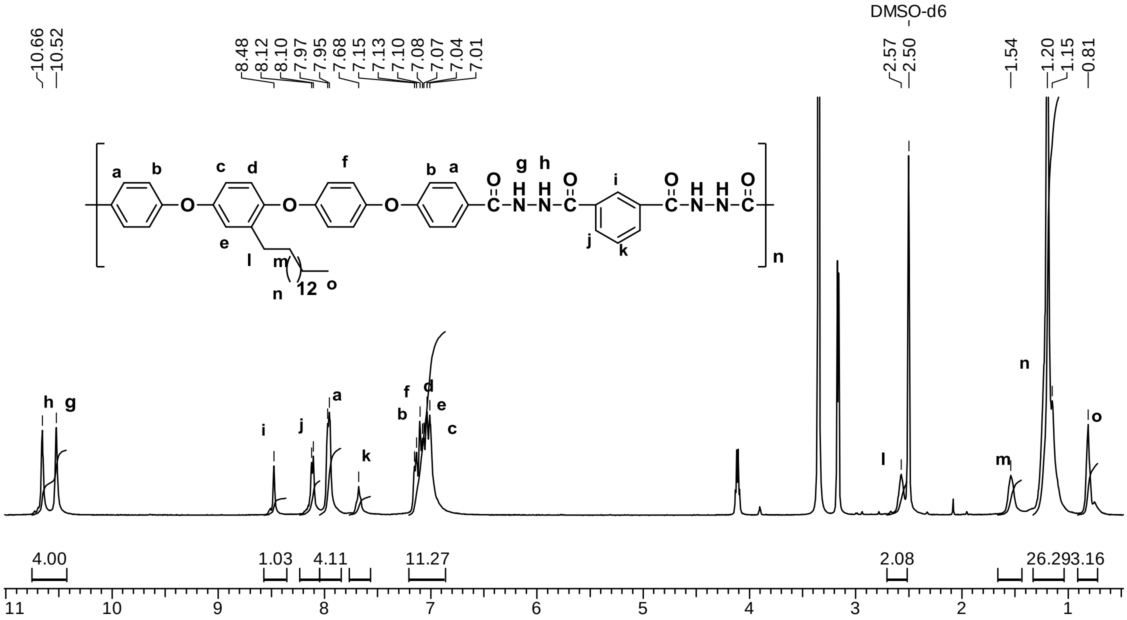


Figure 6.4 ^{1}H NMR spectrum (in DMSO-d$_6$) of polyhydrazide (PHA-II) derived from HPPDPB and IPC

In ^{1}H NMR spectrum of polyhydrazide PHA-II, the two hydrazide protons h and g appeared at 10.52 and 10.66 δ ppm and no difference in the chemical shift of hydrazide protons of PHA-I and PHA-II could be observed even though the two acid chlorides (i.e. TPC and IPC) used in their synthesis are different. The protons of IPC moiety i, j and k exhibited a singlet at 8.84 δ ppm, a doublet at 8.11 δ ppm and a broad peak at 7.63 δ ppm, respectively. The protons of HPPDPB moiety *ortho* to carbonyl group appeared as a doublet at 7.96 δ ppm and remaining aromatic protons displayed a multiplet over the range 7.01-7.15 δ ppm. The benzylic $–CH_2$ group protons exhibited a triplet at 2.57 δ ppm while protons of $–CH_2$ group β to aromatic ring appeared as a broad peak at 1.54 δ ppm. The rest of methylene group protons displayed a multiplet in the range 1.33-1.21 δ ppm and terminal $–CH_3$ group appeared as a triplet at 0.81 δ ppm.

^{1}H NMR spectrum of polyhydrazide (PHA-III) derived HPPDPB and mixture of terephthaloyl chloride and isophthaloyl chloride is presented in **Figure 6.5.**

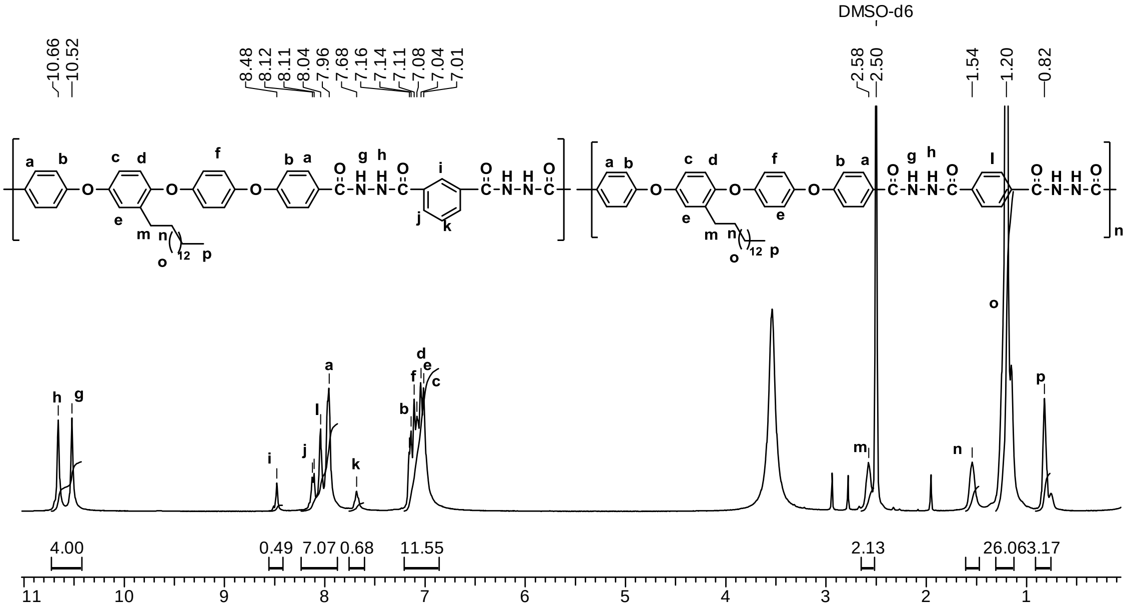


Figure 6.5 ^{1}H NMR spectrum (in DMSO-d$_6$) of polyhydrazide (PHA-III) derived from HPPDPB and mixture of TPC and IPC (50:50 mol %)

Similar to polyhydrazide PHA-I and PHA-II, ^{1}H NMR spectrum of polyhydrazide PHA-III showed the two singlets at 10.52 and 10.66 δ ppm which correspond to hydrazide protons g and h, respectively. The protons of IPC moiety i, j and k appeared as a singlet at 8.84 δ ppm, a doublet at 8.11 δ ppm and a doublet at 7.63 δ ppm, respectively. The four protons TPC ‘l’ and four protons of HPPDPB ‘a’ *ortho* to carbonyl exhibited a multiplet in the range 7.94-8.02 δ ppm. The rest of aromatic protons of HPPDPB exhibited a multiplet in the range 7.01-7.16 δ ppm. The benzylic methylene protons displayed a triplet at 2.58 δ ppm whereas protons of methylene β to aromatic ring exhibited a multiplet in the range 1.53-1.57 δ ppm. The remaining protons of methylene groups appeared as a multiplet over the range 1.15-1.25 δ ppm. The terminal methyl group exhibited a triplet at 0. 82 δ ppm.

^{1}H NMR spectrum of poly (1,3,4-oxadiazole) (POD-I) derived from HPPDPB and terephthaloyl chloride is reproduced in **Figure 6.6.**

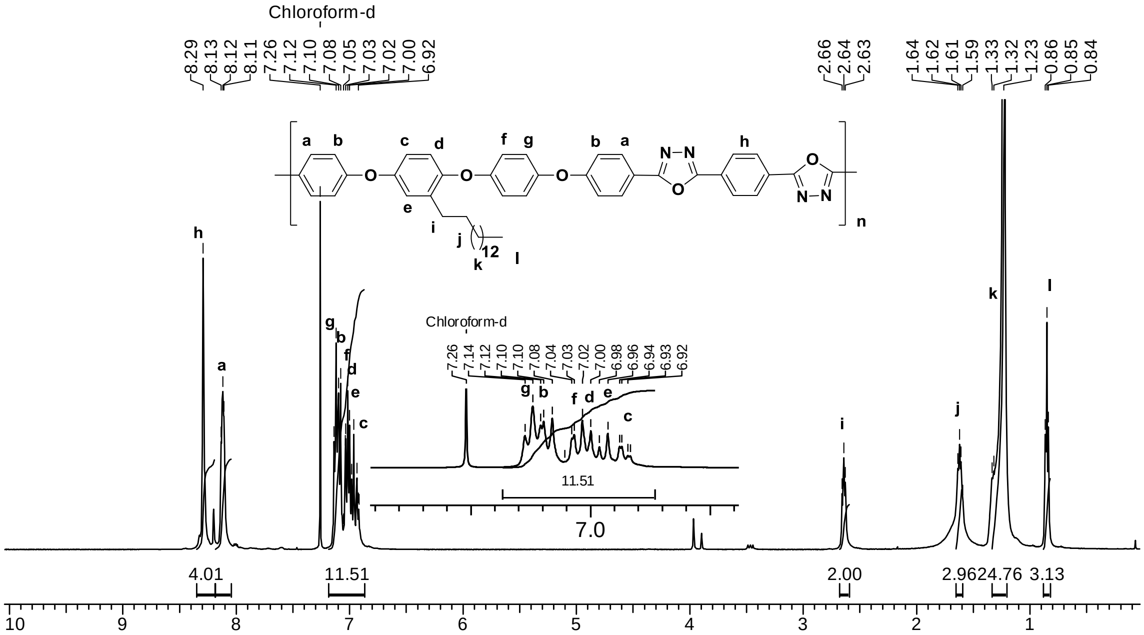


Figure 6.6 ^{1}H NMR spectrum (in CDCl$_3$) of poly(1,3,4-oxadiazole) (POD-I) derived from HPPDPB and TPC

The disappearance of two peaks corresponding to hydrazide protons (**vide Figure 6.3**) confirmed the completion of cyclization of polyhydrazides to poly(1,3,4-oxadiazole). The four protons of TPC moiety exhibited a singlet at 8.29 δ ppm. Aromatic protons 'a' *ortho* to oxadiazole ring and *meta* to the ether linkage exhibited a multiplet in the region 8.10-8.14 δ ppm while the remaining aromatic protons appeared as a multiplet in the range 6.92-7.12 δ ppm. The protons of benzylic $-CH_2$ exhibited a triplet at 2.64 δ ppm. The protons of methylene β to aromatic ring appeared as a multiplet in the range 1.57-1.66 δ ppm. The rest of methylene protons exhibited a multiplet in the range 1.21-1.35 δ ppm. Methyl group protons of the pentadecyl chain displayed a triplet at 0.85 δ ppm.

^{1}H NMR spectrum of poly(1,3,4-oxadiazole) (POD-II) derived from HPPDPB and IPC is represented in **Figure 6.7.** ^{1}H NMR spectrum confirmed the complete of cyclization of polyhydrazide to poly(1,3,4-oxadiazole) as two peaks corresponding to hydrazide protons are absent. The protons of IPC moiety h, i and j displayed a singlet at 8.85 δ ppm, a doublet at 8.31 δ ppm and a doublet at 7.72 δ ppm, respectively. Aromatic protons 'a' *ortho* to oxadiazole ring and *meta* to the ether linkage exhibited a doublet at 8.13 δ ppm while the remaining aromatic protons appeared as a multiplet in the range 6.93-7.11 δ ppm. The protons of benzylic methylene displayed a triplet at 2.64 δ ppm. The protons of methylene β to aromatic ring exhibited a multiplet in the range 1.57-1.66 δ ppm. The rest of methylene protons appeared as a multiplet in the range 1.17-1.29 δ ppm. Methyl group protons displayed a triplet at 0.85 δ ppm.

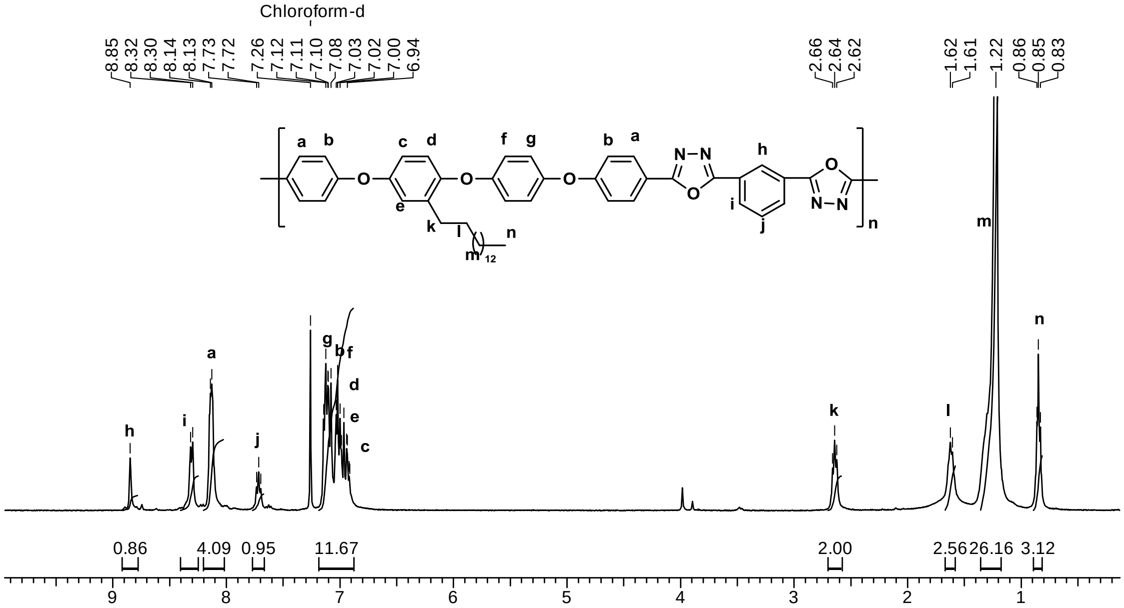


Figure 6.7 ^{1}H NMR spectrum (in $CDCl_3$) of poly (1,3,4-oxadiazole) (POD-II) derived from HPPDPB and IPC

^{1}H NMR spectrum of poly(1,3,4-oxadiazole) (POD-III) derived from HPPDPB and a mixture of TPC and IPC is depicted in **Figure 6.8.** ^{1}H NMR spectrum confirmed the complete of cyclization of polyhydrazide to poly(1,3,4-oxadiazole) as the two peaks of hydrazide protons which were present in ^{1}H NMR spectrum of PHA-III (**vide Figure 6.5**) are absent in ^{1}H NMR spectrum of POD-III. It confirmed the completion of cyclization reaction leading to formation of poly(1,3,4-oxadiazole). ^{1}H NMR spectrum displayed the signals corresponding to the both IPC and TPC moieties. The protons i and k of IPC moiety appeared as a singlet at 8.85 δ ppm and a doublet at 7.72 δ ppm, respectively. The proton j of IPC and protons h of TPC appeared together as a multiplet in the range 8.26-8.32 δ ppm. Aromatic protons ‘a’ *ortho* to oxadiazole ring exhibited a broad signal at 8.13 δ ppm while the remaining aromatic protons appeared as a multiplet in the range 6.93-7.12 δ ppm. The protons of benzylic -CH_2 appeared as broad signal at 2.64 δ ppm. The protons of –CH_2 linkage β to the aromatic ring displayed a multiplet in the range 1.57-1.66 δ ppm. The rest of methylene protons exhibited a multiplet in the range 1.17-1.29 δ ppm. The methyl protons appeared as a triplet at 0.85 δ ppm.

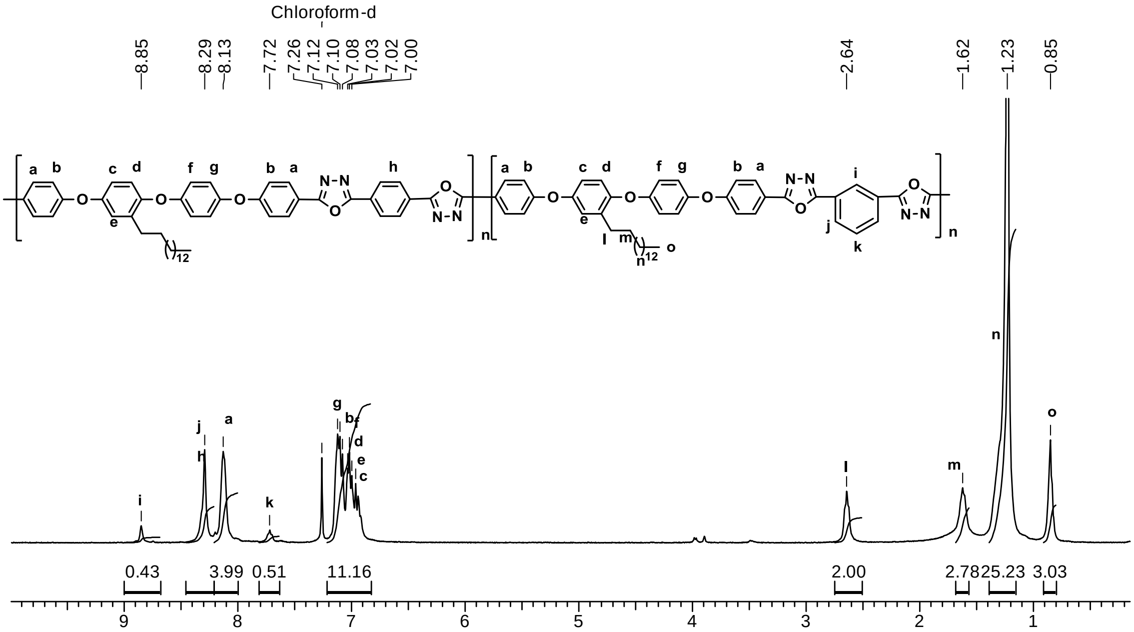


Figure 6.8 ^{1}H NMR spectrum (in $CDCl_3$) of poly(1,3,4-oxadiazole) (POD-III) derived from HPPDPB and a mixture of TPC and IPC

6.4.3 Solubility measurements

The solubilities of polyhydrazides and poly(1,3,4-oxadiazole)s were tested in various organic solvents at 3 wt % concentration and the results are summarized in **Table 6.2.**

Table 6.2 Solubility data of polyhydrazides and poly(1,3,4-oxadiazole)s derived from HPPDPB and aromatic diacid chlorides

Polymer	Diacylhydrazide	Diacid Chlorides		$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	*m*-Cresol	DMSO
		TPC	IPC									
PH-I	HPPDPB	100	0	--	--	--	++	++	++	++	++	++
PH-II	HPPDPB	0	100	--	--	--	++	++	++	++	++	++
PH-III	HPPDPB	50	50	--	--	--	++	++	++	++	++	++
POD-I	HPPDPB	100	0	++	++	++	--	--	--	++	++	--
POD-II	HPPDPB	0	100	++	++	++	+0	+0	+0	++	++	+0
POD-III	HPPDPB	50	50	++	++	++	--	--	--	++	++	--

++ : soluble at room temperature; +0 : partially soluble on heating at 60 °C; -- : insoluble

Polyhydrazides were found to be readily soluble in polar aprotic solvents such as DMAc, NMP, DMF, DMSO and were also soluble in *m*-cresol and pyridine at room temperature. The excellent solubility associated with polyhydrazides could be attributed to the packing disruptive pentadecyl chains and multiple ether linkages in the structure. The incorporation of pendent pentadecyl chain disrupted the close chain packing and reduced interchain interactions like hydrogen bonding. Additionally, the multiple ether linkages provided increased chain flexibility. Therefore solvent molecules can easily penetrate the into polymer chains leading to the enhanced solubility.

Regardless of rigid oxadiazole rings in the poly(1,3,4-oxadiazole) backbone, poly(1,3,4-oxadiazole)s were fairly soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine and *m*-cresol at room temperature. Pasquale et al. synthesized poly(arylene ether 1,3,4-oxadiazoles) and observed that along with ether linkages presence of pendent alkyl group is necessary to enhance solubility.[37] The improved solubility of poly(1,3,4-oxadiazole)s is due to the presence of pendant pentadecyl chains and multiple ether linkages as pentadecyl worked as packing disruptive group and multiple ether linkages gave flexibility to polymer backbone. Thus, objective of synthesizing soluble PODs was achieved. The enhanced solubility offers poly(1,3,4-oxadiazole)s processability characteristic as well as broadens their study by virtue of feasibility in characterizations.

6.4.4 X-Ray diffraction studies

X-Ray diffractograms of polyhydrazides and poly(1,3,4-oxadiazole)s derived from HPPDPB and aromatic diacid chlorides are shown in **Figure 6.9**.

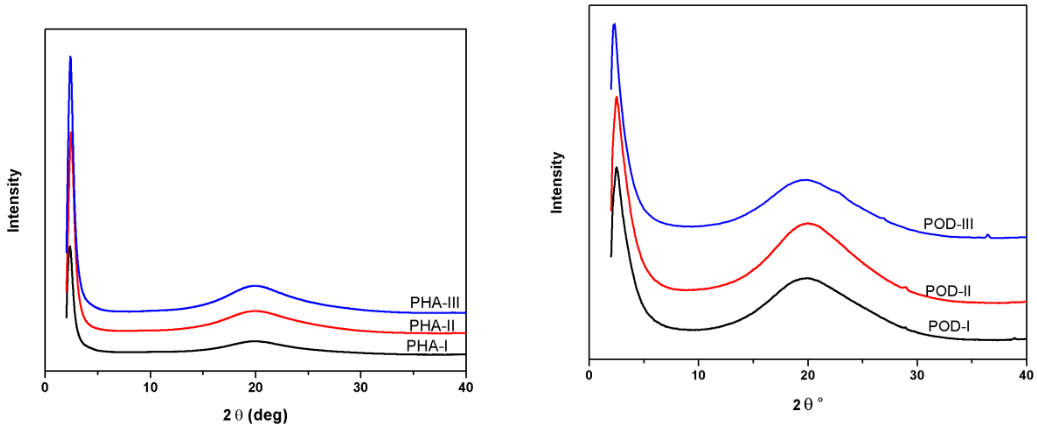


Figure 6.9 X-Ray diffractograms of polyhydrazides and poly(1,3,4-oxadiazole)s derived from HPPDPB and aromatic diacid chlorides

WAXD patterns of polyhydrazides and poly(1,3,4-oxadiazole)s displayed broad halo at around 2θ = ~ 20° which revealed the amorphous nature of the polymers. The amorphous nature could be attributed to the presence of pendant pentadecyl chains in the polymer which disrupt close chain packing. Moreover, polyhydrazides and poly(1,3,4-oxadiazole)s exhibited a strong reflection in the small-angle region at 2θ = ~ 3° which could be attributed to formation layered structure by pentadecyl chains.[37] The amorphous nature of polyhydrazides and poly(1,3,4-oxadiazole)s was also reflected in their superior solubility in common organic solvents.

6.4.5 Thermal properties

Thermal stability of polyhydrazides and poly(1,3,4-oxadiazole)s was evaluated by thermogravimetric analysis (TGA) at a heating rate of 10° C /minute under nitrogen. TG curves of polyhydrazides and poly(1,3,4-oxadiazole)s are represented in **Figure 6.10 and 6.11,** respectively.

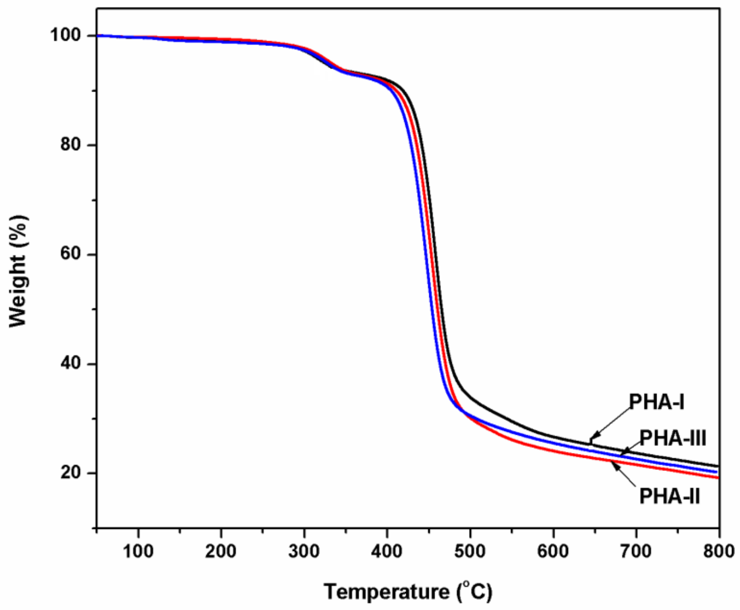
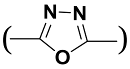


Figure 6.10 TG curves of polyhydrazides derived from HPPDPB and aromatic diacid chlorides

TG curves of polyhydrazides exhibited the initial weight loss at around 300 °C **(Figure 6.10)** due to dehydration of hydrazide moieties (-CO-NH—NH-CO-) in the backbone leading to formation of oxadiazole () units. The 10% decomposition temperatures (T_{10}) and the weight residues at 800 °C for poly(1,3,4-oxadiazole)s are presented in **Table 6.3**. T_{10} values of poly(1,3,4-oxadiazole)s were in the range of 423 to 442 °C indicating their good thermal stability.

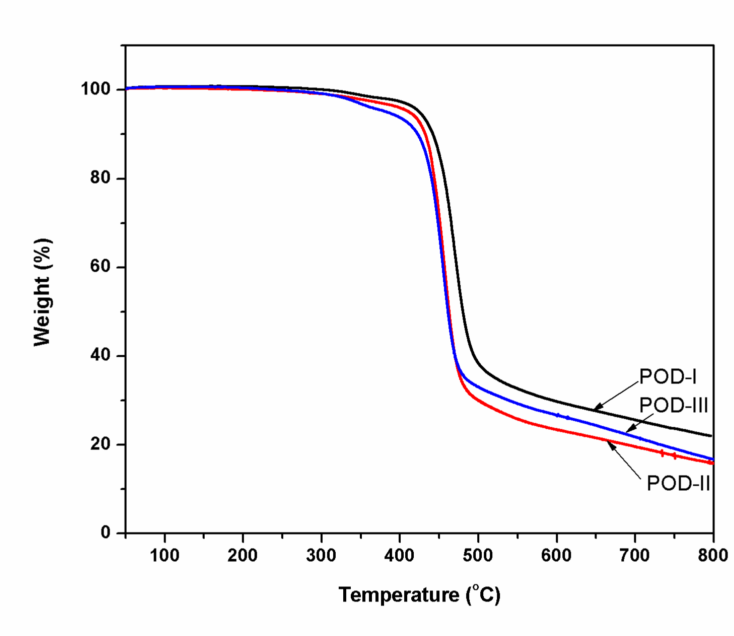


Figure 6.11 TG curves of poly(1,3,4-oxadiazole)s

Table 6.3 Thermal properties of polyhydrazides and poly(1,3,4-oxadiazole)s derived from HPPDPB and aromatic diacid chlorides

Polymer	**Diacylhydrazide**	**Diacid Chlorides**		**T_{10}^{a} (°C)**	**Weight residue at 800° C (%)**	**T_g (°C)**
		TPC	**IPC**			
PH-I	HPPDPB	100	0	-	21	192
PH-II	HPPDPB	0	100	-	19	175
PH-III	HPPDPB	50	50	-	20	183
POD-I	HPPDPB	100	0	440	22	103
POD-II	HPPDPB	0	100	430	16	92
POD-III	HPPDPB	50	50	425	17	97

a : temperature at which 10% weight loss is observed

Polyhydrazides and poly(1,3,4-oxadiazole)s were characterized by differential scanning calorimetry to evaluate their T_g. **Figure 6.12** and **6.13** represent DSC curves of polyhydrazides and poly(1,3,4-oxadiazole)s, respectively. T_g values were calculated from second heating scans of the polymers at a heating rate of 10 °C / minute and T_g values are presented in **Table 6.3**.

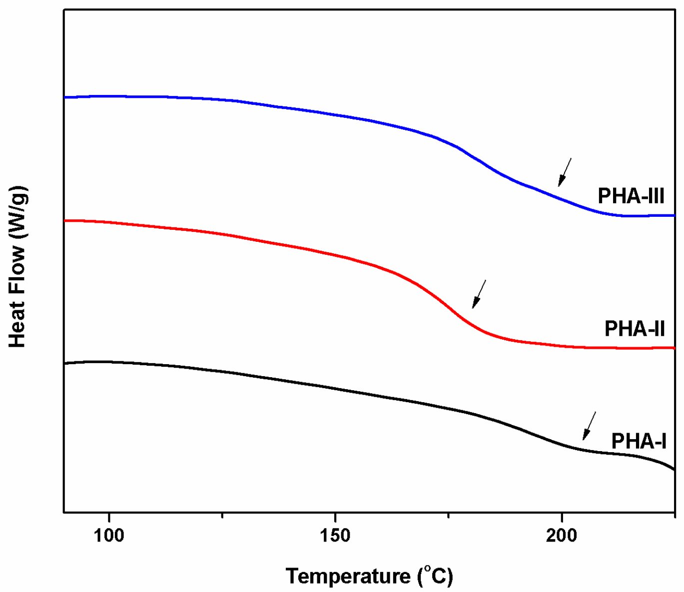


Figure 6.12 DSC curves of polyhydrazides derived from HPPDPB and aromatic diacid chlorides

The T_g values for polyhydrazides PHA-I, PHA-II and PHA-III were 192, 175 and 183 respectively while T_g values of poly(1,3,4-oxadiazole)s POD-I, POD-II, and POD-III were 103, 92 and 97 °C, respectively. T_g value is a function of polymer backbone rigidity since increase in rigidity causes increase in energy required for segmental motion of the polymer chains. Hence, T_g increases with increase in rigidity in polymer backbone. **PHA-I** and **POD-I** showed highest T_g among the series of polyhydrazides and poly(1,3,4-oxadiazole)s which could be attributed to higher rigidity in **PHA-I** and **POD-I** backbone because of rigid 1,4-phenylene units. Moreover, T_g of poly(1,3,4-oxadiazole) based on HPPDPB and TPC (103 °C) is lower than that of poly(1,3,4-oxadiazole) based on 4,4'-oxybisbenzohydrazide and TPC (289 °C).[50] This lowering of T_g values of obtained polyhydrazides could be attributed to packing disruptive effect of pentadecyl chains and to the flexibility offered by the multiple ether linkages.

The T_g values poly(1,3,4-oxadiazole)s were lower than that of parent polyhydrazides. In spite of having rigid 1,3,4-oxadiazole repeat unit in the polymer chain, T_g values observed were in the range 92-103 °C. These results revealed that T_g for poly(1,3,4-oxadiazole)s is strongly dependent on flexible pentadecyl chain present in the polymer backbone, and this conclusion is in agreement with data reported in literature.[25, 51] A large difference between T_g (92-103 °C) and T_{10} values (430-440 °C) offers poly(1,3.4-oxadiazole)s a wide processing window.

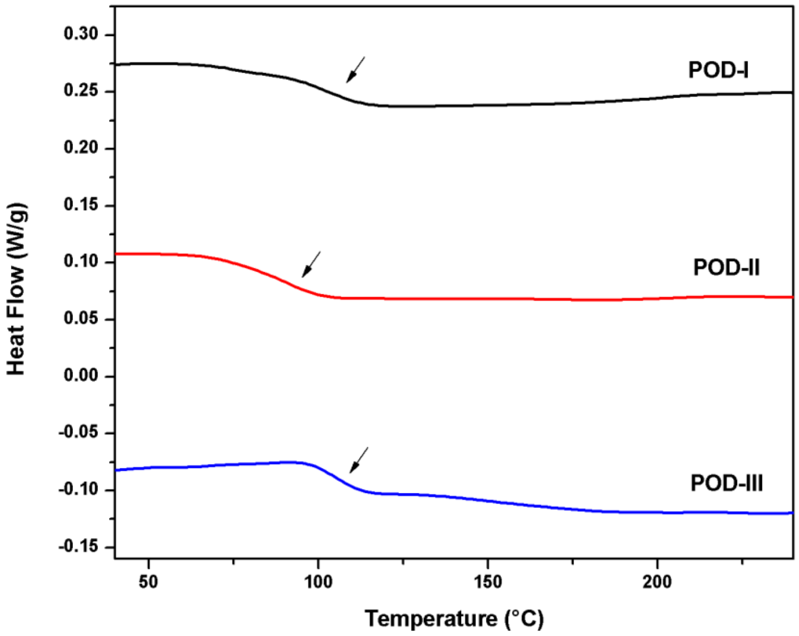


Figure 6.13 DSC curves of poly(1,3,4-oxadiazole)s

6.4.6 Optical properties

The optical properties of poly(1,3,4-oxadiazole)s were investigated by UV-Vis absorption and photoluminescence (PL) spectroscopy in dilute chloroform solution (10^{-5} mol/L). The results are summarized in **Table 6.4**. The UV-Vis absorption and photoluminescence spectra of poly(1,3,4-oxadiazole)s are represented in **Figure 6.14** and **6.15**, respectively.

Table 6.4 Optical and electrochemical properties of poly(1,3,4-oxadiazole)s

Polymer	λ_{max}^{abs} (nm)	λ_{onset}^{abs} (nm)	λ_{max}^{PL} (nm)	E_g^{opt} (eV)	E_{onset}^{Red} Onset (V)	$E_{LUMO/HOMO}$ (eV)
POD-I	337	372	394	3.33	-1.15	3.65/6.98
POD-II	304	340	380	3.65	-1.16	3.64/7.29
POD-III	315	368	394	337	-	-

Calculated by equation: E_g^{opt}= 1240/ λ_{edge} ; The HOMO and LUMO energy levels were calculated from E_{onset} of reduction potential with respect to ferrocene (4.8 eV) and E_g^{opt}

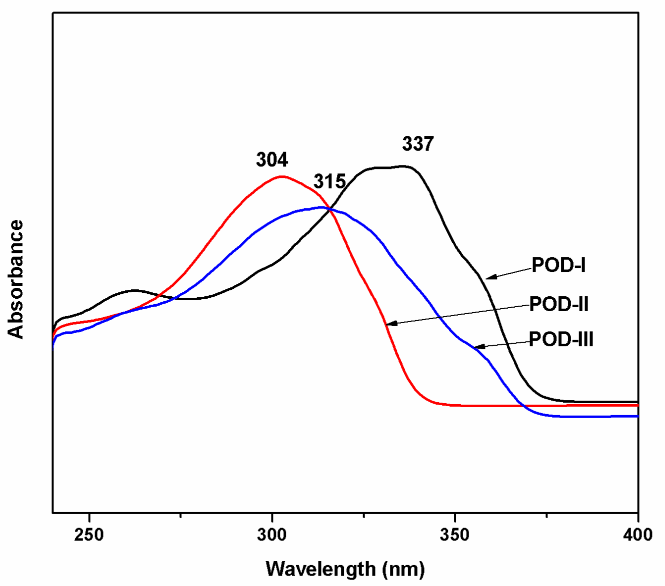


Figure 6.14 UV spectra of poly(1,3,4-oxadiazole)s

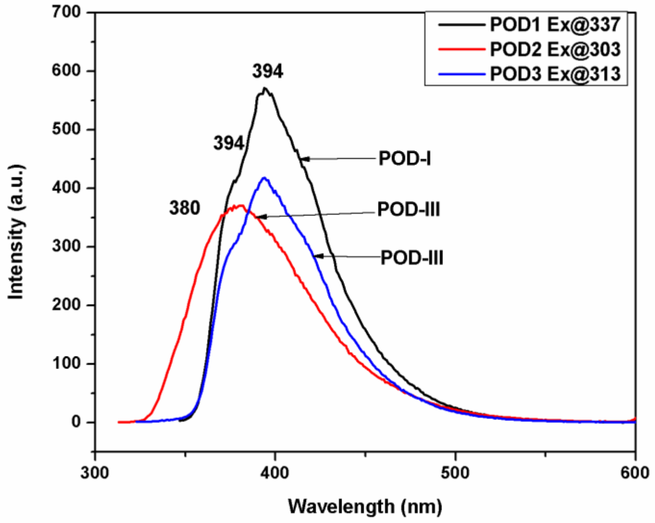


Figure 6.15 Photoluminescence spectra of poly(1,3,4-oxadiazole)s

The optical band gap was calculated from the equation 1.24/ λ_{edge} (eV). The calculated optical bands gap for POD-I, POD-II and POD-III are 3.33, 3.65, 3.37 eV, respectively. Poly(1,3,4-oxadiazole)s I-III exhibited blue fluorescence emission maxima at 394, 380 and 394 nm, respectively in chloroform solution**.** The photoluminescence of poly(1,3,4-oxadiazole)s in solution as well as solid state (POD-I film) under UV irradiation are shown in **Figure 6.16**.

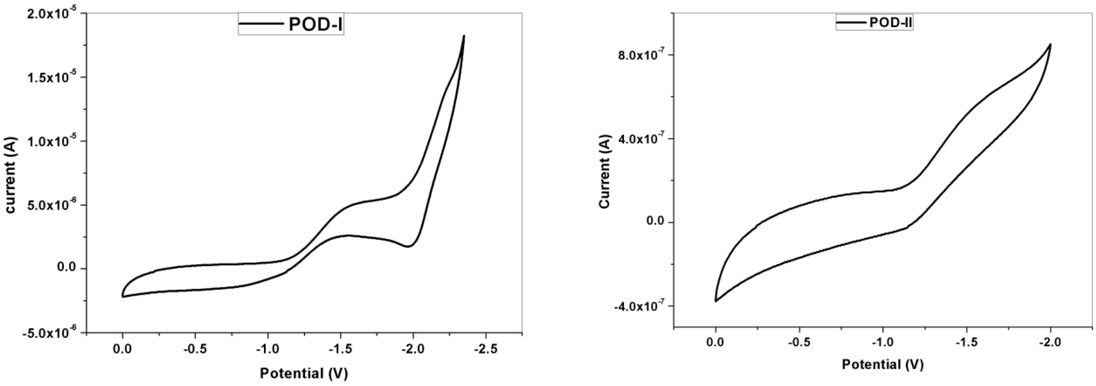
Solution of POD-I, II, III

POD-I film

Figure 6.16 Photoluminescence of poly(1,3,4-oxadiazole)s under UV lamp

6.4.7 Electrochemical properties

The electrochemical properties of poly(1,3,4-oxadiazole)s were studied by cyclic voltammetry. The redox behavior of these polymers was investigated by cyclic voltammetry conducted for the cast films on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere for oxidation and reduction measurements. The electrochemical results were used for calculation of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy of levels for POD-I and II. The LUMO and HOMO energy levels can be determined from the oxidation onset, reduction onset potentials (E) and optical band gap (E_g^{opt}) and the results are presented in **Table 6.4**. The cyclic voltammograms for POD-I and POD-II are represented in **Figure 6.17,** indicating one reduction process at 1.21 and 1.22 V, and onset of reduction potential at -1.15 and -1.16 V, respectively.



A B

Figure 6.17 Cyclic voltammograms for POD-I (A) and POD-II (B)

The external ferrocene/ferrocenium (Fc/Fc^+) redox standard $E_{½}$ is 0.44 V vs Ag/AgCl in CH_3CN. Assuming that the HOMO energy for the Fc /Fc^+ standard is

4.80 eV with respect to the zero vacuum level, the LUMO energy for POD-I and POD-II has been evaluated to be 3.65 eV and 3.64 eV. Thus, the results of optical and electrochemical properties of poly(1,3,4-oxadiazole)s containing pendent pentadecyl chains indicate that they could be potentially utilized in photovoltaic applications.

6.5 Conclusions

1. A new series of polyhydrazides and poly(1,3,4-oxadiazole)s containing pendent pentadecyl chains and multiple ether linkages in the backbone was synthesized from 4-(4-(4-(4-(Hydrazinocarbonyl) phenoxy)-2-pentadecylphenoxy) phenoxy) benzohydrazide and aromatic diacid chlorides.
2. The inherent viscosities of polyhydrazides and poly(1,3,4-oxadiazole)s were in the range 0.65-0.72 dL/g and 0.54-0.62 dL/g, respectively indicating formation of reasonably high molecular weight polymers.
3. Polyhydrazides were soluble in polar aprotic solvents such as DMF, DMAc, pyridine and DMSO. Poly(1,3,4-oxadiazole)s exhibited excellent solubility in solvents, such as chloroform, dichloromethane and tetrahydrofuran. Tough, transparent and flexible films of polyhydrazides and poly(1,3,4-oxadiazole)s could be cast from DMAc and chloroform solutions, respectively.
4. X-Ray diffraction studies of polyhydrazides and poly(1,3,4-oxadiazole)s revealed their amorphous nature. The formation of layered structure was observed for both polyhydrazides and poly(1,3,4-oxadiazole)s because of ordered packing of pentadecyl chains.
5. The T_{10} values for poly(1,3,4-oxadiazole)s were in the range 425-440 °C indicating their good thermal stability.
6. The lowering of T_g of polyhydrazides (175-192 °C) and poly(1,3,4-oxadiazole)s (92-103 °C), could be attributed to presence of packing disruptive pendent pentadecyl chains and flexiblizing multiple ether linkages in the backbone.
7. Poly(1,3,4-oxadiazole)s exhibited maximum UV-Vis absorption in the range 304-337 nm whereas maximum of fluorescence emission was in the range 380-394 nm in chloroform solution.
8. The optical band gap (E_g) values for poly(1,3,4-oxadiazole)s were found to be in the range 3.33-3.65 eV indicating their potential application in opto-electronic devices.

References

1. B. Schulz, M. Bruma and L. Brehmer, *Adv. Mater.*, 1997, **9**, 601-613.
2. H. H. Yang, *Aromatic High-strength Fibers*, Wiley, New York, 1989.
3. S.-H. Yang and C.-S. Hsu, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 2713-2733.
4. M. Bruma and B. Schulz, *J. Macromol. Sci. Part C*, 2001, **41**, 1-40.
5. S. Seo, H. Shin, C. Park, H. Lim and E. Kim, *Macromol. Res.*, 2013, **21**, 284-289.
6. W.-L. Yu, H. Meng, J. Pei, W. Huang, Y. Li and A. J. Heeger, *Macromolecules*, 1998, **31**, 4838-4844.
7. S.-Y. Song, M. S. Jang, H.-K. Shim, D.-H. Hwang and T. Zyung, *Macromolecules*, 1999, **32**, 1482-1487.
8. S.-C. Kim, S.-M. Park, J. S. Park, S.-J. Lee, S.-H. Jin, Y.-S. Gal and J. W. Lee, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 1098-1110.
9. S. Seo, Y. Kim, J. You, B. D. Sarwade, P. P. Wadgaonkar, S. K. Menon, A. S. More and E. Kim, *Macromol. Rapid Commun.*, 2011, **32**, 637-643.
10. Y.-C. Kung and S.-H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.*, 2011, **49**, 4830-4840.
11. A. H. Frazer, W. Sweeny and F. T. Wallenberger, *J. Polym. Sci. Part A*, 1964, **2**, 1157-1169.
12. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci. Part A.*, 1964, **2**, 1171-1179.
13. A. H. Frazer and T. A. Reed, *J. Polym. Sci. Part C: Polym. Symp.*, 1967, **19**, 89-94.
14. E. Leibnitz, C. Eisold and D. Paul, *Die Angew. Makromol. Chem.*, 1993, **210**, 197-205.
15. I. Hajdok, A. Bona, H.-J. Werner and J. Kerres, *Eur. Polym. J.*, 2014, **52**, 76-87.
16. M. Fahmy, R. Al-Ghamdi and N. Mohamed, *Polym. Bull.*, 2010, **66**, 609-625.
17. D. Gomes and S. P. Nunes, *J. Membr. Sci.*, 2008, **321**, 114-122.
18. X. Yang, E. Jia, G. Ye and J. Xu, *Polym. Bull.*, 2015, **72**, 1067-1080.
19. A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556-4573.

20. W. Huang, W.-L. Yu, H. Meng, J. Pei and S. F. Y. Li, *Chem. Mater.*, 1998, **10**, 3340-3345.
21. S.-W. Hwang and Y. Chen, *Macromolecules*, 2002, **35**, 5438-5443.
22. J. Ding and M. Day, *Macromolecules*, 2006, **39**, 6054-6062.
23. D. Acierno, E. Amendola, S. Bellone, S. Concilio, P. Iannelli, H.-C. Neitzert, A. Rubino and F. Villani, *Macromolecules*, 2003, **36**, 6410-6415.
24. D. Udayakumar, A. J. Kiran, A. V. Adhikari, K. Chandrasekharan and H. D. Shashikala, *J. Appl. Polym. Sci.*, 2007, **106**, 3033-3039.
25. A. S. More, S. K. Menon and P. P. Wadgaonkar, *J. Appl. Polym. Sci.*, 2011, **124**, 1281-1289.
26. J. L. Hedrick, *Polymer*, 1992, **33**, 3375-3381.
27. Y. Saegusa, T. Iwasaki and S. Nakamura, *Macromol. Chem. Phys.*, 1997, **198**, 1799-1808.
28. S.-H. Hsiao and C.-H. Yu, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 1847-1854.
29. S.-H. Hsiao, L.-R. Dai and M.-H. He, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 1169-1181.
30. S.-H. Hsiao and M.-H. He, *Macromol. Chem. Phys.*, 2001, **202**, 3579-3589.
31. H. Kim, S. Kang and J. Do, *Macromol. Res.*, 2008, **16**, 360-366.
32. Y.-Y. Chen and H.-C. Lin, *Polymer*, 2007, **48**, 5268-5278.
33. S. Blumstengel, I. Sokolik, R. Dorsinville, D. Voloschenko, M. He, O. Lavrentovich and L. C. Chien, *Syn. Metals*, 1999, **99**, 85-90.
34. S. Janietz and S. Anlauf, *Macromol. Chem. Phys.*, 2002, **203**, 427-432.
35. R. Stern, M. Ballauff, G. Lieser and G. Wegner, *Polymer*, 1991, **32**, 2096-2105.
36. J. W. Connell, P. M. Hergenrother and P. Wolf, *Polymer*, 1992, **33**, 3507-3511.
37. F. A. Bottino, G. Di Pasquale and P. Iannelli, *Macromolecules*, 2001, **34**, 33-37.
38. P. Mormile, L. Petti, M. Gillo, P. Laurienzo, M. Malinconico, A. Roviello, S. Lipson and W. J. Blau, *Mater. Chem. Phys.*, 2003, **77**, 945-951.
39. C. Wang, M. Kilitziraki, L. O. Pålsson, M. R. Bryce, A. P. Monkman and I. D. W. Samuel, *Adv. Funct. Mater.*, 2001, **11**, 47-50.

40. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals; Pergamon Press: New York*, 1989.
41. N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, 1975, **13**, 1373-1380.
42. F. Higashi and M. Ishikawa, *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18**, 2905-2907.
43. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci. Part A: General Papers*, 1964, **2**, 1147-1156.
44. A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci. Part A: General Papers*, 1964, **2**, 1137-1145.
45. F. Dobinson, C. A. Pelezo, W. B. Black, K. R. Lea and J. H. Saunders, *J. Appl. Polym. Sci.*, 1979, **23**, 2189-2195.
46. V. P. Ubale, A. S. Patil and N. N. Maldar, *Eur. Polym. J.*, 2007, **43**, 1038-1045.
47. K. A. Joseph and M. Srinivasan, *Polym. Int.*, 1993, **32**, 257-264.
48. M. J. Nanjan and D. Jayaprakash, *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21**, 1227-1231.
49. R. Mandal and S. Maiti, *Polym. Int.*, 1997, **44**, 428-434.
50. S. Zhu, B. Schulz, M. Bruma and L. Brehmer, *Polym. Adv. Technol.*, 1996, **7**, 879-887.
51. M. Gillo, P. Iannelli, P. Laurienzo, M. Malinconico, A. Roviello, P. Mormile and L. Petti, *Chem. Mater.*, 2002, **14**, 1539-1547.

Chapter 7

Synthesis and Characterization of Poly(arylene ether)s Based on 3-Pentadecyl 4,4' Biphenol

7.1 Introduction

Poly(arylene ether)s such as poly(ether ketone)s, poly(ether sulfone)s, etc., constitute an important class of high performance thermoplastics because of their attractive properties such as high thermo-oxidative, high chemical stability and excellent mechanical strength. Poly(arylene ether)s are therefore extensively used in aviation, spacecrafts, automobile, food processing sectors, medical devices, gas separation membranes, ultrafilration, fuel cells, electronic/electrical industries, etc.[1-17]

The nucleophilic substitution and electrophilic substitution (Friedal-Crafts acylation) methods are used for preparation of various kinds of poly(arylene ether)s.[5, 6, 18-21] The electrophilic substitution method has some limitations due to the mechanistic problems. Therefore, poly(arylene ether)s are most commonly prepared by nucleophilic substitution method. The method involves nucleophilic aromatic substitution (SNAr) of activated aromatic dihalides with alkali-metal bisphenoxides in polar aprotic solvents which generates an ether linkage. Fluorine is found to be the best leaving group but in some cases, chlorine or nitro can be used as good leaving groups.[22-28]

In spite of outstanding properties of poly(ether ketone)s, their applications have been limited due to difficulties in the processing as well as synthesis which could be attributed to their insolubility in common organic solvents because of high crystallinity which originates from the high chain packing density. A number of approaches have been developed towards the enhancement of solubility and processibility of poly(arylene ether)s by the inclusion of *meta*-linkages, flexible linkages, or pendent bulky groups.[4, 9, 10, 12, 16, 29-35]

This chapter includes synthesis of poly(ether ether ketone), poly(ether ether ketone ketone) and poly(ether sulfone) based on 3-pentadecyl 4,4’-biphenol and commercially available aromatic dihalides by nucleophilic substitution method. Poly(arylene ether)s were characterized by inherent viscosity measurements, gel permeation chromatography, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, solubility measurements, X-ray diffraction studies, thermogravimetric analysis, and DSC. Poly(ether sulfone) was evaluated as a membrane material for gas separation studies.

7.2 Experimental

7.2.1 Materials

3-Pentadecyl 4,4’-biphenol (PDBP) was prepared as described in **Chapter 3**. 4,4’-Difluorobenzophenone (DFB), 1,3-bis(4–fluorobenzoyl)benzene (BFB) and bis(4-fluorophenyl)sulfone (FPS) (Aldrich, USA) were recrystallized from toluene before use. Anhydrous potassium carbonate (Aldrich, USA) was used after drying at 150 °C for 24 h under vacuum. N, N-Dimethylacetamide (DMAc) was dried by stirring on calcium hydride for 24 h and then distilled under reduced pressure. All solvents were of reagent grade and were used after purification by the standard procedures.[36]

7.2.2 Measurements

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

η_{inh} was calculated using the equation: $n_{inh} = \frac{2.303}{C} x \log \frac{t}{t_0}$

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

Molecular weights of poly(arylene ether)s were measured on ThermoFinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5 Å to 50 Å), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2 μ SS-filter.

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

NMR spectra were recorded on a Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

The solubility of poly(arylene ether)s was determined at 3 wt.% concentration (w/v) in various solvents at room temperature or on heating.

X-Ray diffraction patterns of polymers were obtained on a Rigaku MicroMax-007HF X-ray diffractometer operating at 40 kV and 30 mA. Dried polymer films or powder samples were exposed to the X-ray beam for 3 min and the scattering pattern was imaged by Rigaku R-AXIS IV++ area detector. The 2D pattern was converted to 1D pattern by Rigaku 2DP software.

Thermogravimetric analysis was performed on Perkin-Elmer STA 6000 system at a heating rate of 10 °C / minute under nitrogen atmosphere. ~5 mg sample was taken for analysis.

DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C / minute in nitrogen atmosphere.

7.3 Synthesis of poly(arylene ether)s

A representative polymerization procedure for the synthesis of poly(arylene ether)s is described below:

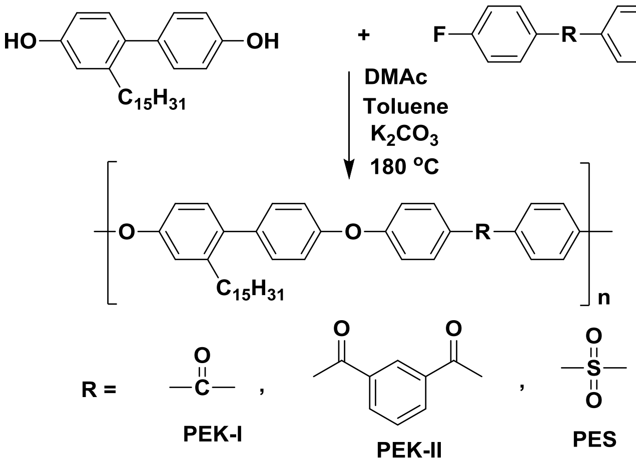
Into a 100 mL three necked round bottom flask equipped with a reflux condenser, a nitrogen inlet, a magnetic stirring bar and a Dean-Stark trap were charged PDBP (0.395 g, 1 mmol), bis(4-fluorophenyl) sulfone (0.254 g, 1 mmol), anhydrous potassium carbonate (0.346 g, 2.5 mmol), N,N-dimethylacetamide (10 mL) and toluene (10 mL). The reaction mixture was heated at reflux with stirring for 3 h and water was removed by azeotropic distillation with toluene. Toluene was removed by distillation, and the reaction mixture was heated at 180 °C for 8 h. After cooling, the viscous reaction mixture was poured into methanol (100 mL); the precipitated polymer was filtered and washed several times with water to remove the metal salt. The polymer was dissolved in chloroform and reprecipitated into methanol. The polymer was filtered, washed with methanol and dried under reduced pressure at room temperature for 24 h.

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

7.4 Results and Discussion

7.4.1 Synthesis of poly(arylene ether)s

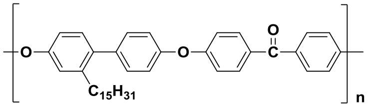
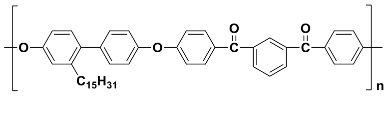
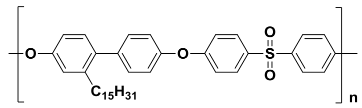
Scheme 7.1 illustrates synthesis of poly(arylene ether)s from PDBP and commercially available aromatic dihalides viz., 4,4’-difluorobenzophenone (DFB), 1,3-bis(4–fluorobenzoyl)benzene (BFB) and bis(4-fluorophenyl)sulfone (FPS).



Scheme 7.1 Synthesis of poly(arylene ether)s from PDBP and activated aromatic dihalides

The polymerization reactions were carried out in N,N-dimethylacetamide in the presence of anhydrous potassium carbonate under conditions described in the experimental section. The excess of anhydrous potassium carbonate was used to convert the biphenol into corresponding phenolate anions. Azeotropic distillation with toluene was used to remove water formed from disproportionation of potassium carbonate.[3] Then the polycondensation of these phenolate anions with the activated difluorides were readily accomplished at 180 °C. Poly(arylene ether)s were isolated by precipitating the reaction mixture into excess methanol. The results of polymerization reactions are summarized in **Table 7.1.**

Table 7.1 Synthesis of poly(arylene ether)s from PDBP and aromatic dihalides

Polymer	**Structure**	**η_{inh} (dL/g)^a**	**Molecular Weight^b**		**PDI**
			M_n (x 10^4)	**M_w (x 10^4)**	**(M_w/M_n)**
PEK-I		0.81	8.3	18.2	2.2
PEK-II		0.50	2.2	4.9	2.2
PES		0.67	5.8	12.9	2.2

a: η_{inh} was measured with 0.5 % (w/v) solution of poly(arylene ether)s in $CHCl_3$ at 30 ± 0.1°C

b: GPC in chloroform, (calibration standard: polystyrene)

Inherent viscosity (η_{inh}) of poly(arylene ether)s was in the range 0.50-0.81 dL/g indicating formation of reasonably high molecular weight polymers. The results of GPC measurements of poly(arylene ether)s are presented in **Table 7.1.** Number average molecular weights (Mn) of poly(arylene ether)s were in the range 2.2 x 10^4 to 8.3 x 10^4 with polydispersity index of 2.2. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards. Poly(arylene ether)s could be cast into tough, transparent, and flexible films by casting from solution of polymers in chloroform.

7.4.2 Structural characterization

FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy was used to confirm the chemical structures of poly(arylene ether)s.

FT-IR spectrum of poly(ether ether ketone) **(PEK-I)** obtained from PDBP and DFB is represented in **Figure 7.1**. A characteristic absorption band of the carbonyl stretching was observed 1661 cm^{-1} and band of the ether linkage appeared at 1230 cm^{-1}.

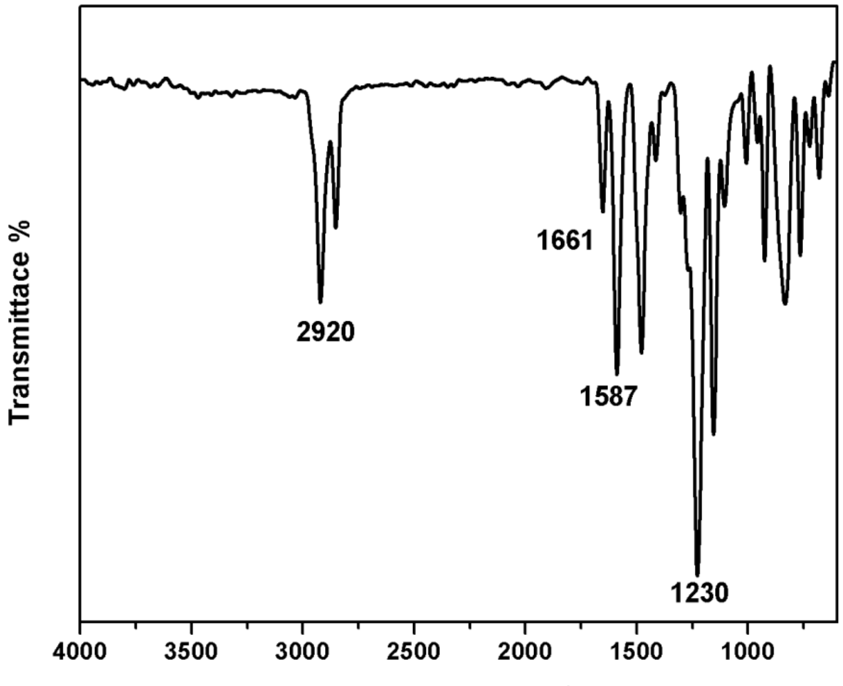


Figure 7.1 FT-IR spectrum of poly(ether ether ketone) (PEK-I) derived from PDBP and DFB

FT-IR spectrum of poly(ether ether ketone ketone) **(PEK-II)** obtained from PDBP and BFB is represented in **Figure 7.2**. A characteristic absorption peak of the carbonyl stretching was observed 1654 cm^{-1}.

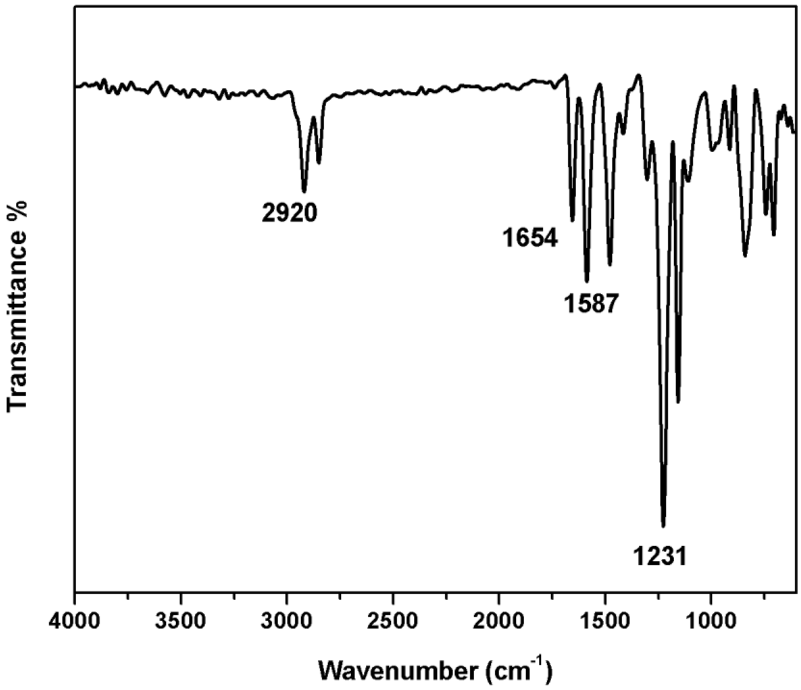


Figure 7.2 FT-IR spectrum of poly(ether ether ketone ketone) (PEK-II) derived from PDBP and BFB

FT-IR spectrum of poly(ether sulfone) (PES) obtained from PDBP and FPS is shown in **Figure 7.3.** The two bands of the sulfone group appeared at 1320 cm^{-1} and 1150 cm^{-1} due to asymmetric and symmetric stretching, respectively whereas band of the ether linkage appeared at 1235 cm^{-1}.

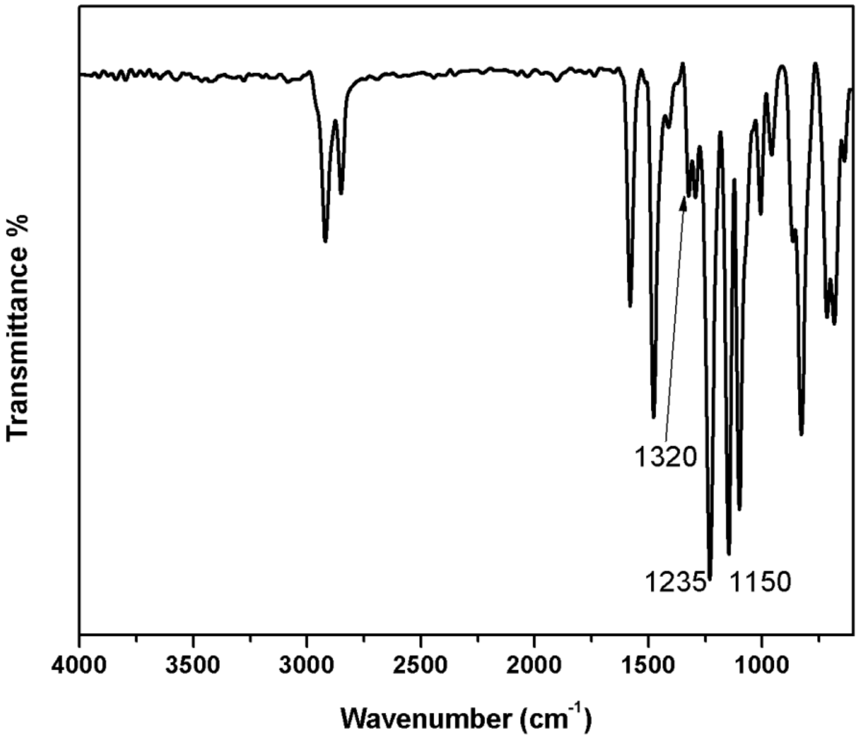


Figure 7.3 FT-IR spectrum of poly(ether sulfone) (PES) derived from PDBP and FPS

^{1}H and ^{13}C NMR spectra of poly(ether ether ketone) (PEK-I) obtained from PDBP and DFB along with assignments are shown in **Figure 7.4** and **7.6**, respectively.

The four protons *ortho* to carbonyl group appeared as four signals in the region 7.85-7.90 δ ppm. The remaining aromatic protons viz, protons *meta* to carbonyl group and aromatic protons of biphenol exhibited multiplet in the range 6.98-7.38 δ ppm. The benzylic methylene protons appeared as a triplet at 2.61 δ ppm. The protons of methylene group β to aromatic ring exhibited a broad peak at δ 1.51 ppm. The other methylene protons displayed a multiplet over the range δ 1.18-1.32 ppm. Methyl protons of the pentadecyl chain appeared as a triplet at 0.89 δ ppm. It was interesting to note the appearance of four peaks for protons *ortho* to carbonyl. In order to study whether the peaks are independent signals or arising out of spin-spin coupling, ^{1}H NMR spectra of PEK-I were recorded at three different magnetic field strengths viz, 200, 400 and 500 MHz. **(Figure 7.5)** The spectra showed that increase in the field strength caused increase in the separation of the signals whereas J- values indicated that these signals are either two distinct doublets or separate signals but not the doublet of doublet. Further, this behavior could be explained on the basis of constitutional isomerism.

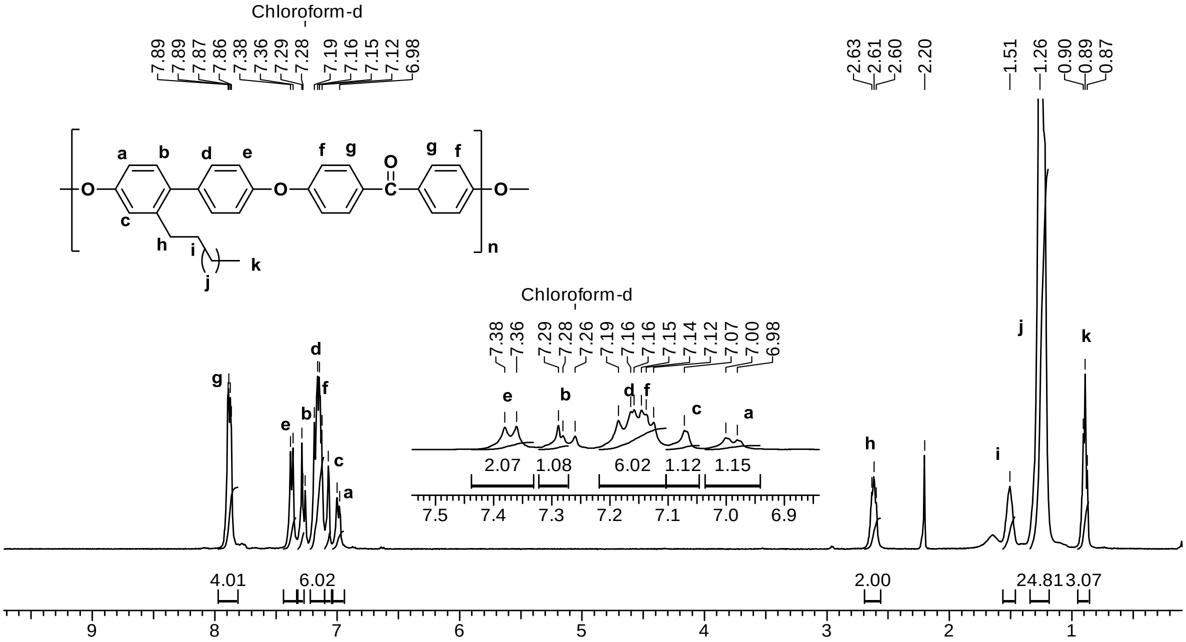


Figure 7.4 ^{1}H NMR spectrum (in $CDCl_3$) of poly(ether ether ketone) (PEK-I) derived from PDBP and DFB

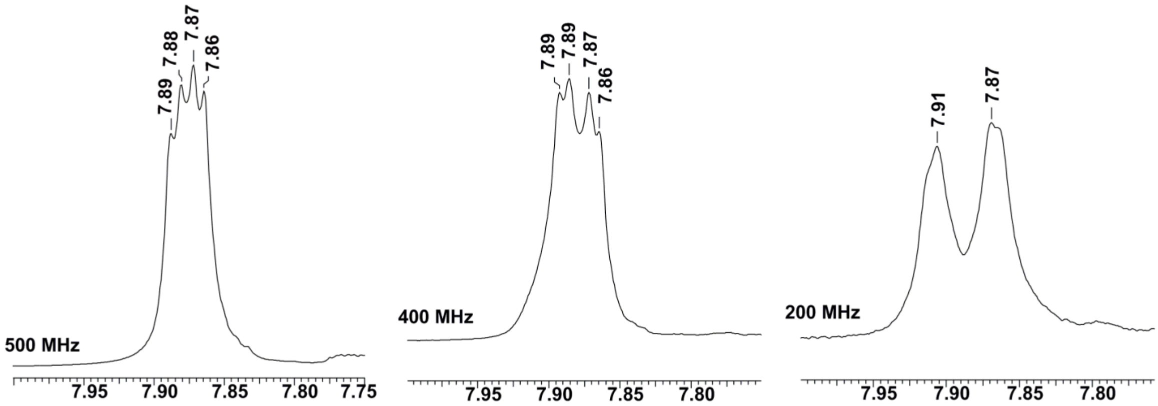


Figure 7.5 Partial ^{1}H NMR spectrum of PEK-I at three different magnetic strengths (500, 400 and 200 MHz)

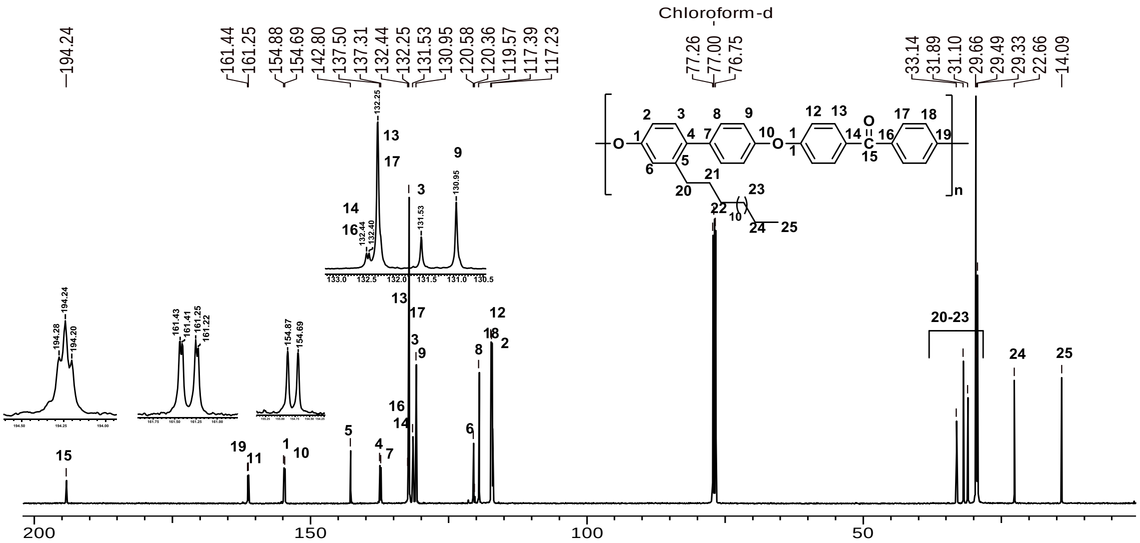


Figure 7.6 ^{13}C NMR spectrum (in CDCl$_3$) of PEK-I derived from PDBP and DFB

In ^{13}C NMR spectrum of **PEK-I (Figure 7.6)**, the carbonyl carbon exhibited three distinct signals at 194.21, 194.24 and 194.28 δ ppm. This could be attributed to the different types of carbonyl carbons of different types of constitutional isomers which is explained later. Similarly, C19 exhibited two signals at 161.41 and 161.44 δ ppm while C11 showed two signals at 161.22 and 161.25 δ ppm. The chemical shifts of other carbon atoms were in good agreement with the assigned structure.

^{1}H NMR spectrum of poly(ether ether ketone ketone) **(PEK-II)** derived from PDBP and BFB along with assignments is shown in **Figure 7.7**

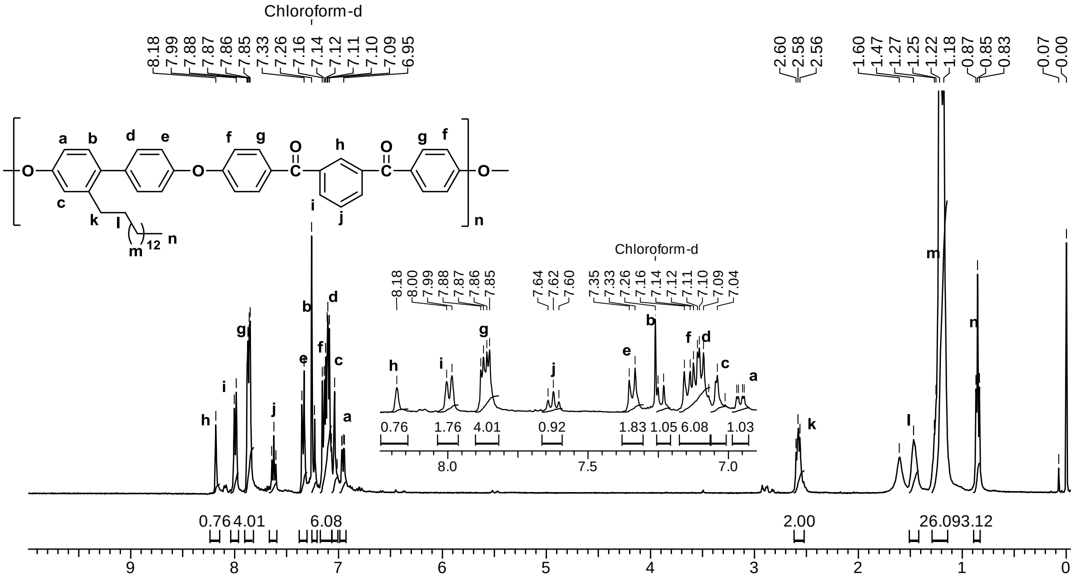


Figure 7.7 ^{1}H NMR spectrum (in CDCl$_3$) of poly(ether ether ketone ketone) (PEK-II) derived from PDBP and BFB

The proton flanked by two carbonyl groups appeared at δ 8.10 ppm. The doublet at δ 7.99 ppm is due to protons ‘i’ whereas triplet at δ 7.62 ppm is due to proton ‘j’. The four aromatic protons *ortho* to carbonyl group appeared as four distinct signals at 7.85, 7.86, 7.87 and 7.88 δ ppm. The rest of aromatic protons appeared as multiplet over the range δ 6.95-7.35 ppm.

^{1}H and ^{13}C NMR spectra of poly(ether sulfone) (PES) derived from PDBP and FPS along with assignments are shown in **Figure 7.8** and **7.9,** respectively.

In ^{1}H NMR of PES, the four signals at δ 7.89.7.90. 7.91 and 7.92 δ ppm are assignable to the aromatic protons *ortho* to sulfone group and remaining aromatic protons appeared as a multiplet in the range δ 6.88-7.33 ppm. The benzylic methylene protons exhibited a triplet at δ 2.55 ppm and protons of carbon β to the ring appeared as multiplet in the range δ 1.42-1.46 ppm. The rest of the methylene protons of the aliphatic chain exhibited multiplet in the range δ 1.17-1.128 ppm. Methyl group of pentadecyl chain appeared at δ 0.86 ppm.

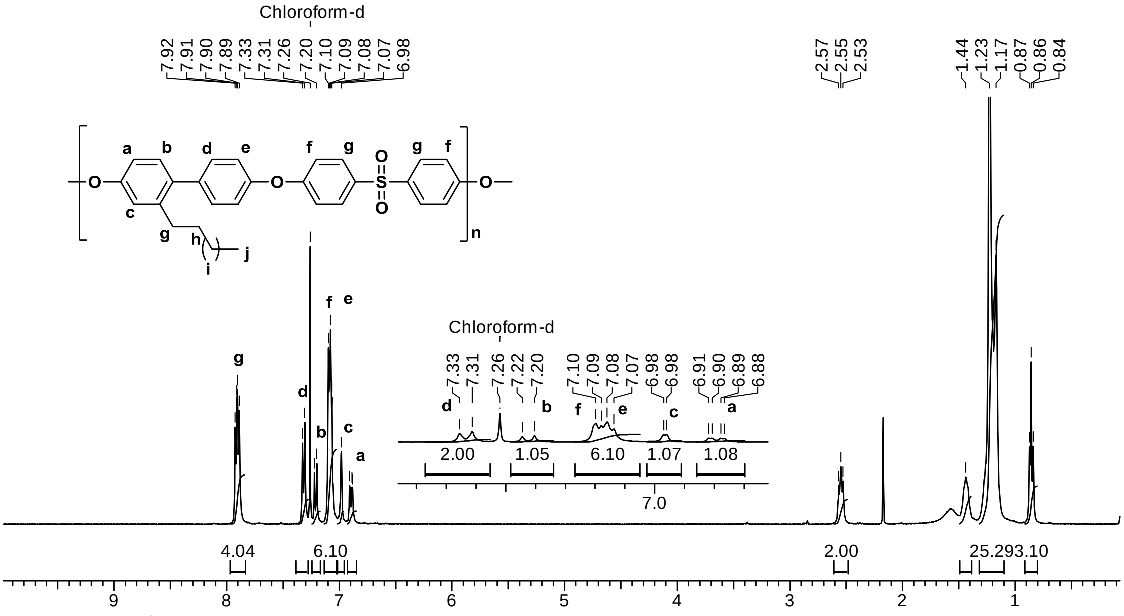


Figure 7.8 ^{1}H NMR spectrum (in $CDCl_3$) of PES derived from PDBP and FPS

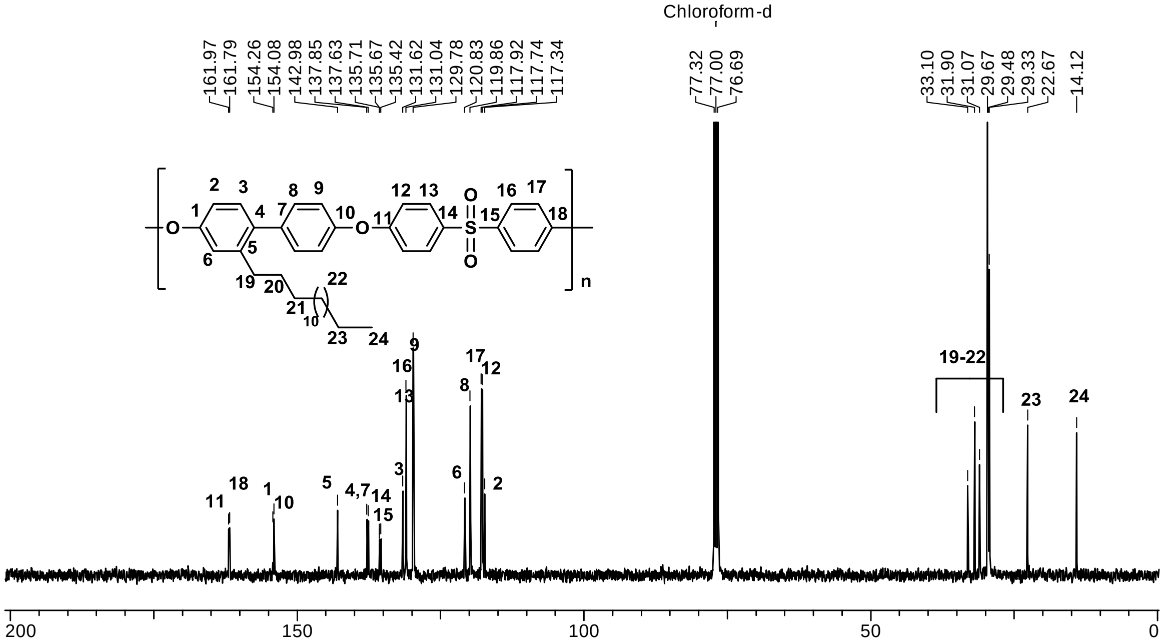
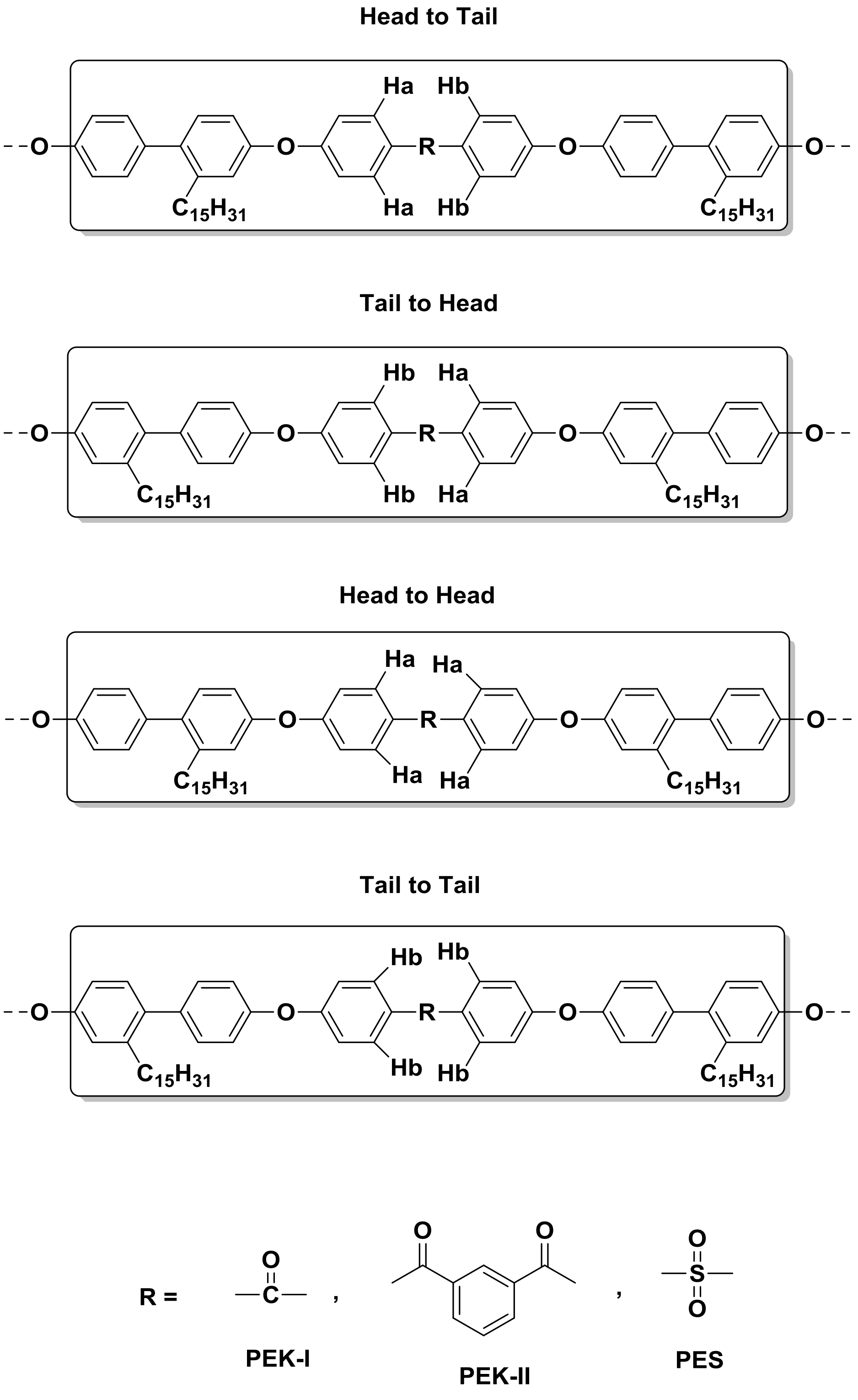


Figure 7.9 ^{13}C NMR spectrum (in CDCl$_3$) of PES derived from PDBP and FPS

The four signals were observed for the protons *ortho* to carbonyl/sulfone group of poly(arylene ether)s. The appearance of four signals could be due to the constitutional isomerism resulting from the use of non-symmetrical biphenol monomer. As discussed in **Chapter 5,** the feasible 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 possible structural orientations of poly(arylene ether)s are depicted in **Figure 7.10**.

In ^{1}H NMR spectra of poly(arylene ether)s, theoretically one would expect three doublets corresponding to protons *ortho* to carbonyl/sulfonyl group, if constitutional isomers were present. However, 400 MHz NMR spectra of poly(arylene ether)s displayed only four signals corresponding to protons *ortho* to carbonyl/sulfonyl group.


Head to Tail

Tail to Head

Head to Head

Tail to Tail

Figure 7.10 Plausible sequences in poly(arylene ether)s derived from PDBP and aromatic dihalides

In order to make definitive conclusions, 2 D NMR experiments were carried out. COSY and HMBC spectra of PEK-I are reproduced in **Figure 7.11-7.14**. In COSY spectrum, protons 'g' and f, d and e, a and b showed correlation with each other, indicating that they are placed *ortho* to each other. In aliphatic region, protons are showing correlation with the protons on adjacent carbon atoms. (**Figure 7.11**). The expanded region showing aromatic proton correlation is represented in **Figure 7.12.**

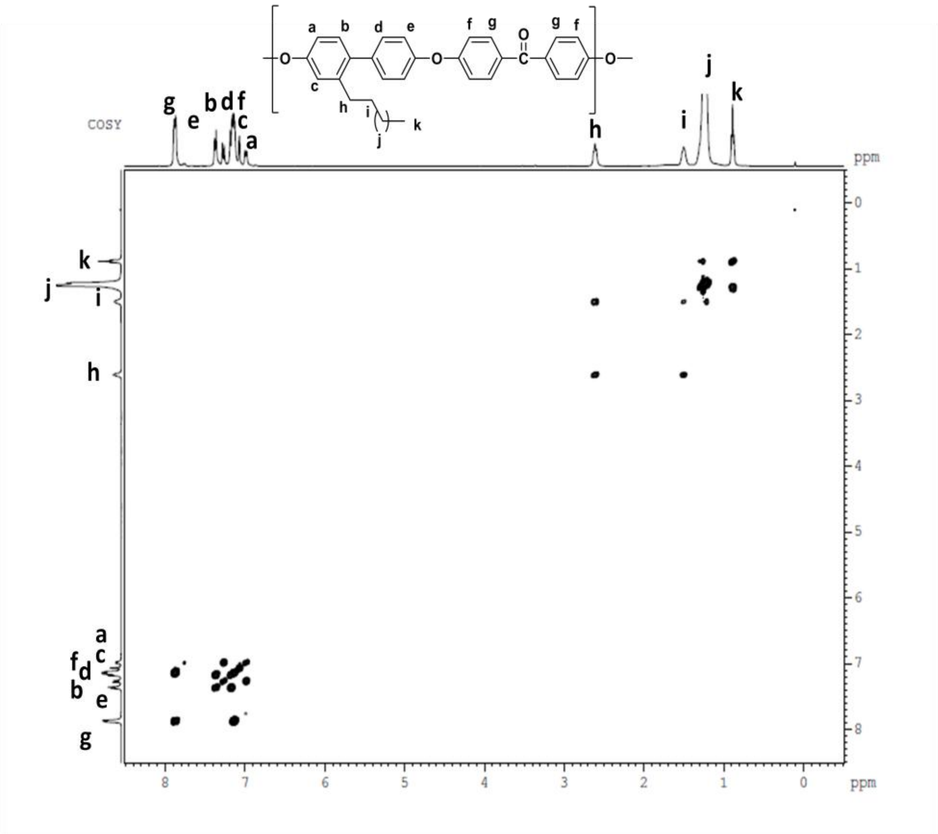


Figure 7.11 ^{1}H-^{1}H COSY spectrum of PEK-I

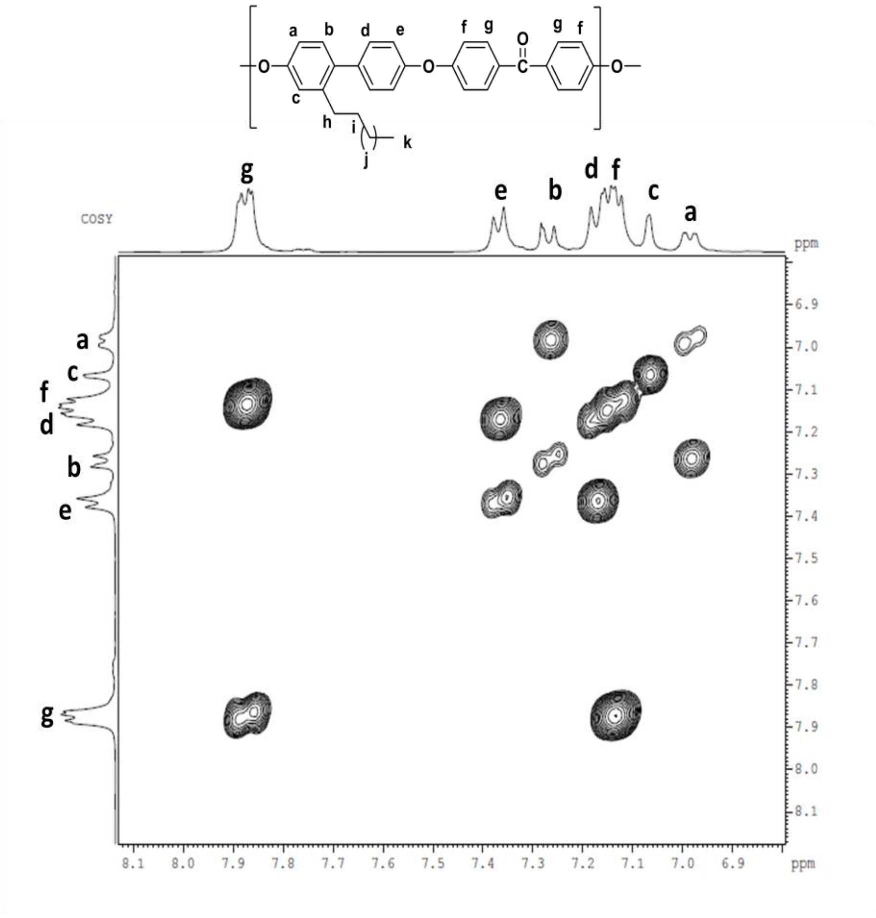


Figure 7.12 ^{1}H-^{1}H COSY spectrum of PEK-I: Expanded region

The correlation between protons and carbons were studied by heteronuclear multiple-bond correlation spectroscopy (HMBC) and heteronuclear single-quantum correlation spectroscopy (HSQC). The assignments of carbons in ^{13}C spectrum of PEK-I were confirmed by HMBC and HSQC correlations. The HMBC spectrum along with assignments is reproduced in **Figure 7.13.** In HMBC spectrum, carbonyl carbon (15) showed correlation with protons ‘g’ which are placed *ortho* to carbonyl group. Moreover, the carbonyl carbon appeared as three signals at 194.21, 194.24 and 194.28 δ ppm, in approximately 1:2:1 proportion (**Figure 7.14**) which further supports the presence of constitutional isomerism.

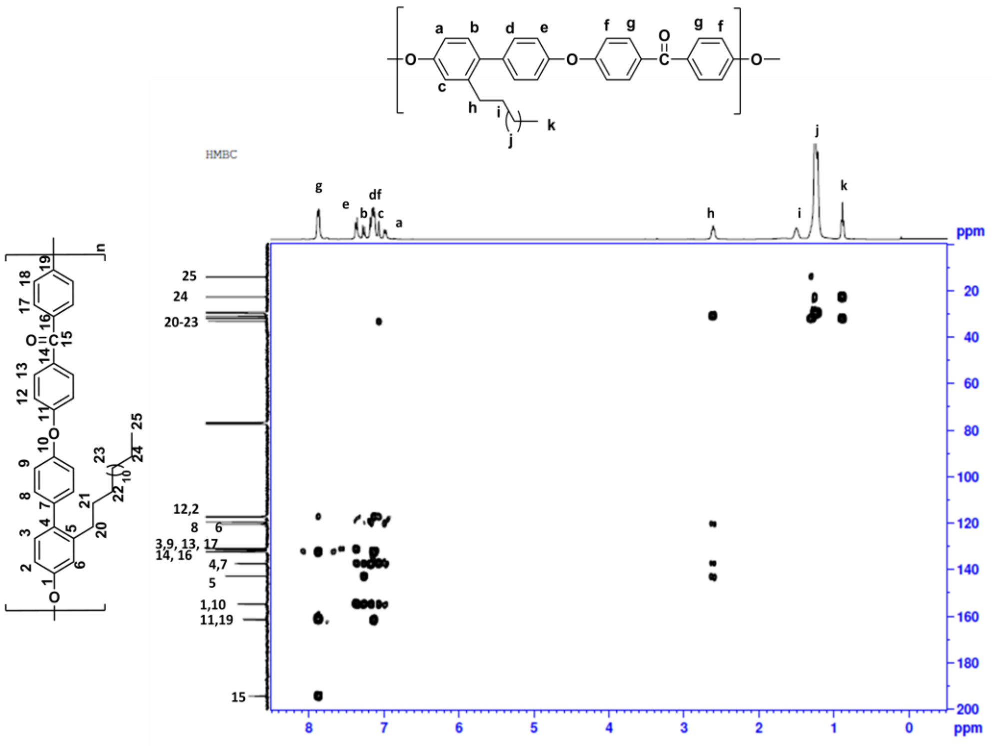


Figure 7.13 HMBC spectrum of PEK-I

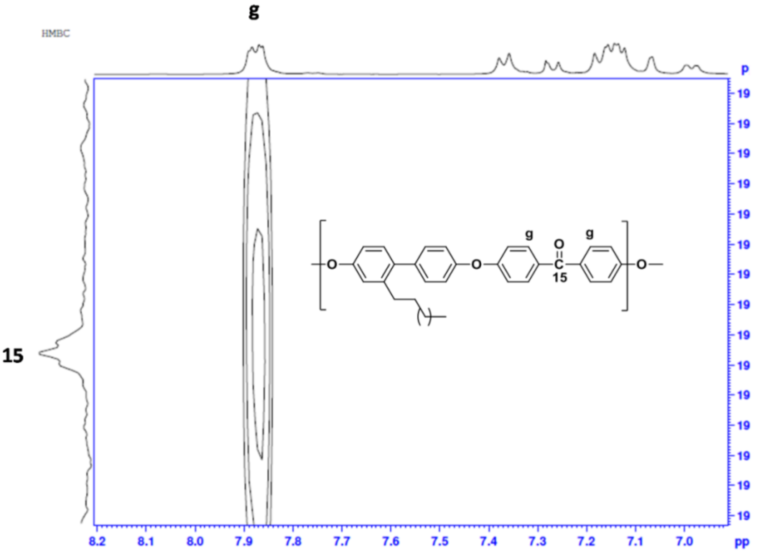


Figure 7.14 HMBC spectrum of PEK-I: Expanded region

7.4.3 Solubility of poly(arylene ether)s

The solubility behavior of poly(arylene ether)s was tested in organic solvents at 3.0 % (w/v) and the data is presented in **Table 7.2**.

Table 7.2 Solubility data of poly(arylene ether)s

Polymer	Dihalide	$CHCl_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	DMSO
PEK-I	**DFB**	++	++	++	+-	+-	++	++	--
PEK-II	**BFB**	++	++	++	+-	+-	++	++	--
PES	**FPS**	++	++	++	+-	++	++	++	--

++ : soluble at room temperature; +- : soluble on heating; -- : insoluble on heating at 80 °C

It is well known that the conventional PEEKs are insoluble in most of the common organic solvents. PEK-I and PEK-II were soluble at room temperature in solvents such as dichloromethane, chloroform, tetrahydrofuran, pyridine, and 1-methyl-2-pyrrolidinone and were soluble in solvents such as N,N-dimethylformamide and N,N-dimethylacetamide upon heating. In light of the organosolubility of poly(ether ketone)s containing pendent pentadecyl chains, they could be considered as good candidates for applications such as gas separation and microelectronic devices where the combination of solubility plus good thermal properties is desired.

Poly(ether sulfone) was soluble in organic solvents such as chloroform, dichloromethane and THF at room temperature.

Overall, poly(arylene ethers) containing pentadecyl chains exhibited improved solubility than analogous poly(arylene ether)s based on 4,4’-biphenol which are reported to be insoluble in common organic solvents.[17] Obviously, the improved solubility poly(arylene ethers)s synthesized in the present work could be attributed to the incorporation of pendent pentadecyl chains, which prevent the close packaging of the polymer chain and lead to the increased free volume, which, in turn, facilitates the penetration of the solvent molecules resulting in improved solubility.

7.4.4 X-Ray diffraction studies

The crystallinity of poly(arylene ether)s was characterized by wide angle X-ray diffraction (WAXD) studies. All the polymers exhibited amorphous halos over the 2θ range 15-25° which indicated their amorphous nature **(Figure 7.15).**

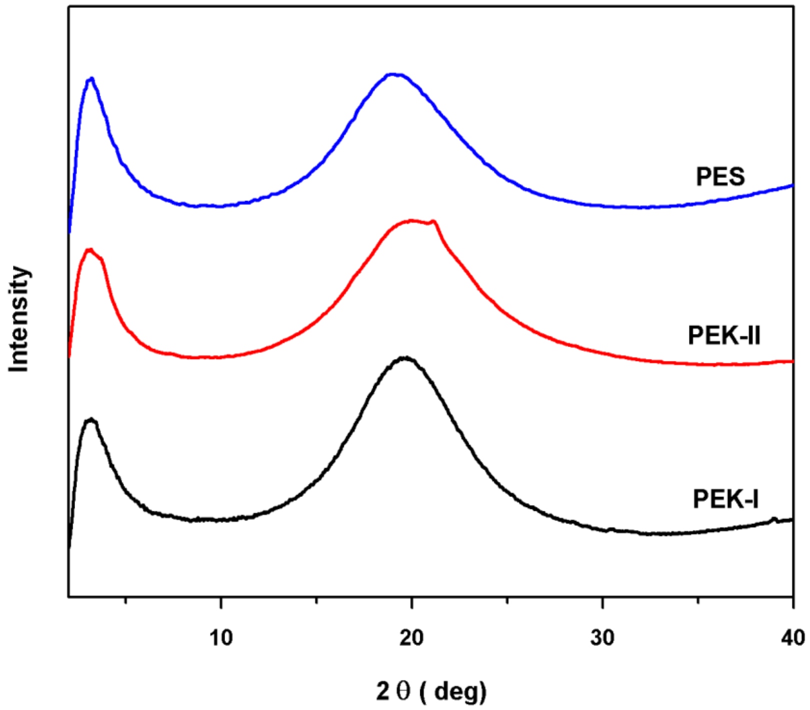


Figure 7.15 X-Ray diffractograms of poly(arylene ether)s derived from PDBP and activated aromatic dihalides

A broad reflection in the small-angle region at about 2θ ≈ 3° was observed for all poly(arylene ether)s. This could be attributed to the presence of layered structure developed due to the packing of pentadecyl chains. There are reports in which layered crystalline structure was showed by the polymers with flexible long chains.[35] The amorphous nature was mainly ascribed to the introduction of pentadecyl chains which prevent close chain packing with increased free volume, this resulted in a decrease in crystallinity. Additionally, amorphous nature of polymers was also reflected in their excellent solubilities.

7.4.5 Thermal properties

Thermal properties of poly(arylene ether)s were characterized by thermogravimetric analysis (TGA) at a heating rate of 10 °C / minute under nitrogen atmosphere **(Figure 7.16)**. The decomposition temperature at 10% weight loss (T_{10}) and char yields at 800 °C for poly(arylene ether)s are given in **Table 7.3**

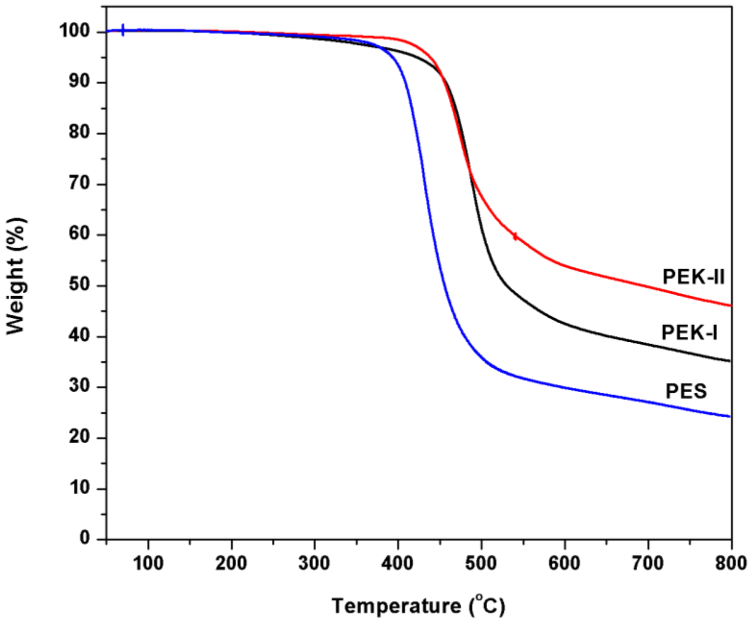
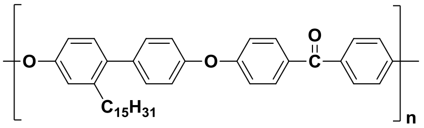
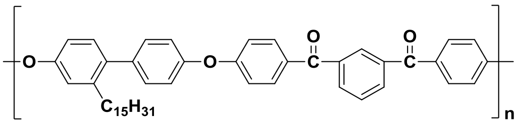
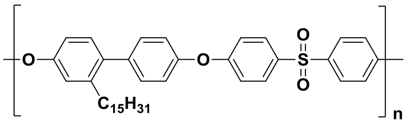


Figure 7.16 TG curves of poly(arylene ether)s derived from PDBP and activated aromatic dihalides

T_{10} values of poly(arylene ether)s were in the range 410-455 ^{o}C indicating their good thermal stability. The weight residue at 800 °C for PEK-I, PEK-II and PES were 35, 46 and 24, respectively. The T_{10} values indicated that the thermal stability trend in the poly(arylene ether)s was PEK-II > PEK-I > PES. A similar trend has been reported in the literature.[37]

Table 7.3 Thermal properties of poly(arylene ether)s

Polymer	Structure	T_{10} (°C)	Weight residue at 800 °C (%)	T_g (°C)
PEK-I		455	35	35 (143[a],158[b])
PEK-II		455	46	51
PES		410	24	60 (186[c], 221[d])

a : T_g of BPA-based PEEK; b : T_g of 4, 4'-biphenol-based PEEK; c : T_g of BPA-based PES; d : T_g of 4,4'-biphenol based PES

Glass transition temperatures (T_g) of poly(arylene ether)s were evaluated by differential scanning calorimetry (DSC) at a heating rate of 10 ^{o}C / min under nitrogen atmosphere. DSC curves of poly(arylene ether)s obtained from second heating scans are represented in **Figure 7.17** and the T_g values are presented in **Table 7.3.** The reported[17, 38] T_g values of BPA and 4,4'-biphenol based poly(arylene ether)s are also included in **Table 7.3.** The T_g values of PEK-I, PEK-II and PES were 35, 51 and 60 °C, respectively. It was observed that T_g of poly(arylene ether)s based on PDBP are lower than the corresponding poly(arylene ether)s based on bisphenol-A and 4.4'-biphenol. The significant drop in T_g could be attributed to presence of pendent flexible pentadecyl chains, which hinders close chain packing.

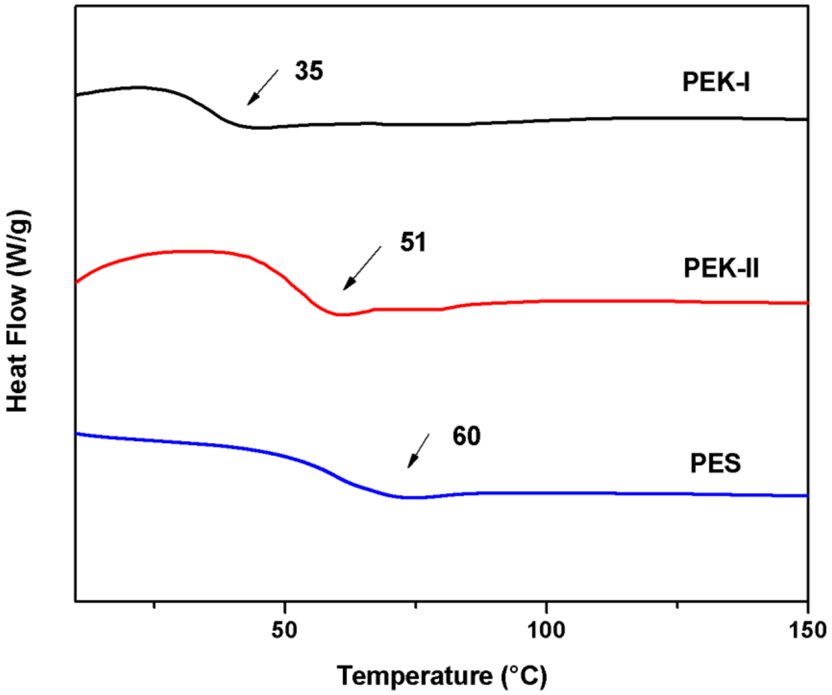


Figure 7.17 DSC curves of poly(arylene ether)s obtained from second heating scans

7.4.6 Gas permeability studies

Gas permeation using polymeric membranes is gaining importance due to techno-economical demands for gas separation applications in the various industries. Membrane-based separation techniques are modular in nature and therefore are easy to implement on large-scale. They need lower operational costs, lower maintenance and have operational simplicity over conventional processes like cryogenic and pressure swing adsorption (PSA). The main drawbacks of polymeric membrane-based gas separation processes are that (i) achieving very high level of purity is cost intensive and (ii) operations cannot be done at high temperatures due to polymer material characteristics. In such cases, the hybrid technology combining membranes with conventional ones are coming forward as promising alternatives. Newer polymeric materials are being investigated to meet demands of various types. The basic understanding towards polymer structure-gas permeation property is required to systematically architecture the polymer structure for required applications to meet a particular demand. For example, the separation of He from spent gas which is used as a diluent in breathing gas mixtures used by deep sea divers, would need polymeric materials that have high diffusivity selectivity. The separation of hydrocarbon mixtures is achieved with materials that have high solubility selectivity. .

7.4.6.1 Effect of structural modification on gas separation

Gas separation based on polymeric membranes is a dynamic and rapidly growing field. Polysulfone has adequate gas separation performance as well as good thermal stability, mechanical properties and chemical resistance.[39-41] Permeability and permselectivity of polymers significantly depend on the components and structure of polymers. Numerous studies on the relationship between the molecular structure of polymers and their gas transport properties have been reported in an attempt to gain a better understanding of the transport mechanism.[13, 17, 42, 43] Generally, chain rigidity imparts increased permselectivity but lower permeability. In terms of polymer molecular design, chain stiffness should be coupled with an increase in interchain separation in order to achieve simultaneously higher permeability and permselectivity.[43]

The effect of connector group and substituent symmetry on bisphenol plays an important role in governing permeation properties of poly(arylene ether)s,[42, 43] polycarbonates[44] and polyarylates.[45] Moreover, polymers derived from non-symmetrically substituted bisphenols have generally higher permselectivity than the polymers derived from unsubstituted or symmetrically substituted bisphenols. The substitution of polar groups like nitro, bromo, in combination with non-symmetric substitution on bisphenol increases permselectivity upto six times while decreasing permeability by half the value than unsubstituted one.[46] There are very few reports on permeability of long alkyl chain containing polysulfones.[47] Therefore, it was interesting to study effect of pendent pentadecyl chains on the permeation behavior of polysulfone. As a consequence, polyether sulfone containing pendent pentadecyl chains was evaluated for the gas permeation analysis.

7.4.6.2 Preparation of dense membrane for gas permeation

A 3-5 % (w/v) solution of PES in chloroform was prepared, filtered through 5μ ss-filter and poured onto a flat bottom glass plate. Chloroform was evaporated under dry conditions at ambient temperature. The formed film was peeled off and kept in a vacuum oven at 50 °C for seven days.

The permeability measurement using pure gases (He, H_2, N_2 and CO_2) was carried out by standard variable volume method at upstream gas pressure of 20 atm and at 35$\pm$0.1 °C; while maintaining the permeate side at the atmospheric pressure.[48] Membrane samples (5 cm in diameter) after removing from the vacuum oven were immediately mounted in the permeation cell. The gas permeability was calculated using the following equation:

$$P = \frac{N \cdot l}{(p_1 - p_2)} \qquad (1)$$

where, 'P', the permeability coefficient expressed in Barrer, 'N' is the steady-state penetrant flux (cm^3/cm^2.sec), 'p_1' and 'p_2' are the feed and permeate side pressures (cm Hg), while '*l*' is the membrane thickness (cm). The permeability measurements were repeated with at least three different membrane samples prepared under identical conditions and the data averaged. The dense membranes were prepared by solution casting method. These films were used for pure gas permeability determination by variable volume method at 35 °C ± 0.1 ^oC and 10 Kg/cm^2 upstream pressure.

The permeation cell was opened and circular coupon (size ~ 50 mm) of membrane was mounted into the permeation cell. The O-ring was kept on the top of the membrane (vacuum grease was applied to the O-ring to ensure the leak-proof assembly). The cell was fixed with inlet (connected to the gas cylinder and a pressure gauge) and outlet tubing and tightened. Using the regulator knob and the inlet valve, the pressure was adjusted in the cell while keeping the exhaust closed. Gas was flushed through the outlet valve seven to eight times in the system to ensure the removal of earlier gas to the maximum possible extent. The flow meter was attached to the permeate side through a flexible pipe. A desired pressure was applied to the upstream side of the cell while outlet valves were kept closed. **(Figure 7.18 and 7.19)**

Figure 7.18 Photograph of gas permeation unit

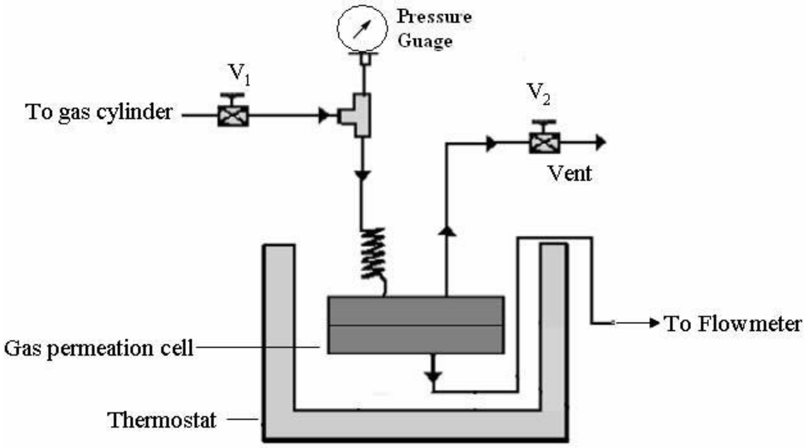
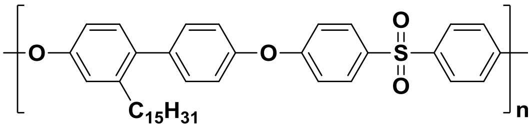
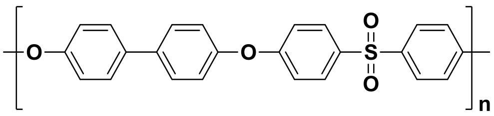


Figure 7.19 Schematic diagram of gas permeation equipment

7.4.6.3 Gas permeability analysis

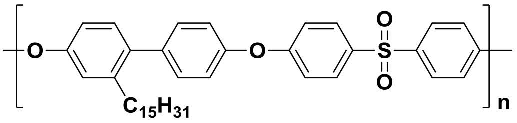
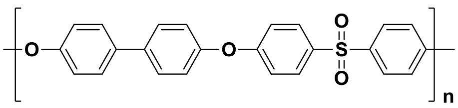
In the present study, poly(ether sulfone) containing biphenylene linkages and pendent pentadecyl chains was used for the permeability measurements of four gases viz., He, H_2, N_2, and CO_2. The permeability and permselectivity data is given in **Table 7.4 and 7.5,** respectively.

Table 7.4 Permeation[a] data of PES and BIPSF

Gas	 **PES**	 **BIPSF[b]**
P_{He}	16.6	12.0
P_{H_2}	15.3	14.0
P_{N_2}	0.62	0.24
P_{CO_2}	15.0	5.6

a-Determined at 20 atm upstream pressure, expressed in Barrer (1 Barrer = 10-10 cm^3(STP).cm/cm^2.s.cmHg); b –data taken form ref.17

Table 7.5 Permselectivity[a] data of PES and BIPSF

Gas	 **PES**	 **BIPSF[b]**
P_{He}/P_{N_2}	26.7	50.0
P_{H_2}/P_{N_2}	24.5	58.0
P_{CO_2}/P_{N_2}	24.0	23.0
P_{CO_2}/P_{H_2}	1.0	0.4

a-Determined at 20 atm upstream pressure, expressed in Barrer (1 Barrer = 10-10 cm^3(STP).cm/cm^2.s.cmHg); b –data taken form ref.17

The gas permeation analysis of poly(ether sulfone) containing pendent pentadecyl chains was compared with reference poly(ether sulfone) based on 4,4'-biphenol (BIPSF) (**Table 7.4 and 7.5).** The permeation data showed that there was increase in permeability for all gases. However, for small gases such as He and H_2 the increment was marginal. For N_2 and CO_2 the gas permeability increased almost three times than the reference polymer BIPSF. The increment in permeability can be explained by increase in chain mobility by flexible pentadecyl chains. The significant enhancement in case of N_2 and CO_2 can be attributed to their higher condensability in polymer matrix. This was also reflected in the respective selectivities. It was observed that, P_{He}/P_{N_2} and P_{H_2}/P_{N_2} were decreased as compared to the reference poly(ether sulfone) without pentadecyl chains while CO_2 based selectivities, P_{CO_2}/P_{N_2} and P_{CO_2}/P_{H_2} were increased significantly. This could be attributed to the internal plasticization effect of pentadecyl chain.

7.5 Conclusions

1. A series of new poly(arylene ether)s containing biphenylene linkages in the backbone and pendent pentadecyl chains were synthesized by polycondensation of 3-pentadecyl biphenol with commercially available activated aromatic dihalides.
2. Poly(arylene ether)s exhibited inherent viscosity in the range 0.50-0.81 dL/g indicating formation of reasonably high molecular weight polymers.
3. The number average molecular weights (M_n) measured by GPC were in the range 2.2-8.3 x 10^4 with polydispersity of 2.2.
4. The existence of constitutional isomerism in poly(arylene ether)s based on 3-pentadecyl biphenol-a non-symmetric monomer- was evidenced from detailed NMR spectroscopy studies.
5. Poly(arylene ether)s were soluble in common organic solvents such as dichloromethane, chloroform and tetrahydrofuran. Tough, transparent and flexible films could be cast from their chloroform solutions.
6. X-Ray diffraction analysis showed that the poly(arylene ether)s were amorphous and a reflection in small angle region indicated layered packing of pentadecyl chains
7. T_g values of the poly(arylene ether)s were in the range of 35-60 °C, the lowering of the T_g could be attributed to the packing disruptive effect of flexible pentadecyl chains.
8. T_{10} values of poly(arylene ether)s were in the range 410-455 °C, indicating their good thermal stability.
9. The gas permeation study of poly(ether sulfone) containing pendent pentadecyl chains exhibited moderate increase in permeability for helium and hydrogen with lower permselectivity as compared to reference poly(ether sulfone) based on 4,4’-biphenol. However, there was large increase in permeability for carbon dioxide and nitrogen due to internal plasticization effect of pentadecyl chains which led to higher CO_2 based selectivity.

References

1. P. E. Cassidy, *Thermally stable Polymers, Synthesis and Properties*, Dekker, New York, 1986.
2. R. J. Cotter, *Engineering Plastics: A Hand Book of Polyarylethers,* Gordon and Breach Publishers, Amsterdam, 1995.
3. P. M. Hergenrother, *High Perform. Polym.*, 2003, **15**, 3-45.
4. L. J. Mathias, C. M. Lewis and K. N. Wiegel, *Macromolecules,* 1997, **30**, 5970-5975.
5. C. Maes, J. Devaux, R. Legras and P. T. McGrail, *Polymer*, 1995, **36**, 3159-3164.
6. F. Liu, J. Ding, M. Li, M. Day, G. Robertson and M. Zhou, *Macromol. Rapid Commun.*, 2002, **23**, 844-848.
7. C. Gao and A. S. Hay, *J. Polym. Sci. Part A: Polym. Chem.*, 1995, **33**, 2731-2739.
8. X. C. Ge, Y. Xu, M. Xiao, Y. Z. Meng and A. S. Hay, *Eur. Polym. J.*, 2006, **42**, 1206-1214.
9. S. Watanabe, A. Kobayashi, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 1994, **32**, 909-915.
10. Z. Y. Wang and A. S. Hay, *J. Polym. Sci. Part A: Polym. Chem.*, 1991, **29**, 1045-1052.
11. M. R. Pixton and D. R. Paul, *Polymer*, 1995, **36**, 3165-3172.
12. M. Strukelj and A. S. Hay, *Macromolecules*, 1991, **24**, 6870-6871.
13. M. Aguilar-Vega and D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.*, 1993, **31**, 1599-1610.
14. J. L. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkes and J. E. McGrath, *Polymer*, 1991, **32**, 2020-2032.
15. J. Hedrick, I. Yilgor, G. Wilkes and J. McGrath, *Polym. Bull.*, 1985, **13**, 201-208.
16. H. J. Jeong, K. Iwasaki, M. A. Kakimoto and Y. Imai, *J. Macromol. Sci. Part A*, 1994, **31**, 1975-1983.
17. C. L. Aitken, W. J. Koros and D. R. Paul, *Macromolecules*, 1992, **25**, 3424-3434.

18. G. L. Tullos, P. E. Cassidy and A. K. St. Clair, *Macromolecules*, 1991, **24**, 6059-6064.
19. M. Jayakannan and S. Ramakrishnan, *Macromol. Rapid Commun.*, 2001, **22**, 1463-1473.
20. D. Shukla, Y. S. Negi, J. S. Uppadhyaya and V. Kumar, *Polym. Rev.*, 2012, **52**, 189-228.
21. P. T. McGrail, *Polym. Int.*, 1996, **41**, 103-121.
22. Y. J. Kim, I. S. Chung and S. Y. Kim, *Macromolecules*, 2003, **36**, 3809-3811.
23. I. S. Chung and S. Y. Kim, *Macromolecules*, 2000, **33**, 9474-9476.
24. I. S. Chung and S. Y. Kim, *J. Am. Chem. Soc.*, 2001, **123**, 11071-11072.
25. P. M. Hergenrother, B. J. Jensen and S. J. Havens, *Polymer*, 1988, **29**, 358-369.
26. S. K. Park and S. Y. Kim, *Macromolecules*, 1998, **31**, 3385-3387.
27. R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale and C. N. Merriam, *J. Polym. Sci. Part A-1: Polym. Chem.*, 1967, **5**, 2375-2398.
28. B. E. Jennings, M. E. B. Jones and J. B. Rose, *J. Polym. Sci. Part C: Polym. Symp.*, 1967, **16**, 715-724.
29. B. Liu, W. Hu, C. Chen, Z. Jiang, W. Zhang, Z. Wu and T. Matsumoto, *Polymer*, 2004, **45**, 3241-3247.
30. B. Liu, W. Hu, X. Rao, G. Wang, Z. jiang, Z. Wu and T. Matsumoto, *Polym. Bull.*, 2004, **52**, 235-242.
31. B. Liu, W. Hu, Y. Jin, C. Chen, Z. Jiang, Z. Wu, T. Matsumoto and A. Matsumura, *Macromol. Chem. Phys.*, 2004, **205**, 1677-1683.
32. Y. Y. Liu, W. M. Li, A. R. Hlil, Y. Z. Meng and A. S. Hay, *J. Macromol. Sci. Part A*, 2010, **47**, 1051-1054.
33. T. Yan, M. Chen, Q. Xu and M. Cai, *J. Polym. Res. C7 - 336*, 2015, **21**, 1-8.
34. G. Yu, C. Liu, J. Wang, J. Xu and X. Jian, *Polym. Int.*, 2010, **59**, 1233-1239.
35. A. S. More, S. K. Pasale, P. N. Honkhambe and P. P. Wadgaonkar, *J. Appl. Polym. Sci.*, 2011, **121**, 3689-3695.
36. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals; Pergamon Press: New York*, 1989.
37. V. L. Rao, P. U. Sabeena and K. N. Ninan, *Eur. Polym. J.*, 1998, **34**, 567-570.
38. D. J. Blundell and V. Bayon, *Polymer*, 1993, **34**, 1354-1360.

39. L. M. Robeson, *J. Membr. Sci.*, 1991, **62**, 165-185.
40. J. Y. Park and D. R. Paul, *J. Membr. Sci.,* 1997, **125**, 23-39.
41. L. M. Robeson, C. D. Smith and M. Langsam, *J. Membr. Sci.*, 1997, **132**, 33-54.
42. J. S. McHattie, W. J. Koros and D. R. Paul, *Polymer*, 1991, **32**, 840-850.
43. J. S. McHattie, W. J. Koros and D. R. Paul, *Polymer*, 1991, **32**, 2618-2625.
44. J. S. McHattie, W. J. Koros and D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.*, 1991, **29**, 731-746.
45. U. K. Kharul and S. S. Kulkarni, *Bull. Mater. Sci.*, 1994, **17**, 1071-1077.
46. U. K. Kharul and S. S. Kulkarni, *US 6420511*, 2002.
47. J. W. Simmons, US 5393323, 1995.
48. S. C. Kumbharkar, *Ph.D. Thesis submitted to University of Pune*, 2008.

Chapter 8

Synthesis and Characterization of Thermosetting Resins Containing Pentadecyl Chains

Chapter 8a

Synthesis and Characterization of Cyanate Ester Based on 4-(4-Hydroxyphenoxy)-3-pentadecylphenol

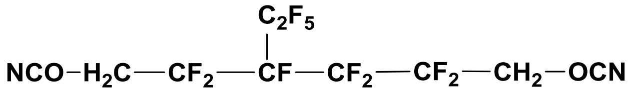
8a.1 Introduction

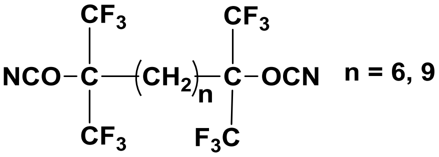
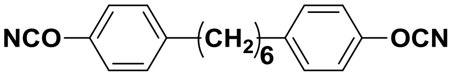
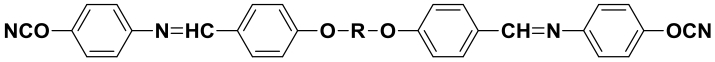
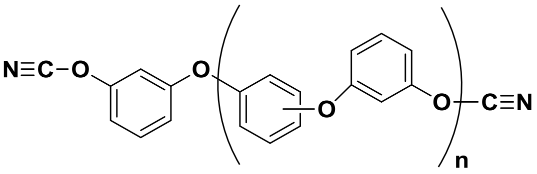
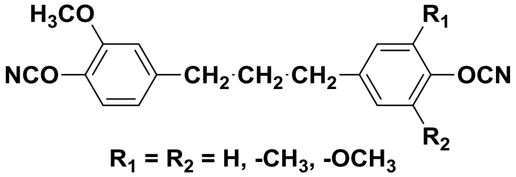
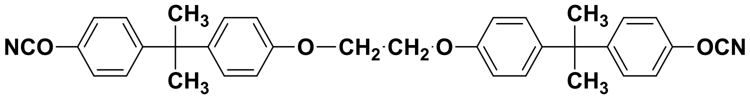
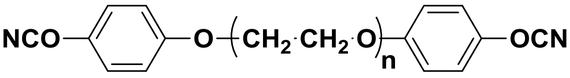
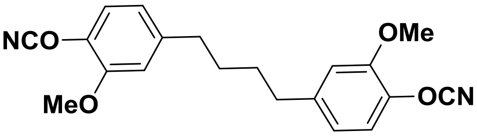
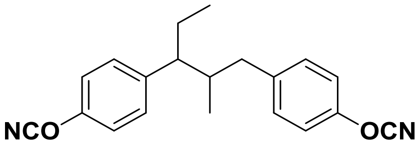
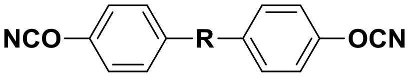
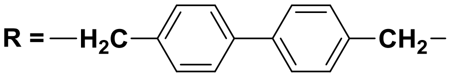
Cyanate ester resins are an influential class of thermosettings which have grown rapidly in the last four decades because of their properties such as good mechanical strength, low dielectric constant, radar transparency and superior adhesive properties. They dominate over other thermosets such as phenolic resins, epoxy resins, bismaleimides, etc. due to lower curing temperatures and high thermal stability. The important criterion that affects properties of polycyanurates is the structure of the cyanate ester monomers and properties of polycyanurates could be tuned with the proper selection of the monomers.[1-3]

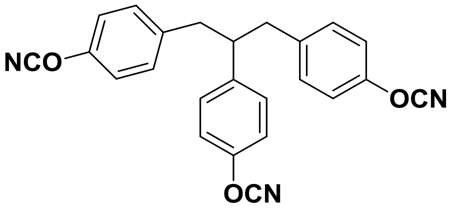
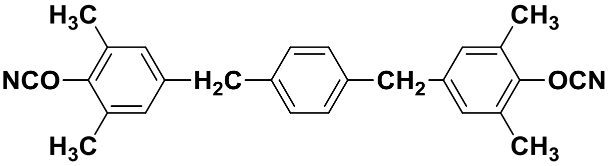
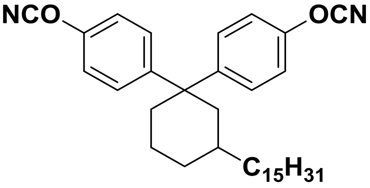
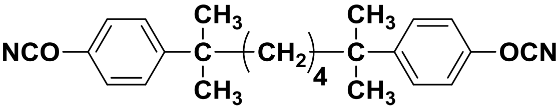
The method used for synthesis of cyanate ester monomers was introduced by Grigat and Putter[4, 5] in 1967. With the application of the Grigat and Putter method, a wide variety of cyanate ester monomers containing different moieties e.g. aliphatic, cycloaliphatic, fluoroaliphatic, ether linkages, siloxane, sulfone, phosphine oxide, phosphazene, biphenylene, triazole, pentadecyl chains, decahydronaphthalene, perhydrocumyl cyclohexane, etc. have been synthesized till date.[2, 6-13]

The number of cyanate ester monomers reported in the literature with different structural variations is too large to be catalogued here. Cyanate ester monomers containing flexible linkages/ side chains are collected in **Table 8.1.** Polycyanurates derived from cyanate ester monomers with such groups exhibit lower moisture absorption and dielectric contant.[2, 12, 14] On the other hand, the incorporation of aliphatic/cycloaliphatic spacer in the cyanate ester monomer structure contributes to lower crosslink density in polycyanurate network. The reduced crosslink density offers enhanced impact strength to polycyanurates.[7, 15]

Table 8.1 List of selected cyanate ester monomers containing flexible groups

Sr. No.	Cyanate ester monomer	Reference
1	$NCO-H_2C-O-(CF_2)_2-O-(CF_2)_4-O-(CF_2)_2-O-CH_2-OCN$	16
2	$NCO-H_2C-O-(CF_2)_2-O-(CF_2)_2-O-CH_2-OCN$	16
3	$NCO-H_2C-(CF_2)_n-CH_2-OCN$ n = 3, 4, 6, 8, 10	7, 16
4	 $NCO-H_2C-CF_2-CF(C_2F_5)-CF_2-CF_2-CH_2-OCN$	16

Sr. No.	Cyanate ester monomer	Reference
5		17
6		18
7	 R = $-(CH_2\cdot CH_2\cdot O)_n-CH_2\cdot CH_2\cdot O-$ n = 1, 2	19
8	 n = 1,3	20
9	 $R_1 = R_2 = H, -CH_3, -OCH_3$	21
10		22
11	 n = 1, 2, 3	23
12		24
13		25
14	 	26

Sr. No.	Cyanate ester monomer	Reference
15		27
16		28
17		29
18		30

In this work, new cyanate ester monomer viz., 4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene (HPPDPCN) containing pentadecyl chain and ether linkage and synthesized. HPPDPCN was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The non-isothermal curing kinetics of HPPDPCN was studied by DSC.

8a.2 Experimental

8a.2.1 Materials

4-(4-Hydroxyphenoxy)-3-pentadecylphenol (HPPDP) was synthesized as described in **Chapter 3**. Acetone, acetic anhydride, triethylamine, sodium chloride, sodium sulfate, sodium acetate, potassium hydroxide, celite and silica gel were received from Merck, India. Cyanogen bromide was procured from SRL, India. The solvents were of reagent grade quality and were used as received.

8a.2.2 Measurements

FT-IR spectra were recorded using a Perkin-Elmer Spectrum GX spectrophotometer. The spectra were recorded by depositing samples as solvent-cast thin films on sodium chloride cells.

NMR spectra were recorded on 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

DSC measurements were performed on TA Instrument (Q10) supported by TA Universal Analysis software for data acquisition. The samples (5-7 mg) were taken in aluminum pans and experiments were performed under a nitrogen flow of 50 mL / min. The samples were subjected to a dynamic DSC scan at the heating rate of 10 °C/min. The enthalpy of curing (ΔH) was determined from the area under the exothermic curve. The cure onset temperature (T_o) was considered as intersect of slope of baseline and tangent of curve leading to peak of transition.

8a.3 Synthesis of 4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene

Into a 250 mL three-necked round bottom flask equipped with a magnetic stirring bar, a pressure equalizing dropping funnel and a thermowell were added cyanogen bromide (4.77 g, 0.05 mol) and 4-(4-hydroxyphenoxy)-3-pentadecylphenol (6.28 g, 0.02 mol). The reactants were dissolved in acetone (100 mL). The solution of freshly distilled triethylamine (stored over KOH) (6.0 mL, 0.05 mol) in acetone (10 mL) was added at –15 °C over a period of 30 minutes to the reaction mixture with a constant stirring. After the completion of addition, the reaction mixture was stirred at –15 ^{o}C for 3 h and then filtered through a sintered funnel. The residue was washed with acetone (2 x 15 mL). The filtrate was concentrated under reduced pressure at room temperature and then dissolved in dichloromethane (150 mL). The dichloromethane solution was washed successively with 4% aqueous sodium chloride solution (3 x 25 mL) and water (2 x 25 mL). The dichloromethane solution was dried over sodium sulfate, filtered and concentrated on a rotary evaporator at room temperature under reduced pressure to yield a colorless viscous liquid which was purified by passing through a bed of silica gel. The product solidified on storing in the refrigerator for 24 h.

Yield: 7.67 g (83 %).

MP: 30 °C.

IR (cm^{-1}): 2270 (triple bond stretching of –O-CN)

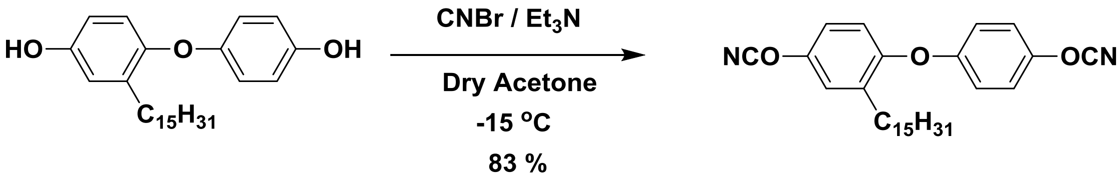
^{1}H NMR: (200 MHz, $CDCl_3$) δ = 7.27 (d, 2H), 7.22 (d, 1H), 7.11 (dd, 1H), 6.96 (d, 2H), 6.92 (d, 1H), 2.61 (t, 2H), 1.54-1.60 (m, 2H), 1.25 (bs, 24H), 0.88 (t, 3H)

^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.90, 152.09, 148.94, 148.06, 137.53, 121.01, 118.91, 117.28, 116.85, 114.00, 108.86, 31.88, 30.08, 29.64, 25.46, 29.27, 22.65, 14.09.

8a.4 Results and Discussion

8a.4.1 Synthesis of 4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene

A new cyanate ester monomer *viz;* 4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene (HPPDPCN) containing pendent pentadecyl chain was synthesized starting from 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP) (**Scheme 8.1**).



Scheme 8.1 Synthesis of HPPDPCN

The cyanation of HPPDP was carried out by following the protocol developed by Grigat and Putter.[5] The reaction was carried out by addition of triethyl amine to a mixture of HPPDP and cyanogen bromide in dry acetone as a solvent at -15 °C. The reaction progressed with the precipitation of triethyl ammonium bromide salt. The role of reaction temperature was very crucial as Von Braun reaction[31] is reported to compete with cyanate ester formation to produce diethylcyanamide; an unwanted by-product.[31]

8a. 4.2 Structural characterization

The cyanate ester monomer was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. **Figure 8.1** depicts FT-IR spectrum of HPPDPCN.

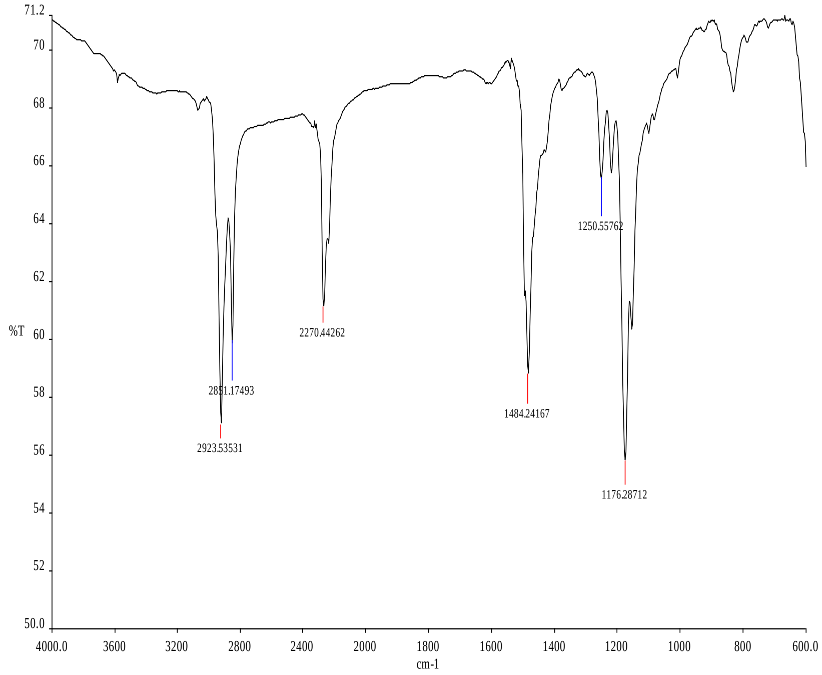


Figure 8.1 FT-IR spectrum of HPPDPCN

FT-IR spectrum confirmed complete conversion of HPPDP into HPPDPCN as band corresponding to –O-H stretching was absent. The characteristic triple bond stretching of –OCN group was observed at 2270 cm^{-1} along with a small notch. The splitting could be attributed to dimer complex formation,[32] but the exact mechanism of it is not yet clear. For alkyl cyanates, the splitting has been reported to be due to a Fermi resonance between 2270 cm^{-1} stretching and the first overtone of C-O-C asymmetric stretching mode.[32, 33] However, for aryl cyanates, the understanding of splitting is less clear.

^{1}H-NMR spectrum of HPPDPCN is shown in **Figure 8.2**.

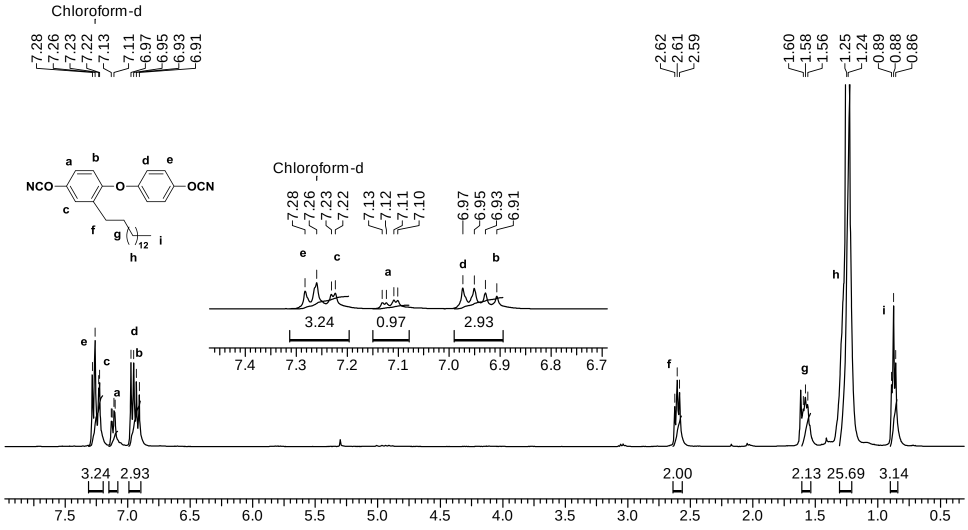


Figure 8.2 ^{1}H NMR spectrum (in $CDCl_3$) of HPPDPCN

Due to electron withdrawing effect of –OCN group the protons *ortho* to –OCN groups were found to be deshielded. The protons *ortho* to –OCN group of aromatic ring without pentadecyl chain exhibited a doublet at 7.27 δ ppm. The proton *ortho* to pentadecyl chain appeared as a doublet at 7.22 δ ppm while the proton *para* to pentadecyl chain appeared as a doublet of doublet at 7.11 δ ppm. The multiplet in the range 6.91-6.97 δ ppm could be assigned to three protons *meta* to –OCN groups. The benzylic methylene protons appeared as a triplet at 2.61 δ ppm, the methylene protons *β* to aromatic ring appeared as a multiplet in the range 1.56-1.60 δ ppm. The other methylene protons exhibited a multiplet over the range 1.20–1.30 δ ppm. The terminal $–CH_3$ showed a triplet at 0.88 δ ppm.

Figure 8.3 represents ^{13}C NMR spectrum of HPPDPCN.

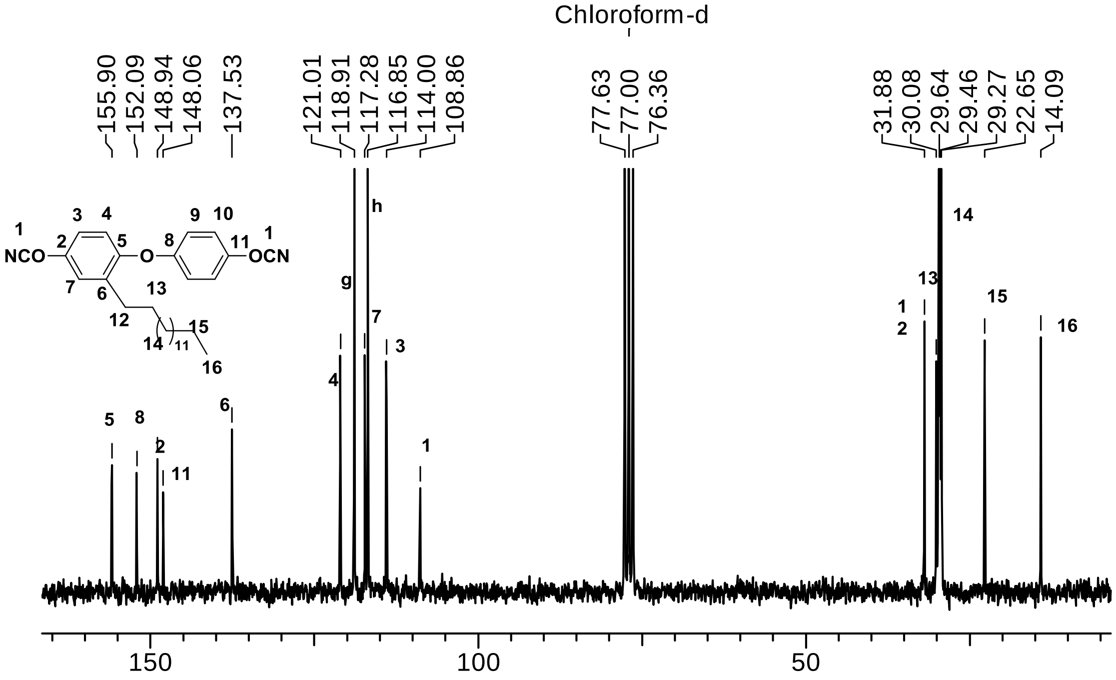


Figure 8.3 ^{13}C NMR spectrum (in $CDCl_3$) of HPPDPCN

In ^{13}C NMR spectrum, the peak appeared at 108.86 δ ppm corresponds to cyanate carbon which confirmed the formation of cyanate ester. The aromatic carbons (C5, C8) attached to ethereal oxygen appeared at 155.90, 152.09 δ ppm, respectively. The carbon attached to –OCN (C2, C11) appeared at 148.94, 148.06 δ ppm, respectively. The peak at 137.54 δ ppm is due to the quaternary carbon (C6) to which pentadecyl chain is attached. The carbons of the aromatic ring substituted with pentadecyl chain are shielded than that of carbons of aromatic ring without pentadecyl chain. The benzylic carbon showed a peak at 31.88 δ ppm and other methylene carbons except adjacent to methyl carbon appeared in the range 30.08-29.27 δ ppm.

The carbon adjacent to the methyl exhibited a peak at 22.65 δ ppm and terminal methyl carbon appeared as peak at 14.09 δ ppm.

8a.4.3 Non-isothermal cure kinetics

In order to design the processing conditions/parameters of newly synthesized cyanate ester monomer, it was imperative to understand the cure kinetics. **Figure 8.4** represents DSC curve of cyanate ester monomer (neat) under study.

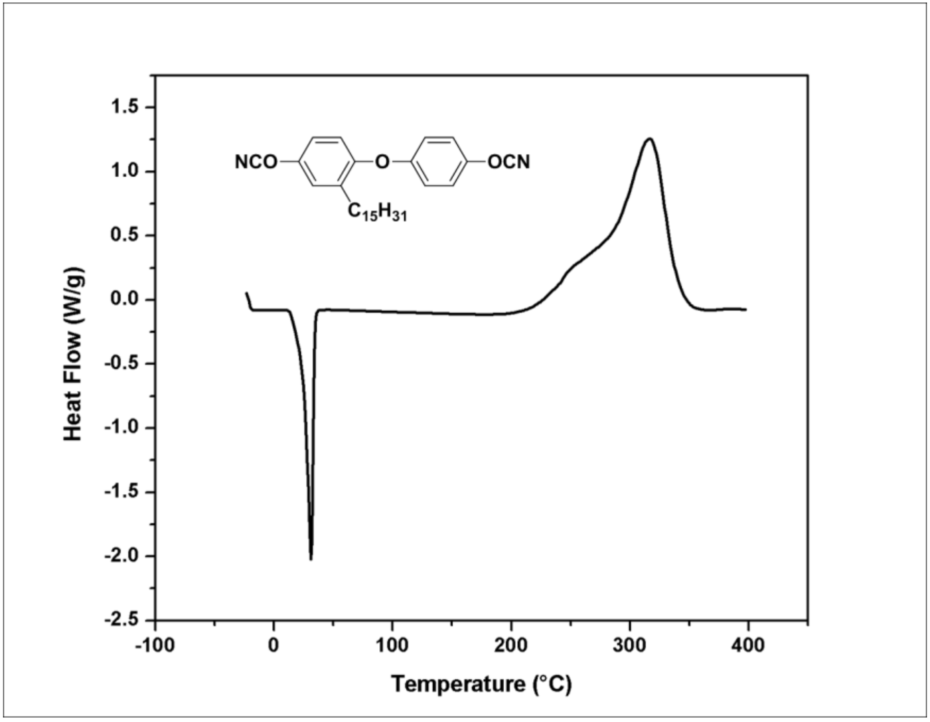


Figure 8.4 DSC curve of HPPDPCN

DSC thermogram was not found to be perfectly mono-modal in nature and had some inhomogeneity during initial phase of curing. As the apparent activation energy of the overall reaction is obtained from averages of the various reaction steps, this small inhomogeneity would not affect the overall kinetics of curing reaction to a large extent. The onset temperature (T_o), peak temperature (T_p) and final temperature (T_f) of uncatalyzed curing reaction was obtained from DSC curve and the values are given in **Table 8.2**. DSC curve showed an endotherm at 31 °C corresponding to melting phenomenon. The melting point of HPPDPCN is lower than that of bisphenol A dicyanate (BPACN, mp. 84 °C). The lowering of melting point could be attributed to the presence of pendent pentadecyl chains along with flexible ether linkage in the structure of HPPDPCN. This lower melting point helps in providing a wider processing window of 219 °C.[29]

Table 8.2 Cure characteristics and kinetic parameters of curing reaction of HPPDPCN and BPACN

Cyanate ester Monomer	T_m (°C)	Processing window (T_o-T_m) (°C)	Cure Characteristics				Kinetic Parameters	
			T_o (°C)	T_p (°C)	T_f (°C)	ΔH (KJ/mol)	Ea (KJ/mol)	Ln A (S^{-1})
HPPDPCN	31	219	250	317	356	209	108.06	9.97
BPACN[a]	84	124	208	286	334	189	174.80	33.17

T_m – Melting point, T_o – Cure onset temperature, T_p - Peak temperature, T_f –Final cure temperature, ΔH – Enthalpy of curing reaction, Ea – Activation energy, A – Arrhenius frequency factor, a – data taken from ref. 34

The enthalpy (ΔH) of curing reaction for the monomer under present study was found to be 209 KJ/mol. The curing of cyanate monomers is known to proceed with an enthalpy of ΔH ≈ - 105 KJ/mol per cyanate groups. For various dicyanates, ΔH has been observed to be around 210 KJ/mol.[33] The curing of uncatalyzed cyanate ester exhibits onset temperature (T_o) at 250 °C. As per literature, if absolutely pure monomer is heated, no curing reaction would take place. The curing of cyanate ester monomers in the absence of added catalyst could be catalysed by hydrogen donating impurities such as residual phenol, moisture, etc. Since the presence of such trace impurities catalyzes the curing reaction (influencing thereby onset temperature T_o), the correlation of reactivity based on variation in structure of monomer becomes difficult. For catalysed curing reaction, different catalysts such as transition metal carboxylates, acetyl acetonates, carbonyls, phenols, adventitious water, etc., are commonly employed.[2, 35, 36]

The curing kinetics of cyanate ester resins[34] has been well-known to obey a classical n^th order kinetic model as:

$$\frac{d\alpha}{dT} = k_1 (1-\alpha)^n \qquad \text{…......(1)}$$

For non-isothermal reactions, the rate equation can be given by:

$$\frac{d\alpha}{dT} = (A/\varphi) e^{-E/RT} (1-\alpha)^n \qquad \text{……. (2)}$$

Where, α is fractional conversion at temperature T, φ is heating rate, E is activation energy, A is Arrhenius frequency factor, R is gas constant, and n is the order of reaction.

In the present study, Coats-Redfern equation[37] (eq. 3) was used to study cure kinetics which can be represented as:

$$\ln\{g(\alpha)/T^2\} = \ln\{(AR/\varphi E)(1-2RT/E)\} - E/RT \qquad \text{….. (3)}$$

Where, $g(\alpha) = [1-(1-\alpha)^{1-n}]/(1-n)$; for n = 1, $g(\alpha) = -\ln(1-\alpha)$; R is the gas constant.

To arrive at kinetic parameters, equation (3) was employed to calculate fractional conversion 'α' using fractional enthalpy of curing reaction. The curve of $\ln\{g(\alpha)/T^2\}$ versus 1/T with the different predetermined values of order of reaction, n = 0.5, 1, 1.5, 2, 2.5 and 3, were plotted. The best linear fit indicated the order of reaction 'n'. For the present cyanate ester monomer under investigation, the best fit was found to be for n = 1 for most of the conversion region. **Figure 8.5** shows plots of determination of order of reaction and curing parameters.

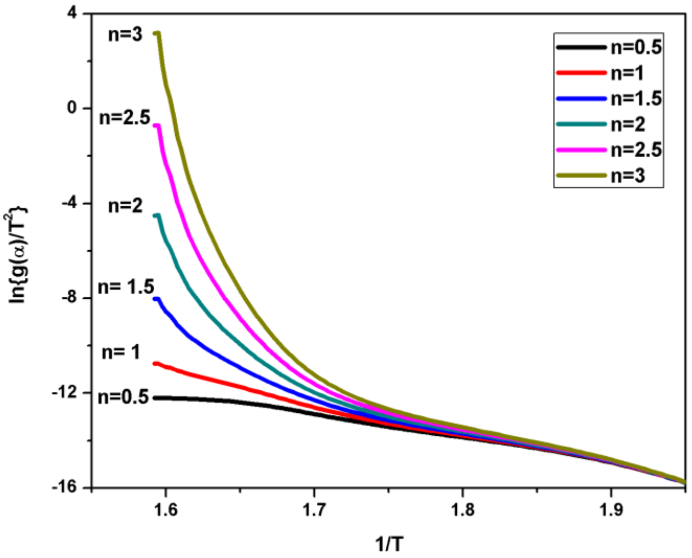


Figure 8.5 Determination of order of cyanate ester curing reaction by Coats-Redfern equation

The curing parameters (activation energy and Arrhenius frequency factor) were computed from slope and intercept of the plot with n = 1 and data is collected in **Table 8.2**. The kinetics of uncatalysed curing reaction of cyanate ester is known to be affected by hydrogen donating impurities such as residual phenol, moisture, etc.

Therefore, a direct comparison of curing parameters viz., order of reaction and activation energy of HPPDPCN and that of BPACN was not made.

8a.5 Conclusions

1. A new cyanate ester monomer *viz*; 4-cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene, containing ether linkage and pendent pentadecyl chain was synthesized from 4-(4-hydroxyphenoxy)-3-pentadecylphenol by its reaction with cyanogen bromide and was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy.
2. The lower melting point (31 °C) of HPPDPCN provided wider processing window of 219 °C than that of BPACN monomer which has a processing window of 124 °C.
3. The enthalpy and activation energy of curing reaction of HPPDPCN in uncatalyzed mode was found to be -209 KJ/mol and 108.06 KJ/mol, respectively.

Chapter 8b

Synthesis and Characterization of Bismaleimide Based on 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)-aniline

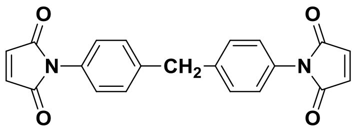
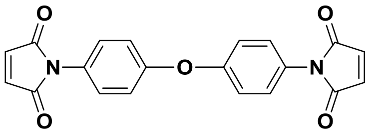
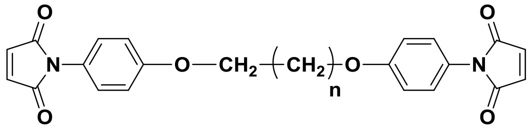
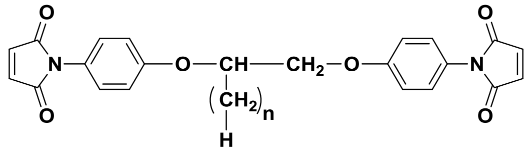
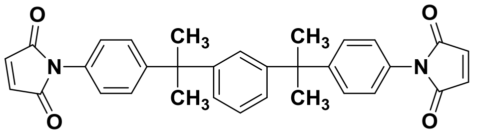
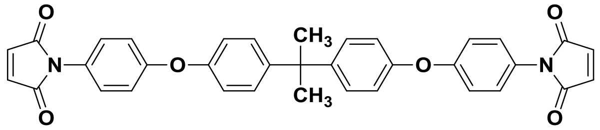
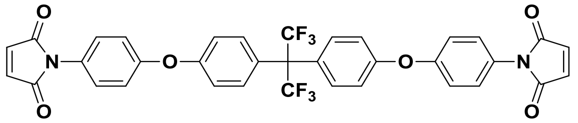
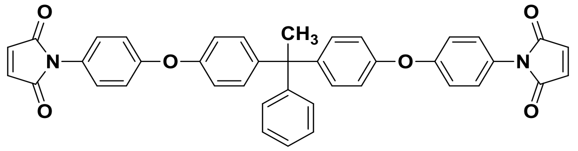
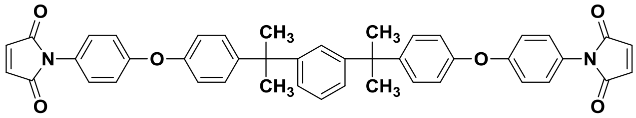
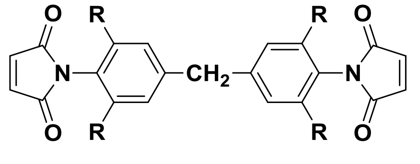
8b.1 Introduction

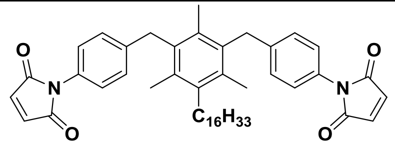
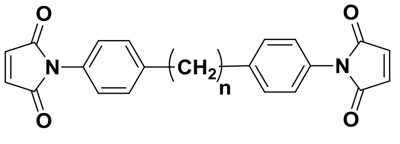
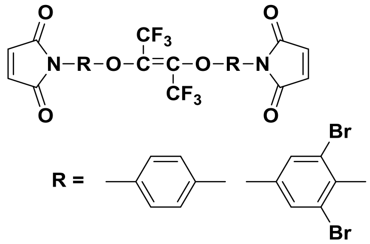
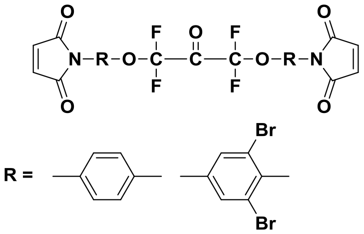
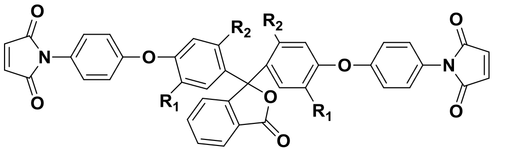
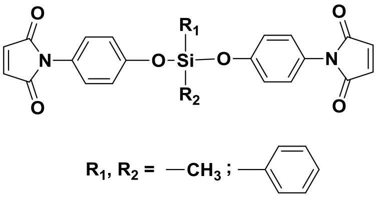
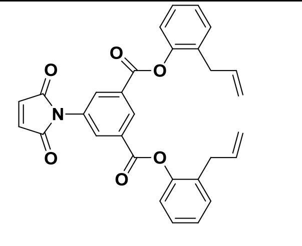
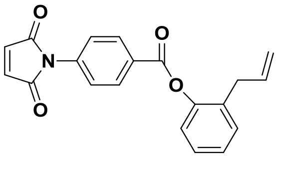
Bismaleimides (BMIs) are addition-type polyimides comprising thermally curable monomer or oligomers and cured resins.[38] As mentioned in **Chapter 5,** aromatic polyimides have a wide range of applications in microelectronics, aerospace and automobile industries due to their excellent thermal stability, mechanical strength and chemical resistance.[39-42] BMIs have ability to be fabricated with processing conditions like epoxies without evolution of void forming volatiles which makes them the resin of choice in aforementioned applications. Additionally, BMIs possess higher stiffness as well as higher dimensional stability because of their higher crosslink networks.[43, 44]

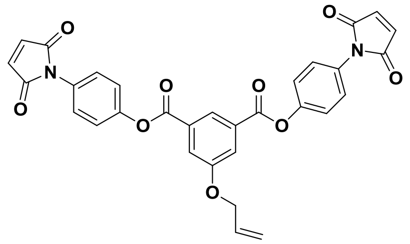
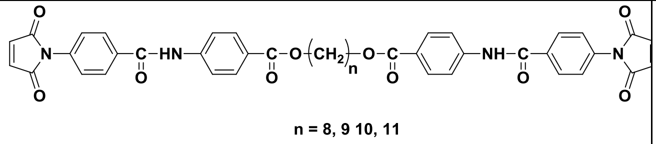
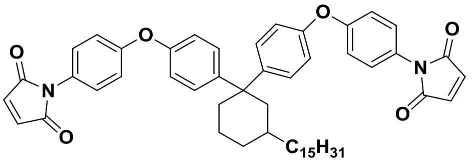
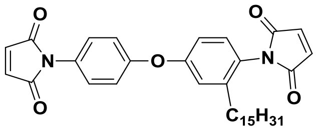
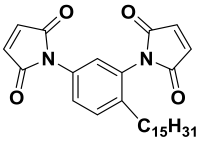
However, conventional BMI monomers with rigid and symmetrical structures have melting temperatures higher than 150 °C. The higher melting points (>150 °C) of BMIs result into narrow processing window, shorter gel time or shorter potlife of the melt making their processing difficult. Moreover, poor solubility of BMIs in common organic solvents and inherent brittleness of cured BMI resins remain the other drawbacks. These set of drawbacks limit the widespread applications of BMI resins to a greater extent.[45, 46]

To surmount these difficulties, great efforts have been made to develop new BMI monomers with improved solubility, lower melting points and enhanced facture toughness in corresponding cured resins. The preferred approach has been synthesis of new BMI monomers with flexible linkages/spacers.[47-51] The introduction of flexible spacer decreases the interaction between two reactive end groups leading to lowered melting points and improved solubility of BMI monomers. The lowering of melting points offers sufficient temperature gap between melting and cure onset. It is observed that introduction of aromatic ether linkages decrease T_g, and enhance toughness without compromising thermal stability. Barton et al[52, 53] reported synthesis of BMIs with melting points lower than 100 °C and observed that the purity of BMI monomer has marked effect on the thermal cure characteristics. In literature, there are number of reports on BMI monomers containing flexible spacers such as alkylene, oxyalkylene, ether, pendent alkyl groups, etc.[51, 54, 55] **Table 8.3** lists selected BMI monomers containing flexible linkages and common BMIs with their melting points.

Table 8.3 List of bismaleimide monomers containing flexible linkages

Sr. No.	Bismaleimide	Melting Point (°C)	Ref.
1		155-157	55
		157-158	56
		160-163(Purity: 95-99.3 %)	57
2		173-174	55
		176-178	58
3	 n = 2, 4	130-132 (n= 2) 98-100 (n= 4)	49
4	 n = 2, 3, 4	53-54 (n= 2) 48-49 (n= 3) 46-47 (n= 4)	49
5		135	50
6		85	50, 59
7		90	50
8		131	50
9		90	50
10	 R = $-CH_3$, $-C_2H_5$, $-CH(CH_3)_2$	210 (R = CH_3) 162 (R = C_2H_5) 221(R= $H(CH_3)_2$)	60

Sr. No.	Bismaleimide	Melting Point (°C)	Ref.
11		45	61
12	 n = 5, 6, 7, 8	101-103 (n = 5) 138-142 (n = 6) 75-78 (n = 7) 123-126 (n = 8)	62
13		161 (R = C_6H_4) 159 R = $C_6H_2Br_2$	63
14		152 (R = C_6H_4) 150 (R= $C_6H_2Br_2$)	63
15	 R_1 = -H, $-CH_3$, $-CH(CH_3)_2$ R_2 = -H, $-CH_3$,	145 (R_1= -H, R_2= -H) 119 (R_1=$-CH_3$, R_2=-H) 122(R_1=$CH(CH_3)_2$ R_2= $-CH_3$)	64
16		170 (R_1=R_2=$-CH_3$) 171 (R_1=$-CH_3$, R_2=$-C_6H_5$) 174 (R_1,R_2=$-C_6H_5$)	65
17		88	66
18		87	66

Sr. No.	Bismaleimide	Melting Point (°C)	Ref.
19		214	66
20		219 (n = 8) 159 (n = 9) 210 (n = 10) 165 (n = 11)	67
21		Viscous liquid	30
22		78	30
23		98	30

The present work reports the synthesis of new BMI monomer viz., 4’-bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether (C15BMI), containing multiple ether linkages and pendent pentadecyl chain. The multiple ether linkages and pendent pentadecyl chain introduced in C15BMI were expected to offer lower melting point and improved solubility in common organic solvents. C15BMI was synthesized from CNSL-derived diamine viz., 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline (APPPA) and was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The curing kinetics of C15BMI was studied by DSC and thermal stability of cured resin was evaluated by TGA.

8b.2 Experimental

8b.2.1 Materials

4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline (APPPA) was synthesized as described in **Chapter 3**. 4,4’-Bis(maleimido)diphenylether (ODABMI) was synthesized using reported procedure.[30] Acetone, acetic anhydride, sodium chloride, sodium sulfate, sodium acetate, potassium hydroxide, celite and silica gel were received from Merck, India. The solvents were of reagent grade quality and were used as received.

8b.2.2 Measurements

FT-IR spectrum of C15BMI was recorded using a Perkin-Elmer Spectrum GX spectrophotometer. The spectrum was recorded by depositing sample as solvent-cast thin film on sodium chloride cells.

NMR spectra were recorded on a Bruker 200 MHz spectrometer at resonance frequency of 200 MHz for ^{1}H and 50 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

DSC analysis was performed on TA Instrument (Q10) supported by TA Universal Analysis software for data acquisition. The samples (5-7 mg) were taken in aluminum pans and experiments were performed under a nitrogen flow of 50 mL / min. The samples were subjected to a dynamic DSC scan at the heating rate of 10 °C/min. The enthalpy of curing (ΔH) was determined from the area under the exothermic curve. The cure onset temperature (T_o) was considered as intersect of slope of baseline and tangent of curve leading to peak of transition.

Thermogravimetric analysis was performed on Perkin-Elmer STA 6000 system at a heating rate of 10 °C / minute under nitrogen atmosphere. ~5 mg sample was taken for analysis.

8b.3 Synthesis of 4, 4’-bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether

Into a 100 mL two necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a reflux condenser were placed 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline (2.0 g, 3.36 mmol), maleic anhydride (0.70 g, 7.1 mmol) and acetone (25 mL). The reaction mixture was stirred at room temperature for 4 h and then refluxed for 1 h. To the reaction mixture were added acetic anhydride (10 mL) and sodium acetate (1.64 g, 20 mmol) and the mixture was refluxed for 6 h. The reaction mixture was cooled to room temperature and poured into water (100 mL). The solid obtained was washed with water (4 x 10 mL) and then with methanol (2 x 10 mL).The product was recrystallized from methanol.

Yield: 1.60 g (63 %).

MP: 90 °C (by DSC)

IR (cm^{-1}): 1704 (C=O stretching of imide ring), 1215 (-C-O-C- stretching)

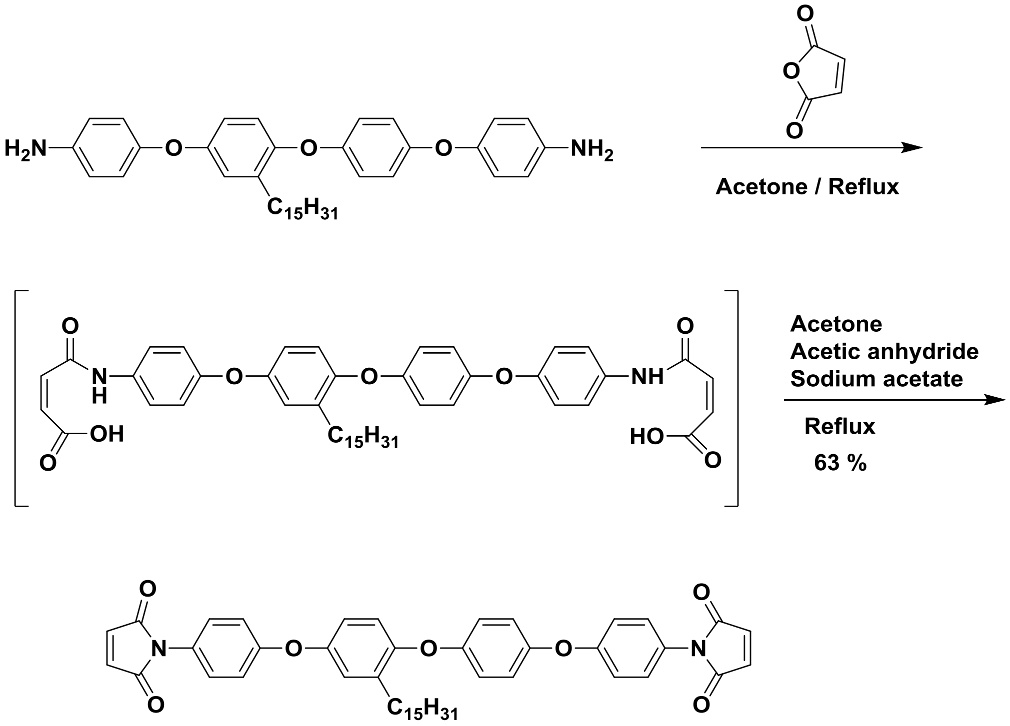
^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.25-7.30 (m, 4H), 6.88-7.09 (m, 11 H), 6.86 (d, 4 H), 2.60 (t, 3 H), 1.59 (br. s., 3 H), 1.25 (br. s., 24 H), 0.88 (t, 6 H)

^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.55, 157.64, 157.50, 154.46, 151.95, 150.97, 150.67, 136.28, 134.09, 127.55, 125.548, 121.62, 121.03, 120.59, 118.59, 118.05, 31.82, 30.08, 29.90, 29.60, 29.49, 29.33, 22.60, 14.05

8b.4 Results and Discussion

8b.4.1 Synthesis of 4, 4’-bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether

A new BMI monomer *viz*; 4, 4’-bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether (C15BMI), containing flexible ether linkages and pendent pentadecyl chain was synthesized starting from 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline (APPPA) (**Scheme 8.2**). The synthesis of the starting diamine, APPPA has been discussed in **Chapter 3**.



Scheme 8.2 Synthesis of C15BMI

Searl’s[68] procedure was adopted for synthesis of C15BMI from the diamine APPPA. Firstly, the diamine APPPA was treated with maleic anhydride to form bismaleamic acid. The exothermic reaction proceeded with formation of precipitate of bismaleamic acid. Next, the obtained bismaleamic acid was converted into C15BMI by *in situ* cyclodehydration using acetic anhydride and sodium acetate.

8b.4.2 Structural characterization

The chemical structure of bismaleimide was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. FT-IR spectrum (**Figure 8.6)** of BMI exhibited a strong absorption band at 1707 cm^{-1} which is characteristic of imide C=O stretching.

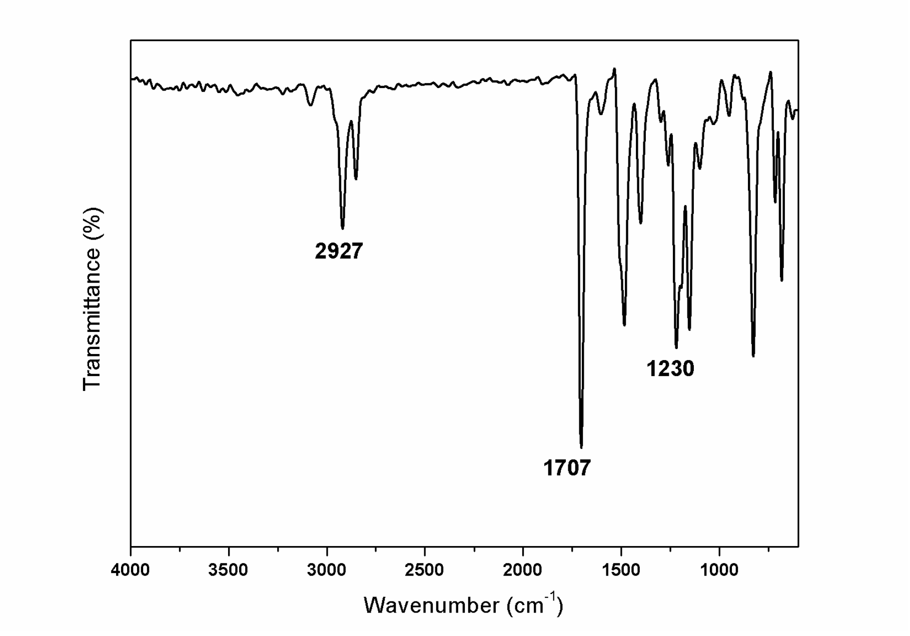


Figure 8.6 FT-IR spectrum C15BMI

^{1}H NMR spectrum of C15BMI is represented in **Figure 8.7**.

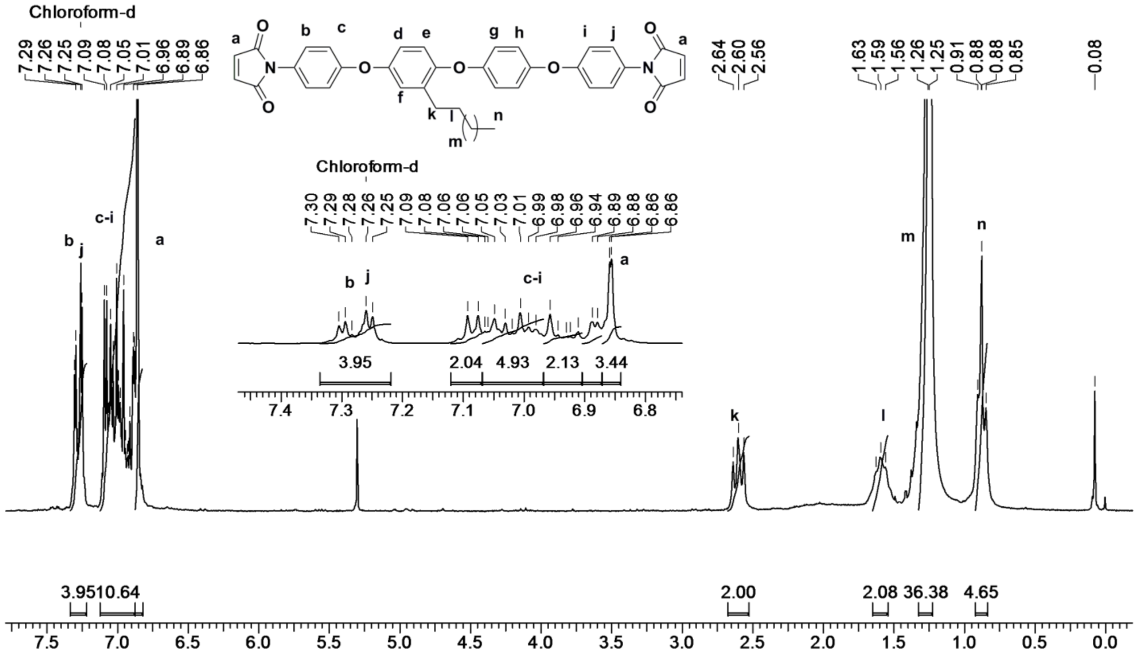


Figure 8.7 ^{1}H NMR spectrum (in CDCl$_3$) of C15BMI

The protons of imide ring appeared as two very close but distinct peaks at 6.86 and 6.86 δ ppm because of non-symmetry in the structure. The aromatic protons *ortho* to imide nitrogen (b, j) appeared as two separate doublets at 7.28 and 7.27 δ ppm. The remaining aromatic protons (c-i) exhibited multiplet in the range 6.96-7.09 δ ppm. The benzylic –CH_2 group showed a triplet at 2.60 δ ppm, the –CH_2 group *β* to aromatic ring appeared as a multiplet in the range 1.56-1.63 δ ppm. The remaining –CH_2 groups exhibited a multiplet in the range 1.23–1.27 δ ppm. The terminal –CH_3 group showed a triplet at 0.88 δ ppm.

Figure 8.8 represents ^{13}C NMR of spectrum of C15BMI

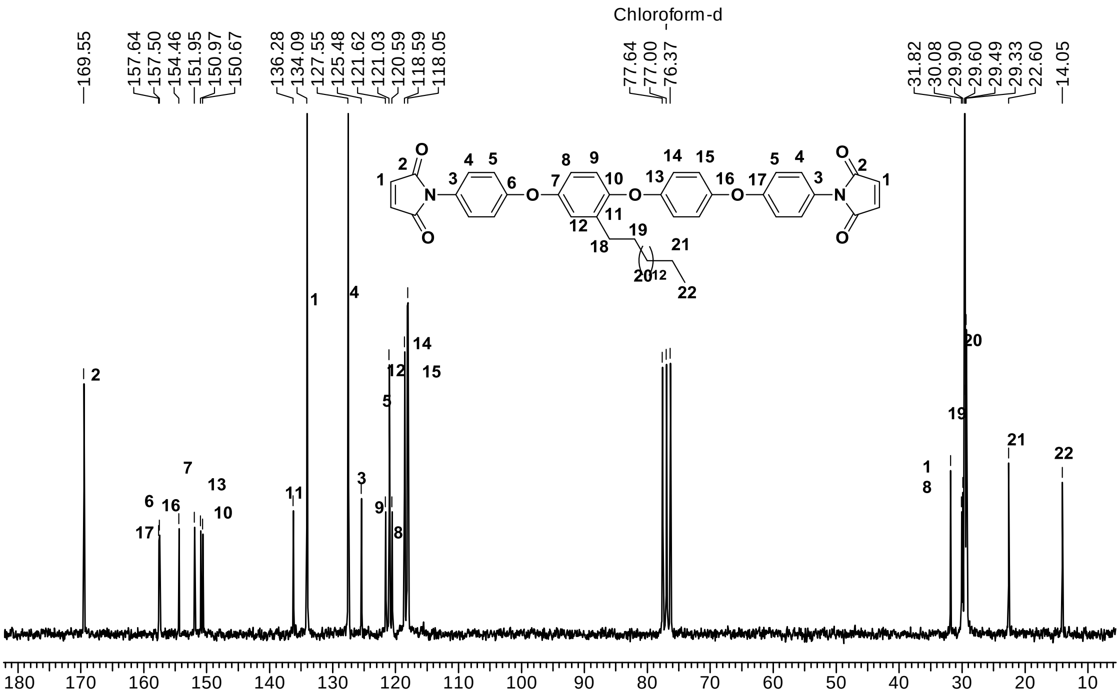


Figure 8.8 ^{13}C NMR spectrum (in $CDCl_3$) of C15BMI

In ^{13}C NMR spectrum, the olefinic carbons of imide rings appeared at 134.09 δ ppm while carbonyl carbons exhibited a peak at 169.55 δ ppm. The quaternary aromatic carbon to which pentadecyl chain is attached displayed a peak at 136.28 δ ppm while quaternary carbons to which the imide ring is attached exhibited a peak at 125.48 δ ppm. The aromatic carbons (17, 6, 16, 7, 13, 10) attached to ethereal oxygens appeared at 157.64, 157.50, 154.46, 151.95, 150.97, 150.67 δ ppm, respectively. The pentadecyl chain carbons exhibited peaks in the aliphatic region.

The assignments of ^{13}C NMR were further confirmed by ^{13}C DEPT spectrum (**Figure 8.9**)

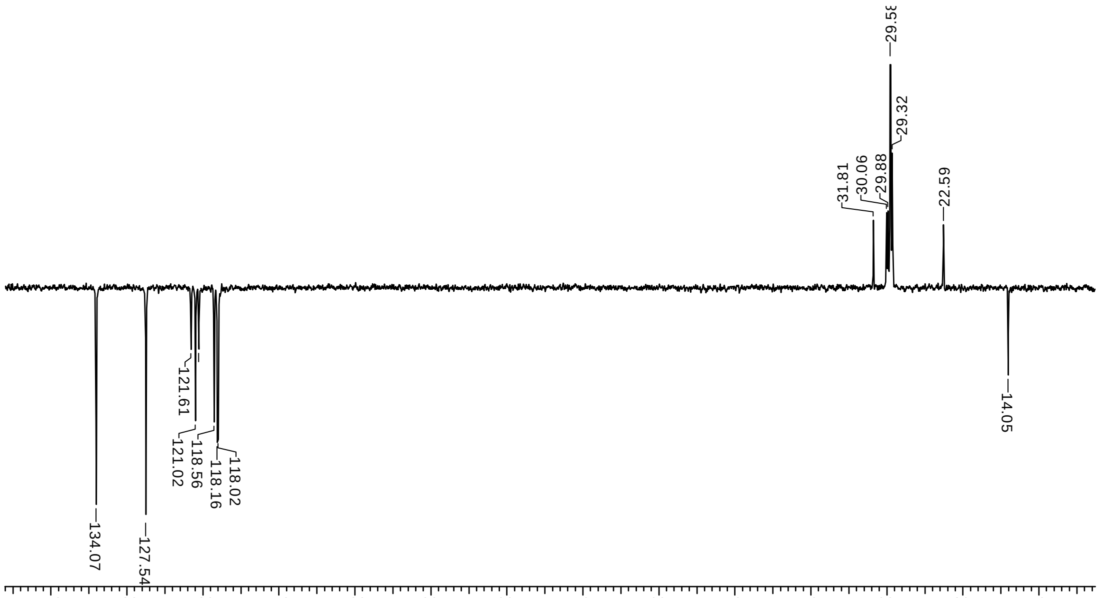
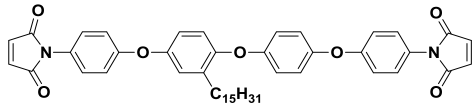
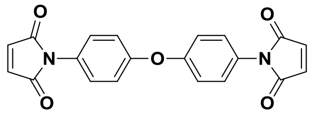


Figure 8.9 ^{13}C DEPT spectrum (in $CDCl_3$) of C15BMI

8b.4.3 Solubility of bismaleimide

The solubility tests of C15BMI and that of reference BMI namely; 4,4'-bis(maleimido)diphenylether (ODABMI) were carried out in different organic solvents at 5 wt % concentration and results are summarized in **Table 8.4**

Table 8.4 Solubility data of C15BMI and ODABMI

BMI Structure	Chloroform	DCM	Acetone	THF	DMF	DMSO	NMP	Ethanol
	++	++	++	++	++	++	++	--
	--	--	--	++	++	++	++	--

++ : Soluble at room temperature; -- : Insoluble at room temperature

C15BMI was found to be soluble in acetone, chloroform, dichloromethane, THF, NMP, DMSO and DMF. ODABMI was soluble in THF, DMF, DMSO and NMP and was insoluble in chloroform, dichloromethane and acetone. The improved solubility of C15BMI in common organic solvents could be attributed to the presence pentadecyl chain and multiple ether linkages.

8b.4.4 Non-isothermal curing kinetics

The presence of two electron withdrawing carbonyl groups adjacent to C=C bond in BMIs, offers an ability to undergo homo or copolymerization. The polymerization/ curing can be carried out thermally or by free radicals or anions to form a three dimensional network with high cross-link density *via* addition reaction. The curing reaction of BMI obeys autocatalytic first order kinetics. The literature revealed that curing kinetics can be studied by different analytical techniques such as IR, DSC, NMR, etc. In the present study, the curing kinetics of BMI was studied by DSC. DSC thermogram of curing process of C15BMI is represented in **Figure 8.10.**

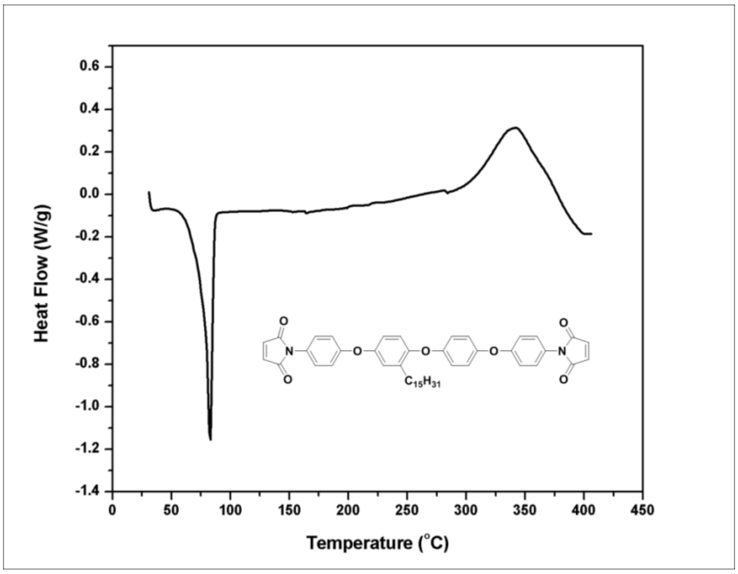
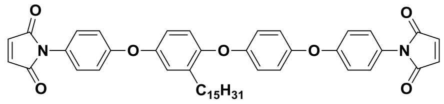
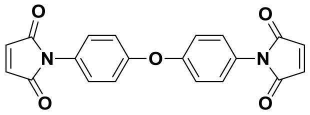


Figure 8.10 DSC curing thermogram of C15BMI

In the DSC thermogram, a sharp endothermic peak at 90 °C corresponds to the melting point followed by a curing exotherm with maximum at 342 °C and heat of polymerization (ΔH) of 117 KJ/mol. As can be observed from data in **Table 8.5**, due to comparatively lower melting point of C15BMI a larger processing window of 170 °C (temperature interval between melting and curing) was observed than that of ODABMI (processing window of 42 °C).The curing of various BMI monomers has been reported to proceed with enthalpy in the range of 50-140 KJ/mol and ΔH (117 KJ/mol) value of the C15BMI falls in this range of that reported for the other BMI monomers.[50, 52, 53, 69-71] The curing characteristics C15BMI and that of ODABMI are collected in **Table 8.5**.

Table 8.5 Cure characteristics of C15BMI and ODABMI

BMI Monomer	**T_m (°C)**	**Processing window (T_o-T_m)(°C)**	**Cure Characteristics**			
			T_o (°C)	**T_p (°C)**	**T_f (°C)**	**ΔH (KJ/mol)**
 C15 BMI	90	170	280	342	398	117
 ODABMI[a]	183	42	225	282	340	73

T_m – Melting point, T_o – Cure onset temperature, T_p – Peak temperature, T_f –Final cure temperature,
a- data taken from from reference[30]

For non-isothermal reactions, the rate equation can be given by equation 2:

$$\frac{d\alpha}{dT}=(A/\varphi)e^{-E/RT}(1-\alpha)^n \qquad ……(2)$$

Where, α is fractional conversion at temperature T, φ is heating rate, E is activation energy, A is Arrhenius frequency factor, R is gas constant, and n is the order of reaction.

In the present study, Coats-Redfern equation (equation 3) was applied to compute activation energy.

$$F=\ln\{(AR/\varphi E)(1-2RT/E)\}-E/RT \qquad …… (3)$$

Where, $g(\alpha)=[1-(1-\alpha)^{1-n}]/(1-n)$; for n = 1, $g(\alpha) = -\ln(1-\alpha)$; R is the gas constant.

For calculation of kinetic parameters, equation 1 was used to calculate fractional conversion 'α' using fractional enthalpy of curing reaction. The plots of $\ln\{g(\alpha)/T^2\}$ versus 1/T with assuming order of reaction as n = 0.5, 1, 1.5, 2, 2.5 and 3, were plotted (**Figure 8.11)** as per the Coats-Redfern equation and the best fit provided the order of reaction 'n'.

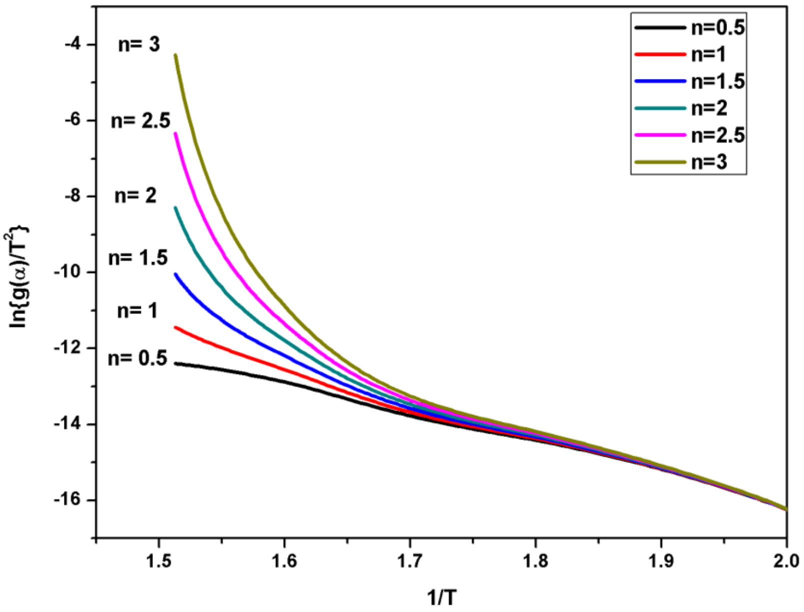
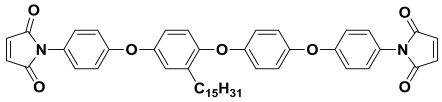
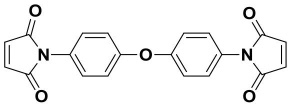


Figure 8.11 Coats-Redfern plots for determination of order of C15BMI curing reaction

Table 8.6 Kinetic parameters of curing reaction of C15BMI and ODABMI

BMI Monomer	Ea (KJ/mol)	Ln A (S^{-1})
 C15BMI	75.32	1.94
 ODABMI[a]	110	10.3

Ea – Energy of activation, A– Arrhenius frequency factor, and a- data taken from reference 38

The curing kinetic parameters (activation energy and Arrhenius frequency factor) were computed from slope and intersect of the plot with best fitting value of ‘n’. For C15BMI, the best fit was observed for n = 1. The curing kinetic parameters of C15BMI and those of ODABMI taken from literature[30] are tabulated in **Table 8.6.** The activation energy in case of curing of C15 BMI (75.32 KJ/mol) was observed to be lower than that of ODABMI (110 KJ/mol). As the activation energy of BMI curing has been reported to be sensitive to nature and concentration of the impurities present, no efforts were made to establish correlation between structure and curing characteristics and kinetic parameters.

8b.4.5 Thermal properties

The thermal stability of cured BMI was evaluated by TGA at heating rate of 10 °C/minute under nitrogen atmosphere **(Figure 8.12)**.

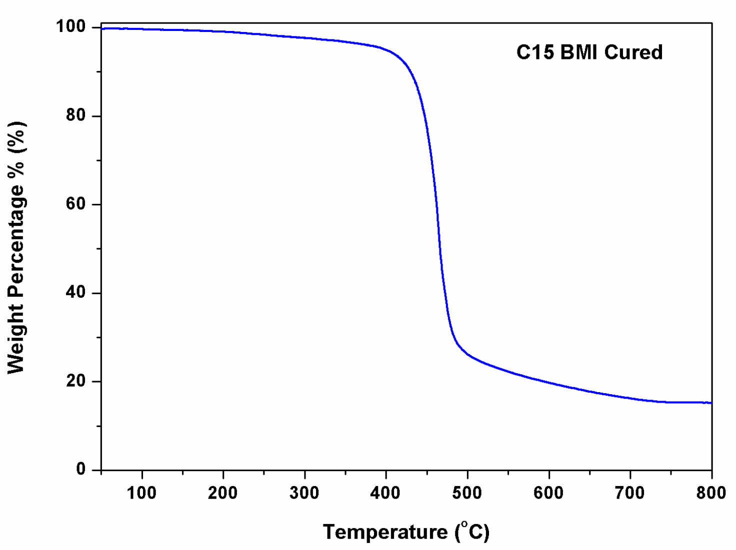


Figure 8.12 TG curve of cured C15BMI

Cured C15BMI showed 10 % decomposition temperature (T_{10}) at 430 °C and char yield at 800 °C was 15 % indicating its good thermal stability. However, thermal stability of cured C15BMI was lower than that of cured ODABMI for which reported[30] value of T_{10} is 485 °C. The decreased thermal stability of cured C15BMI could be attributed to the presence of thermally labile aliphatic pentadecyl chain as well as increased distance between two succinimide rings due to the additional ether linkages.

8b.5 Conclusions

1. A new bismaleimide monomer viz; C15BMI, containing flexible ether linkages and pendent pentadecyl chain was synthesized by the ring-opening addition reaction of the diamine with maleic anhydride followed by cyclodehydration of N,N-bismaleamic acid using acetic anhydride and sodium acetate and its structure was confirmed by IR, ^{1}H NMR, ^{13}C NMR spectroscopy.

2. 4, 4’-Bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether exhibited excellent solubility in common organic solvents such as, chloroform, dichloromethane and THF.
3. Activation energy for cuing of 4, 4’-bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether as determined in non-isothermal curing mode using Coats-Redfern method was found to be 75.32 KJ/mol.
4. The cured BMI resin showed T_{10} value of 430 °C indicating its good thermal stability.

Chapter 8c

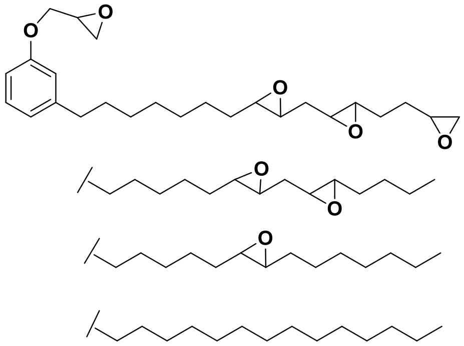
Synthesis and Characterization of Epoxy Resin Based on 4-(4-Hydroxyphenoxy)-3-pentadecylphenol

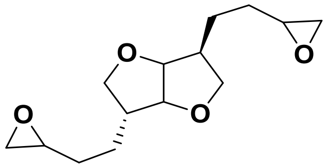
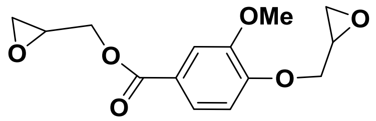
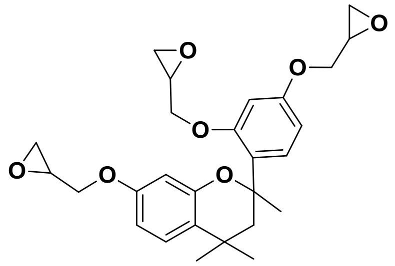
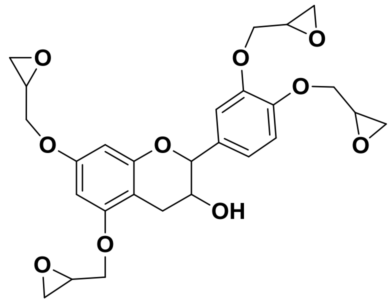
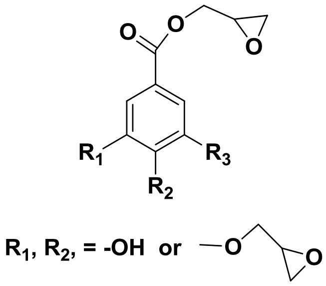
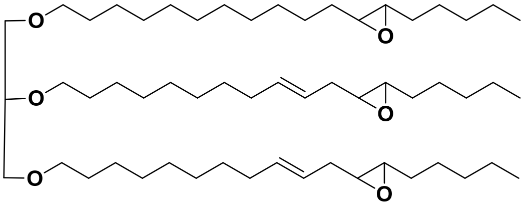
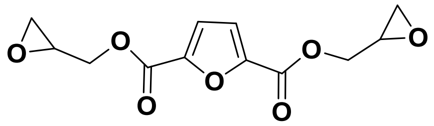
8c.1 Introduction

In 1938, Peirre Castern introduced epoxy resins and since late 1940s, they have been exploited in diverse industrial applications such as adhesives, advanced composite matrices, protective coatings, electrical laminates and packaging materials.[72-74] The epoxy resins have unique features such as combination of good thermal and dimensional stability, high tensile strength and modulus, excellent chemical and corrosion resistance, and also they are easy to handle and process.[75-77] Till date, a variety of epoxy resins have been commercialized depending upon the end use applications. An important criterion that governs the properties of cured epoxy resins is its structure. Therefore, design and synthesis of new epoxies provides range of structural variations and that basically permits structural modifications at molecular level.[76-83]

The diglycidyl ether of bisphenol A (DGEBA) is the most widely used epoxy resin. The properties of DGEBA-based epoxies are acceptable, but there are health and environmental concerns associated with of bisphenol A and also it is petroleum derived. Therefore, there is a growing interest in both academic and industrial laboratories for developing biobased epoxies as a substitute for the non-renewable bisphenol A-based epoxies. Devid et al.[84] have reviewed recent progress and perspectives of utilization of biobased feedstocks for epoxies. Literature reports synthesis of epoxies from polyphenols, tannins, lignin, cardanol, starch, sugars, terpenes, terpenoids, rosin acids, vegetable oil, etc.[85-98] Some selected biobased epoxies are listed in **Table 8.7.** Moreover, hardeners required for epoxy network formulations such as amines and anhydrides could also be obtained from biobased building blocks.[85, 92, 99] An industrial scale process for epichlorohydrin based on bio-derived glycerol is available.[100, 101]

Table 8.7 List of selected bio-based epoxies

Sr. No.	Epoxy monomer	Precursor	Reference
1		CNSL	89

Sr. No.	Epoxy monomer	Precursor	Reference
2		Sugars	90, 91
3		Lignin	92
4		Resorcinol	93
5		Catechin	94
6		Gallic acid	95
7		Vegetable oil	96
8		Furans	97

In the present work, we discuss synthesis and characterization of a new epoxy resin starting from 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP) which is bisphenol-derived from CNSL-a renewable resource material. The diglycidyl ether of HPPDP is expected to have better impact strength and fracture toughness, low moisture absorption and low dielectric constant.[30, 102]

8c.2 Experimental

8c.2.1 Materials

4-(4-Hydroxyphenoxy)-3-pentadecylphenol (HPPDP) was synthesized as described in **Chapter 3**. Potassium hydroxide, sodium chloride, sodium sulfate, celite and silica gel were received from Merck, India. Epichlorohydrin was procured from Loba Chemie Pvt Ltd., India. Phenolphthalein was purchased from S. D. Fine-Chem Ltd, India. The solvents were of reagent grade quality and were used as received.

8c.2.2 Measurements

FT-IR spectrum of diglycidyl ether of HPPDP was recorded using a Perkin-Elmer Spectrum GX spectrophotometer. The spectra were recorded by depositing samples as solvent-cast thin films on sodium chloride cells.

NMR spectrum of diglycidyl ether of HPPDP was recorded on a Bruker 200 MHz spectrometer at resonance frequency of 200 MHz for ^{1}H and 50 MHz for ^{13}C measurements using $CDCl_3$ as a solvent.

8c.3 Synthesis of diglycidyl ether of HPPDP

Into a 250 mL three necked round bottom flask equipped with an overhead stirrer, a reflux condenser and a thermometer were added HPPDP (5 g, 0.012 mol), epichlorohydrin (9.4 mL) and water (0.1 mL). To the reaction mixture NaOH pellets (0.96 g, 0.024 mol) were added in portions. The first portion of NaOH (0.48 g) was added at room temperature and reaction mixture was heated to 90 °C. When reaction temperature reached to 90 °C, another portion (0.48 g) of NaOH was added slowly, so that temperature of reaction mixture does not exceed 100 °C. After the completion of addition, the reaction mixture was heated at 90 °C for 30 minutes. Excess of epichlorohydrin was distilled out under reduced pressure. To the residue was added toluene (10 mL) and the precipitated salt was separated by filtration. Toluene was distilled off under vacuum to obtain a viscous liquid which was purified by column chromatography using dichloromethane as an eluent.

Yield: 5.5 g (87 %)

IR (cm^{-1}): 911 (oxirane ring deformation)

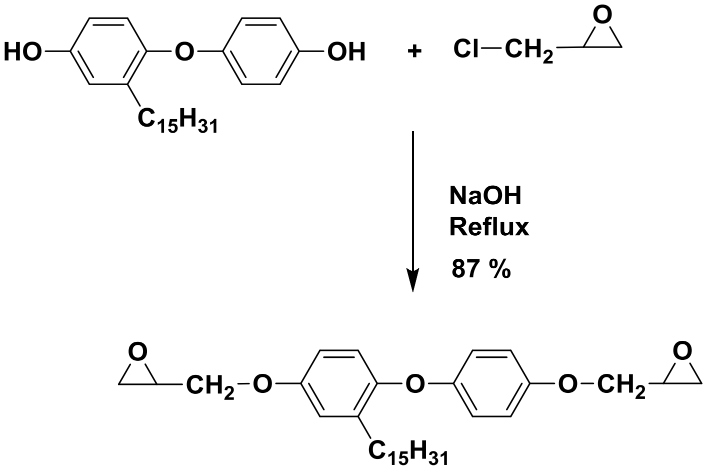
^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.81 - 6.88 (m, 5 H), 6.76 - 6.78 (m, 1 H), 6.68 (dd, 1 H), 4.14 - 4.23 (m, 2 H), 3.84-4.0 (m, 2 H), 3.34 (ddd, J = 2.9, 3.9, 5.7 Hz, 2 H), 2.89 (dt, J = 2.0, 4.5 Hz, 2 H), 2.75 (td, J = 2.7, 5.1 Hz, 2 H), 2.55 (t, 2 H), 1.63 - 1.49 (m, 2 H), 1.25 (br. s., 24 H), 0.88 (t, 3 H)

^{13}CNMR (50 MHz, $CDCl_3$) δ = 154.48, 153.57, 152.73, 148.78, 135.61, 120.32, 117.97, 116.55, 115.52, 112.41, 50.08, 44.52, 31.82, 30.14, 29.93, 29.59, 29.59, 29.33, 22.59, 14.03.

8c.4 Results and Discussion

8c.4.1 Synthesis of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

A new epoxy resin containing flexible ether linkage and pendent pentadecyl chain was synthesized by a conventional one step method by reaction of 4-(4-hydroxyphenoxy)-3-pentadecylphenol with epichlorohydrin as shown in **Scheme 8.3.**



Scheme 8.3 Synthesis of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

8c.4.2 Structural characterization

The diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol was characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. FT-IR spectrum of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol is represented in **Figure 8.13**. The absorption peak at 911 cm^{-1} is due to the oxirane ring deformation.

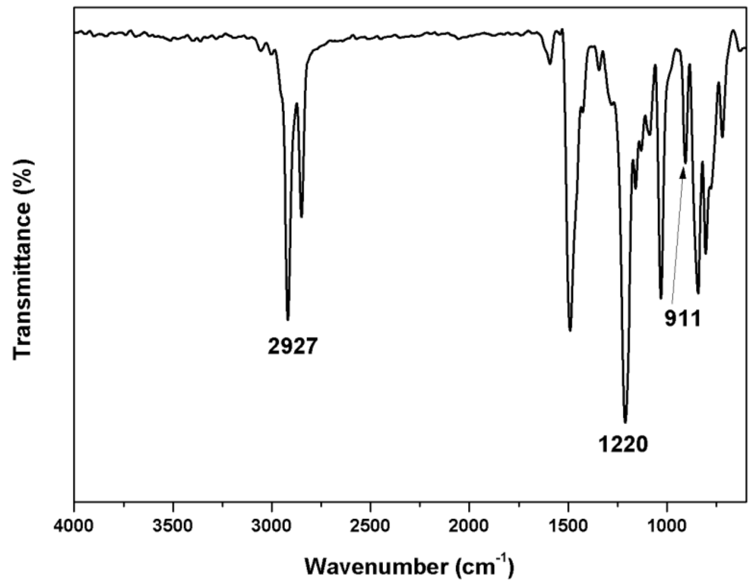


Figure 8.13 FT-IR spectrum of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

Figure 8.14 depicts ^{1}H NMR spectrum diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

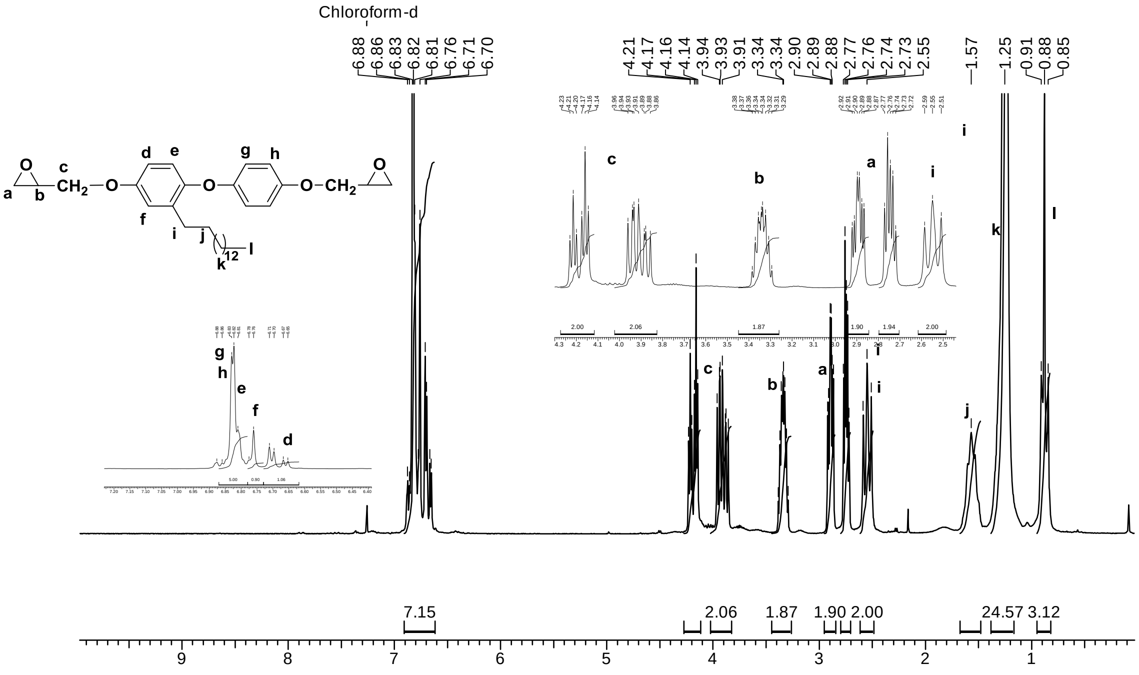


Figure 8.14 ^{1}H NMR spectrum (in $CDCl_3$) of diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol

In ^{1}H NMR spectrum, the four aromatic protons of aromatic ring without pentadecyl chain and a proton *meta* to pentadecyl chain exhibited multiplet in the region 6.80-6.88 δ ppm. The proton *ortho* to pentadecyl chain appeared as a doublet at 6.75 δ ppm while proton *para* to pentadecyl chain appeared as doublet of doublet at 6.68 δ ppm. The methylene group adjacent to ether linkage exhibited a multiplet in the region 3.91-4.21 δ ppm. The octet at 3.34 δ ppm is due to methine protons of oxirane ring. The methylene group of oxirane ring appeared as a multiplet in the range 2.72-2.92 δ ppm. The remaining up-field peaks are assigned to protons of pentadecyl chains and the assignments are made in the spectrum.

^{13}C NMR spectrum diglycidyl ether of HPPDP along with assignments is represented in **Figure 8.15.**

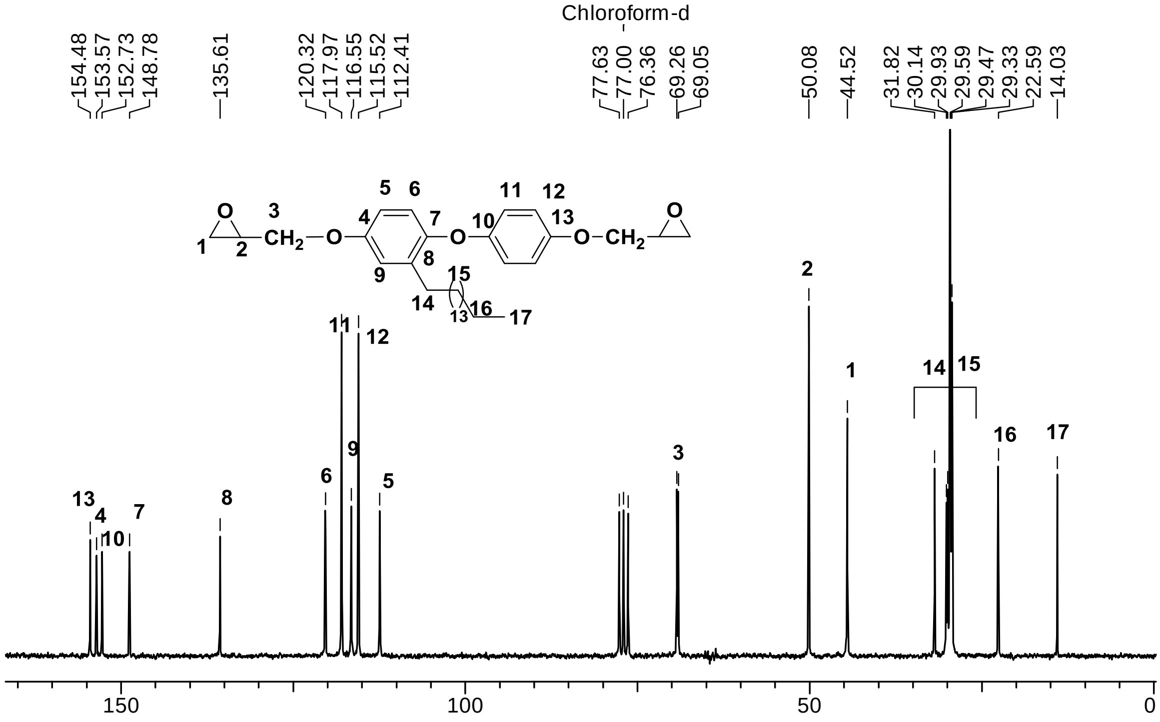


Figure 8.15 ^{13}C NMR spectrum (in $CDCl_3$) of diglycidyl ether of HPPDP

The aromatic carbons attached to epoxide groups (13, 4) showed the peaks at 154.48 and 153.57 δ ppm, respectively. The aromatic carbons attached to ethereal oxygen (10, 7) appeared at 152.73 and 148.78 δ ppm, respectively. The quaternary carbon to which pentadecyl chain is attached exhibited peak at 135.91 δ ppm. The signals at 120.32, 166.55 and 112.41 δ ppm could be assigned to carbons of pentadecyl substituted aromatic ring (6, 9 and 5), respectively. The two strong peaks at 117.79 and 115.92 are due to carbons of aromatic ring without pentadecyl chain which are *meta* and *ortho* to the epoxy group, respectively. The two signal appeared at 69.26 and 69.05 δ ppm could be assigned to methylene carbons (labeled as 3) of epoxide group. The signal corresponding to methine carbon of oxirane ring appeared at 50.05 δ ppm which also confirmed by DEPT spectrum (**Figure 8.16**) as it appeared in negative phase. The methylene proton of oxirane ring appeared at 44.52 δ ppm. The remaining carbons appeared in aliphatic region could be attributed to pentadecyl chain.

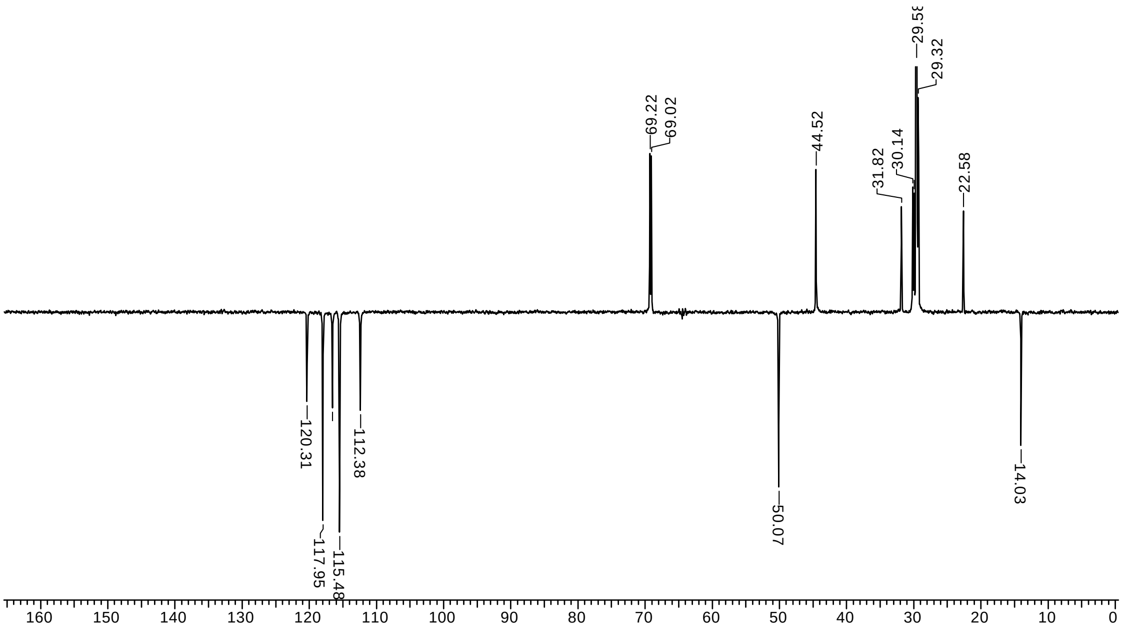


Figure 8.16 ^{13}C DEPT NMR spectrum (in CDCl$_3$) of diglycidyl ether of HPPDP

8c.5 Conclusions

1. Diglycidyl ether of HPPDP containing pendent pentadecyl chain was successfully synthesized from HPPDP-a bisphenol derived from CNSL by the reaction with epichlorohydrin and was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

References

1. I. Hamerton, ed., *Chemistry and Technology of Cyanate Ester Resins*, Glasgow, 1994.
2. C. P. R. Nair, D. Mathew and K. N. Ninan, *Adv. Polym. Sci.*, 2001 **155**, 1-176.
3. V. A. Pankratov, S. V. Vinogradova and V. V. Korshak, *Russ. Chem. Rev.*, 1977, **46**, 278.
4. E. Grigat and R. Pütter, *Ang. Chem. Int. Ed.*, 1967, **6**, 206-218.
5. E. Grigat and R. Putter, *US 4028393*, 1977.
6. J. Abed, R. Mercier and J. E. McGrath, *J. Polym. Sci. Part A: Polym. Chem.*, 1997, **35**, 977-987.
7. A. W. Snow and L. J. Buckely, *Macromolecules*, 1997, **30**, 394-405.
8. A. Marcos-Fernandez, P. Posadas, A. Rodriguez and L. J. Gonzalez, *Polym. Sci. Part. A: Polym. Chem.*, 1999, **37**, 3155-3168.
9. E. M. Maya, A. W. Snow and L. J. Buckely, *Macromolecules*, 2002, **35**, 460-466.
10. E. M. Maya, A. W. Snow and L. J. Buckely, *J. Polym. Sci. Part A: Polym. Chem.*, 2003, **41**, 60-67.
11. H. Yan, S. Chen and G. Qi, *Polymer*, 2003, **44**, 7861-7867.
12. H. J. Hwang, C. H. Li and C. S. Wang, *J. Appl. Polym. Sci.*, 2005, **96**, 2079-2089.
13. D. Mathew, C. P. R. Nair and K. N. Ninan, *Polym. Int.*, 2000, **49**, 48-56.
14. C. H. Lin, H. T. Lin, Y. W. Tian, S. A. Dai and W. C. Su, *J. Polym. Sci. Part A : Polym. Chem.*, 2011, **49**, 4851-4860.
15. A. W. Snow, L. J. Buckley and J. P. Armistead, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 135-150.
16. B. L. Loudas and H. A. Vogel, *US 3733349*, 1973.
17. A. W. Snow and J. R. Griffith, *J. Fluorine Chem.*, 1980, **15**, 471-485.
18. A. W. Snow, J. R. Griffith, R. L. Soulen, J. A. Greathouse and J. K. Lodge, *Am. Chem..Soc.: Poly. Mat. Sci. Eng. Preprints*, 1992, **66**, 466.
19. Y. H. Wang, V. Y. L. Hong and J. L. Hong, *Polymer*, 1993, **34**, 1970-1971.
20. M. Laskoski, D. D. Dominguez and T. M. Keller, *J. Polym. Sci. Part A: Polym. Chem.*, 2006, **44**, 4559-4565.
21. G. Anuradha and M. Sarojadevi, *J. Appl. Polym. Sci.* , 2008, **110**, 938-944.

22. G. Anuradha and M. Sarojadevi, *J. Polym. Res.*, 2008, **15**, 507-514.
23. I. Hamerton, B. J.Howlin, P. Klewpatinond and S. Takeda, *Macromolecules*, 2009, **42**, 7718-7735.
24. B. G. Harvey, A. J. Guenthner, G. R. Yandek, L. R. Cambrea, H. A. Meylemans, L. C. Baldwin and J. T. Reams, *Polymer*, 2015, **55**, 5073-5079.
25. M. C. Davis, A. J. Guenthner, T. J. Groshens, J. T. Reams and J. M. Mabry, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 4127-4136.
26. Z. Zhang, R. Yu, F. Wang, J. Wang and Y. Jiao, *J. Appl. Polym. Sci.*, 2011, **122**, 2609-2615.
27. A. J. Guenthner, M. C. Davis, K. R. Lamison, G. R. Yandek, L. R. Cambrea, T. J. Groshens, L. C. Baldwin and J. M. Mabry, *Polymer*, 2011, **52**, 3933-3942.
28. Z. Zhang, R. Yu, F. Wang, J. Wang and Y. Jiao, *J. Appl. Polym. Sci.*, 2011, **120**, 3716-3723.
29. A. D. Kulkarni, B. V. Tawade and P. P. Wadgaonkar, *High Perform. Polym.*, 2013, **25**, 278-286.
30. A. D. Kulkarni, *Ph.D. Thesis submitted to University of Pune, Pune, India*, 2010.
31. H. A. Hageman, in *Organic Reactions*, John Wiley & Sons, Inc., 1953, pp. 198-259.
32. J. L. Cercena, *Ph.D. Dissertation, University of Connecticut, USA, 1984*.
33. A. W. Snow, in *Chemistry and Technology of Cyanate Ester Resins*, ed. I. Hamerton, Chapman and Hall, Glasgow, 1994, pp. 7-57.
34. D. Mathew, C. P. R. Nair, K. Krishnan and K. N. Ninan, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 1103-1114.
35. T. Fang and D. A. Shimp, *Prog. Polym. Sci.*, 1995, **20**, 61-118.
36. J. N. Hay, in *Chemistry and Technology of Cyanate Ester Resins.*, ed. I. Hamerton, Chapman and Hall, Glasgow, 1994, pp. 151-192.
37. A. W. Coats and J. P. Redfern, *Nature*, 1964, **201**, 68-69.
38. J. V. Crivello, *J. Polym. Sci. Polym. Chem. Ed.*, 1973, **11**, 1185-1200.
39. L. T. Pappalardo, *J. Appl. Polym. Sci.*, 1977, **21**, 809-820.
40. H. D. Stenzenberger, *Adv. Polym. Sci.*, 1994, **117**, 165-162-160.
41. A. S. Brown, *Aerospace Am.*, 1989, **27**, 18.

42. Z. D. Xiang and F. R. Jones, *Comp. Sci. Technol.*, 1993, **47**, 209-215.
43. A. Nagai, A. Takahashi, M. Wajima and K. Tsukanishi, *Polym J*, 1988, **20**, 125-130.
44. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, eds., *Polyimides*, Blackie, Glasgow and London, 1990.
45. H. D. Stenzenberger, M. Herzog, W. Römer, R. Scheiblich and N. J. Reeves, *Br. Polym. J.*, 1983, **15**, 2-12.
46. R. Chandra and L. Rajabi, *J. Macromol. Sci. Part C*, 1997, **37**, 61-96.
47. S. Takeda, H. Akiyama and H. Kakiuchi, *J. Appl. Polym. Sci.*, 1988, **35**, 1341-1350.
48. A. Nagai, A. Takahashi, M. Suzuki and A. Mukoh, *J. Appl. Polym. Sci.*, 1992, **44**, 159-164.
49. I. J. Goldfarb, W. A. Feld and J. Saikumar, *Polymer*, 1993, **34**, 813-818.
50. S. H. Hsiao and C. F. Chang, *J. Polym. Res.*, 1996, **3**, 31-37.
51. C. S. Wang and T. S. Leu, *J. Appl. Polym. Sci.*, 1999, **73**, 833-839.
52. J. M. Barton, I. Hamerton, J. B. Rose and D. Warner, *Polymer*, 1991, **32**, 358-363.
53. J. M. Barton, I. Hamerton, J. B. Rose and D. Warner, *Polymer*, 1991, **32**, 2482-2490.
54. G. Davidson, I. Soutar, P. N. Preston, V. K. Shah, S. W. Simpson and N. J. Stewart, *Polymer*, 1994, **35**, 653-657.
55. H. D. Stenzenberger, K. U. Heinen and D. O. Hummel, *J. Polym. Sci. Polym. Chem. Ed.*, 1976, **14**, 2911-2925.
56. P. Kovacic and R. W. Hein, *J. Am. Chem. Soc.*, 1959, **81**, 1187-1190.
57. A. Seris, M. Feve, F. Mechin and J. P. Pascault, *J. Appl. Polym. Sci.*, 1993, **48**, 257-269.
58. N. D. Kole and W. F. Gruber, *US 3127414*, 1964.
59. C. Vijayakumar, R. Surender, K. Rajakumar and S. Alam, *J. Therm. Anal. Calorim.*, 2012, **103**, 693-699.
60. M.-F. Grenier-Loustalot and L. Da Cunha, *Eur. Polym. J.*, 1998, **34**, 95-102.
61. F. Dumont, M. Visseaux, D. Barbier-Baudry and A. Dormond, *Polymer*, 2000, **41**, 6043-6047.
62. J. L. Feng, C. Y. Yue and K. S. Chian, in *e-Polymers*, 2006, p. 44.

63. W. Shu and J. Ho, *Polym. Sci. Ser. B*, 2014, **56**, 530-537.
64. X. Xiong, P. Chen, Q. Yu, N. Zhu, B. Wang, J. Zhang and J. Li, *Polym. Int.*, 2010, **59**, 1665-1672.
65. W. J. Shu and R. S. Tsai, *Des. Monom. Polym.*, 2010, **13**, 33-49.
66. H. Tang, W. Li, X. Fan, X. Chen, Z. Shen and Q. Zhou, *Polymer*, 2009, **50**, 1414-1422.
67. B. Fache, B. Gallot, M. P. Gelin, J. C. Milano and Q. T. Pham, *J. Appl. Polym. Sci.*, 2013, **127**, 3798-3813.
68. N. E. Searle, *(Du pont) US 2444536*, 1948, Chem. Abstr., 42 (1948), p. 7340.
69. S.-H. Hsiao, C.-P. Yang and S.-H. Chen, *J. Polym. Res.*, 1999, **6**, 141-148.
70. K. N. Ninan, K. Krishnan and J. Mathew, *J. Appl. Polym. Sci.*, 1986, **32**, 6033-6042.
71. I. K. Varma and S. Sharma, *Polymer*, 1985, **26**, 1561-1565.
72. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw Hill, New York, 1967.
73. C. May and Y. Tanaka, eds., *Epoxy Resins Chemistry and Technology*, Marcel Dekker, Inc, New York, 1988.
74. H. Pham and M. Marks, in *Encyclopedia of Polymer Science and Technology*, Wiley Interscience, New Jersey, 2004.
75. A. Serra, V. Cadiz, P. Martinez and A. Mantecon, *Angew. Makromol. Chem.*, 1986, **140**, 113-125.
76. C. B. Bucknall and A. H. Gilbert, *Polymer*, 1989, **30**, 213-217.
77. A. E. Batog, I. P. Petko and P. Penczek, *Adv. Polym. Sci.*, 1999, **144**, 49-113.
78. W. Erich and M. J. Bodnar, *J. Appl. Polym. Sci.*, 1960, **3**, 296-301.
79. S. C. Lin and E. M. Pearce, *J. Polym. Sci. Polym. Chem. Ed.*, 1979, **17**, 3095-3119.
80. S. C. Lin, B. J. Bulkin and E. M. Pearce, *J. Polym. Sci. Part A: Polym. Chem.*, 1979, **17**, 3121-3148.
81. C. S. Chen, B. J. Bulkin and E. M. Pearce, *J. Appl. Polym. Sci.*, 1982, **27**, 1177-1190.
82. C. S. Chen, B. J. Bulkin and E. M. Pearce, *J. Appl. Polym. Sci.*, 1982, **27**, 3289-3312.

83. Z. Dai, Y. Li, S. Yang, C. Zong, X. Lu and J. Xu, *J. Appl. Polym. Sci.*, 2007, **106**, 1476-1481.

84. R. Auvergne, S. Caillol, G. David, B. Boutevin and J.-P. Pascault, *Chem. Rev.*, 2014, **114**, 1082-1115.

85. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, 2014, **5**, 3142-3162.

86. T. Koike, *Polym. Eng. Sci.*, 2012, **52**, 701-717.

87. E. Darroman, N. Durand, B. Boutevin and S. Caillol, *Prog. Org. Coat.*, 2015, **83**, 47-54.

88. A. Maiorana, S. Spinella and R. A. Gross, *Biomacromolecules*, 2015, **16**, 1021-1031.

89. J. Chen, X. Nie, Z. Liu, Z. Mi and Y. Zhou, *ACS Sus. Chem. Eng.*, 2015, 10.1021/acssuschemeng.5b00095.

90. X. Feng, A. J. East, W. B. Hammond, Y. Zhang and M. Jaffe, *Polym. Adv. Technol.*, 2011, **22**, 139-150.

91. F. Xianhong, J. E. Anthony, H. Willis and J. Michael, in *Contemporary Science of Polymeric Materials*, American Chemical Society, 2010, pp. 3-27.

92. M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol and B. Boutevin, *Green Chem.*, 2014, **16**, 1987-1998.

93. J. Robins, *US 4503211*, 1985.

94. H. Nouailhas, C. Aouf, C. Le Guerneve, S. Caillol, B. Boutevin and H. Fulcrand, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **49**, 2261-2270.

95. C. Aouf, C. Le Guerneve, S. Caillol and H. l. n. Fulcrand, *Tetrahedron*, 2013, **69**, 1345-1353.

96. F. Seniha Guner, Y. Yagci and A. Tuncer Erciyes, *Prog. Polym. Sci.*, 2006, **31**, 633-670.

97. J. Deng, X. Liu, C. Li, Y. Jiang and J. Zhu, *RSC Adv.*, 2015, **5**, 15930-15939.

98. S. Laurichesse and L. Averous, *Prog. Polym. Sci.*, 2014, **39**, 1266-1290.

99. C. Ding and A. S. Matharu, *ACS Sus. Chem. Eng.*, 2014, **2**, 2217-2236.

100. P. Krafft, P. Gilbeau, B. Gosselin and S. Classens, *FR 2862644*, 2005.

101. L. Shen, E. Worrell and M. Patel, *Biofuels, Bioprod. Biorefin.*, 2009, **4**, 25-40.

102. M. Ochi, N. Ichikawa, M. Harada, M. Hara and H. Uchida, *J. Appl. Polym. Sci.*, 2011, **124**, 4572-4578.

Chapter 9

Summary and Conclusions

9.1 Summary and Conclusions

The chemical industry today is based on the conversion of fossil resource-based raw materials into value-added products such as fuels, pharmaceuticals, polymers, etc. However, progressive depletion of fossil resources has raised the question of the sustainability and a number of approaches are being undertaken to replace fossil resources with renewable bio-based chemicals. Biorefinery and biotechnology are the emerging areas which can potentially provide the solutions for the sustainable development of the chemical industry. A great deal of polymer science research has also been devoted for replacement of fossil resource-based monomers and polymers with bio-based monomers and polymers having similar or advantageous properties.

The objective of the present dissertation was to explore the utility of CNSL- a by-product of agricultural-based cashew processing industry-as a starting material for the design and synthesis of difunctional step-growth monomers. Another goal was to prepare high performance/ thermally stable polymers *viz.*, polyesters, polyimides, poly(arylene ether)s, polyhydrazides and poly(1,3,4-oxadiazole)s containing pendent flexible pentadecyl chains and/or flexible ether linkages and to investigate the effect of incorporation of pentadecyl chains and/or ether linkages on their solubility behavior as well as thermal properties. Further, cyanate ester, bismaleimide and epoxy resin containing pentadecyl chain were synthesized in order to study their curing characteristics.

The present work has resulted into synthesis of ten new difunctional monomers containing pendent pentadecyl chain making use of 3-pentadecyl phenol as a starting material which in turn is obtained from CNSL, *viz*;

1. 4-(4-Formylphenoxy)-2-pentadecylbenzaldehyde
2. 4-(4-Hydroxyphenoxy)-3-pentadecylphenol
3. 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline
4. 4-(4-(4-(4-Carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid
5. 4-(4-(4-(4-(Hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide
6. 3-Pentadecyl 4,4' biphenol
7. 2, 2-Pentadecyl-[1,1'-biphenyl]-4,4'-diol
8. 4,4’-Dibromo 3-pentadecyl biphenyl
9. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid and

10. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

The difunctional monomers were characterized by IR, ^{1}H NMR, and ^{13}C NMR and mass spectroscopic techniques. The selected difunctional monomers were utilized for the synthesis of high performance polymers such as polyesters, polyimides, poly(arylene ether)s, polyhydrazides and poly(1,3,4-oxadiazole)s. The influence of pendent pentadecyl chains and/or ether linkages on their solubility and thermal properties was investigated. The thermosetting resins, viz.; cyanate ester, bismaleimide, and epoxy resin containing pentadecyl chain were synthesized and the influence of presence of pentadecyl chain on melting point and processing window of these themoset systems was studied.

A series of aromatic (co)polyesters was synthesized from 4-(4-hydroxyphenoxy)-3-pentadecylphenol (HPPDP) and commercially available aromatic diacid chlorides by phase-transfer catalysed interfacial polycondensation. Also a series of copolyesters was synthesized from a mixture of HPPDP and bisphenol A (BPA) with terephthalic acid chloride. Inherent viscosities of (co)polyesters were in the range 0.70-1.21 dL/g. **(**Co)polyesters were soluble in chloroform, dichloromethane, pyridine and *m*-cresol at room temperature and could be cast into tough, transparent and flexible films from chloroform solutions. X-Ray diffractograms showed that polyesters containing pendent pentadecyl chains were amorphous in nature. Temperatures of 10% weight loss (T_{10}) for (co)polyesters were in the range 425-455 °C indicating their good thermal stability. A drop in glass transition temperature (T_g) (27-202 °C) and storage modulus (E’) of (co)polyesters was observed due to the presence of flexible pentadecyl chains which act as packing disruptive groups.

A new diamine viz., 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy) phenoxy)aniline was polycondensed with commercially available aromatic dianhydrides namely 3,3’,4,4’-oxydiphthalic anhydride (ODPA), 4,4’-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA) and 3,3’,4,4’-biphenyl tetracarboxylic dianhydride (BPDA) by one-step solution polycondensation in *m*-cresol to form a series of polyetherimides containing pendent pentadecyl chains and multiple ether linkages. Polyetherimides exhibited inherent viscosity (η_{inh}) in the range 0.66-0.70 dL/g, indicating formation of reasonably high molecular weight polymers. Polyetherimides were soluble in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, pyridine, *m*-cresol and dimethyl sulfoxide. Polyetherimides could be cast into tough, transparent and flexible films from chloroform solution. X-Ray diffraction analysis showed that polyetherimides were amorphous and a reflection in small angle region ($2\theta \approx 3°$) indicated layered packing of pentadecyl chains. DSC study demonstrated lowering of T_g and which were in the range 113-131 °C. T_{10} values of polyetherimides were in the range 460-470 °C indicating their good thermal stability. The incorporation of pendent pentadecyl chain and flexible ether linkages increased the gap between T_g and T_{10} of polyetherimides and thus offered a wider processing window.

Polyhydrazides were synthesized by polycondensation of 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide (HPPPB) with aromatic diacid chlorides and were subsequently cyclized using $POCl_3$ to the corresponding poly(1,3,4-oxadiazole)s. Polyhydrazides and poly(1,3,4-oxadiazole)s exhibited inherent viscosities in the range 0.65-0.72 dL/g and 0.54-0.62 dL/g. Polyhydrazides could be dissolved in polar aprotic solvents viz., N,N-dimethylformamide, N,N-dimethylacetamide, pyridine, dimethyl sulfoxide and *m*-cresol while poly(1,3,4-oxadiazole)s were soluble in solvents such as chloroform, dichloromethane and tetrahydrofuran. The amorphous nature of the polymers was revealed by X-ray diffraction studies. The formation of layered structure was observed for both polyhydrazides and poly(1,3,4-oxadiazole)s because of ordered packing of pentadecyl chains. The T_{10} values for poly(1,3,4-oxadiazole)s were in the range 425-440 °C indicating their good thermal stability. The lowering of T_g in polyhydrazides (175-192 °C) and poly(1,3,4-oxadiazole)s (92-103 °C) could be attributed to packing disruptive pendent pentadecyl chain and flexiblizing ether linkages in the backbone. Poly(1,3,4-oxadiazole)s exhibited maximum UV-Vis absorption in the range 304-337 nm whereas maximum of fluorescence emission was in the range 380-394 nm in chloroform solution. The optical band (E_g) values for poly(1,3,4-oxadiazole)s were found to be in the range 3.33-3.65 eV indicating their potential application in opto-electronic devices.

3-Pentadecyl biphenol was polycondensed with commercially available activated aromatic dihalides by nucleophilic aromatic substitution reaction to afford a series of poly(arylene ether)s containing biphenylene linkages in the backbone and pendent pentadecyl chains. η_{inh} of poly(arylene ether)s were in the range 0.50-0.81 dL/g indicating formation of reasonably high molecular weight polymers. The number average molecular weights (M_n) measured by GPC were in the range 2.2 x 10^4 - 8.3 x 10^4 with polydispersity of 2.2. ^{1}H NMR studies of poly(arylene ether)s indicated the presence of constitutional isomerism which existed due to the non-symmetrical structure of 3-pentadecyl biphenol. Poly(arylene ether)s were soluble in common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. The tough, transparent and flexible films could be cast from their chloroform solutions. X-Ray diffraction patterns showed halos over the range 2θ =15-25° and broad reflections in the small-angle region at about $2\theta \approx 3°$ indicating amorphous nature and layered pentadecyl chain packing, respectively. Poly(arylene ether)s exhibited T_g in the range of 35-60 °C which are lower than that of reference poly(arylene ether)s without pentadecyl chains. The lowering of T_g could be attributed to packing disruptive effect of flexible pendent pentadecyl chains. T_{10} value of poly(arylene ether)s were in the range of 410-455 °C, indicating their good thermal stability. The gas permeation study of poly(ether sulfone) containing pendent pentadecyl chains revealed moderate increase in permeability for helium, hydrogen and oxygen with lower permselectivity as compared to reference poly(ether sulfone) based on 4,4'-biphenol. However, there was large increase in permeability for carbon dioxide due to plasticizing effect pentadecyl chains.

4-Cyanato-1-(4-cyanatophenoxy)-2-pentadecylbenzene (HPPDPCN), containing ether linkages and pendent pentadecyl chain was synthesized from 4-(4-hydroxyphenoxy)-3-pentadecylphenol and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy. The melting point of the HPPDPCN was found to be 31 °C, which is lower than that of bisphenol-A based cyanate ester (MP, 84 °C). Thus, the lower melting point (31 °C) of HPPDPCN provided wider processing window of 219 °C than that of BPACN monomer which has a processing window of 124 °C. The non-isothermal curing kinetics of HPPDPCN was studied by DSC and the activation energy of uncatalyzed curing was found to be 108.06 KJ/mol.

4, 4'-Bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether (C15BMI) containing flexible ether linkages and pendent pentadecyl chain was synthesized by the ring-opening addition reaction of 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline with maleic anhydride followed by cyclodehydration of N,N-bismaleamic acid using acetic anhydride and sodium acetate. The structure of C15BMI was confirmed by IR, ^{1}H NMR, ^{13}C NMR spectroscopy. The melting point of C15BMI was found to be 90 °C, which lower is than that of 4,4’-bis(maleimido)diphenylether (ODABMI) (MP, 183 °C). 4, 4’-Bis-(4-maleimidophenoxy)-2-pentadecyl diphenyl ether exhibited excellent solubility in common organic solvents such as, chloroform, dichloromethane, and tetrahydrofuran at room temperature. Activation energy for curing of C15BMI, as determined in non-isothermal curing mode using Coats-Redfern method, was found to be 75.32 kJ/mol. The cured BMI resin showed T_{10} value of 430 °C indicating its good thermal stability.

Diglycidyl ether of 4-(4-hydroxyphenoxy)-3-pentadecylphenol containing pendent pentadecyl group was successfully synthesized from 4-(4-hydroxyphenoxy)-3-pentadecylphenol by its reaction with epichlorohydrin and was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

In summary, CNSL- a biobased renewable resource- was successfully exploited for synthesis of a range of difunctional monomers. The structural features of the synthesized monomers such as the presence of C15 alkyl chain, ether linkages, and non-symmetrical structure have been found to reduce strong interchain interactions and offer flexibility to the synthesized polymers, resulting in their improved solubility and processability. Thus, processability / solubility of high performance/ thermally stable polymers could be improved by the incorporation of pendant pentadecyl chains as a packing disruptive group which also acts an additional handle for interaction with solvents. The increased gap in values of T_g and T_{10} offered a large processing window to the polymers. Importantly, soluble high performance polymers with reasonably high thermal stability are interesting candidates for applications such as membranes, coatings, electronic devices, etc.

9.2 Perspectives

The work embodied in the thesis dealt with design and synthesis of new difunctional monomers from CNSL for preparation of high performance polymers with improved solubility/processability characteristics and has opened many new avenues for future work.

- The thesis work has added the range of difunctional monomers derived from CNSL which is a cheap, non-edible and abundantly available agricultural waste product.
- The diacids viz., 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid and 4-(4-(4-(4-carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid can be

converted into corresponding diisocyanates on azidation followed Curtius rearrangement. These diisocyanate monomers could be potentially useful for synthesis of polyimides, polyurethanes, etc.

- 3-Pentadecyl 4,4'-biphenyldicarboxaldehyde- a monomer for synthesis of conjugated polyazomethines- can be synthesized by either formylation of 4,4'-dibromo 3-pentadecyl biphenyl or reduction of 4,4'-dicyano 3-pentadecyl biphenyl using diisobutylaluminium hydride (DIBAL-H).
- The monomers containing biphenyl linkage and pendent pentadecyl chain viz., 4,4'-dibromo 3-pentadecyl biphenyl, 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid and 3-pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide have potential to be utilized to synthesize conducting polymers such as polyphenylenes, poly(1,3,4-oxadiazole)s, etc. The pentadecyl chain is expected to grant solubility characteristics to the polymers enabling fabrication of devices.
- High performance polymers synthesized in the present work exhibited wide processing window and therefore it would be worthwhile to study melt processability of these polymers.
- Polyetherimides have multiple ether linkages which would result into lower dielectric constants and therefore evaluation of their dielectric properties would be interesting.
- Gas separation membranes made out of high performance polymers containing pentadecyl chain are expected to interact with hydrocarbon gases and therefore it would be interesting to study permeation characteristics of hydrocarbon gases such as methane, ethane, etc.
- Poly(arylene ether)s and polyesters have lower T_g, therefore it would be interesting to study their applications as 'High Temperature Elastomers'
- The curing and evaluation of mechanical properties of the cyanate ester, bismaleimide and epoxy resin would be of importance as these thermosetting resins are expected to exhibit improved impact strength by virtue of the presence of flexible pentadecyl chains.

Synopsis of the Thesis Entitled

"Exploitation of Cashew Nut Shell Liquid as a Starting Material for the Synthesis of Monomers Useful in the Preparation of Thermally Stable Polymers"

Introduction

The replacement of petroleum-based materials by renewable resource materials is an interesting topic of research for academic and industrial scientists. The approaches concerning development of bio-based polymers include utilization of sugars, polysaccharides, vegetable oils, lignin, and furans.[1, 2] These renewable resources can be turned into viable macromolecular materials and could be potentially useful candidates for the replacement of both thermoplastics and thermosetting materials.

Among vegetable oils (oleochemicals), cashew nut shell liquid (CNSL) is one of the major sources of naturally occurring phenols. CNSL is a non-edible oil and is a by-product of the cashew nut processing industry.[3, 4] CNSL occurs in the soft honeycomb of the shell of the cashew and is a greenish-brown colored liquid. Cashew tree (*Anacardium accidentale Linn*), has origin from Brazil and is now being grown extensively in India, Bangladesh, Tanzania, Kenya, Mozambique, tropical regions of Africa, and South-East and Far-East Asia.[5]

CNSL can be regarded as a versatile and valuable raw material for wide applications in the form of brake linings, surface coatings, paints, and varnishes as well as in polymer production.[6-8] It is used in the preparation of many speciality materials such as phenalkamine cross-linking agents,[9, 10] liquid crystalline polyesters,[11] cross-linkable polyphenols,[12] polyurethanes[13] and a range of other speciality polymers and additives.[4]

The important features of CNSL as a starting material are the following: inexpensive, abundant availability and chemically reactive nature.[14, 15] 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. In spite of extensive literature reported on utilization CNSL, many areas remain which are yet to utilize this attractive raw material. There are only a few reports describing CNSL as a starting material for synthesis of difunctional monomers useful in the preparation of step-growth polymers.[4] Therefore, design and synthesis of difunctional condensation monomers starting from CNSL is an attractive proposition.

High performance / high temperature polymers such as polyesters, polyimides, poly(1,3,4-oxadiazole)s, poly(arylene ether)s, etc. exhibit unique combination of properties such as high thermal stability, high mechanical properties and excellent chemical resistance.[16, 17] These polymers find applications in aviation, automobile, electronic industries, etc. However, the poor solubility in common organic solvents, coupled with high melting (T_m) and glass transition temperature (T_g) results in poor processability which results from the presence of rigid backbone and strong interchain interactions from symmetrical and polar groups. To surmount this, it is desirable to incorporate structural features either in the backbone or as pendent groups to these polymers which will impart greater flexibility and consequently improved solubility and processing characteristics without compromising their attractive characteristics.

Solubility / processability of these polymers may be improved by (i) introducing flexible linkages in the polymer backbone; (ii) introducing monomer with crank shaft or bent units along the backbone or (iii) the use of bulky side groups or flexible side chains.[18-22] These approaches work by forcing the chains apart and lend to the improved solubility and better processability.

For achieving the objective of processability, design and synthesis of difunctional monomers with features that disturb chain packing and structural regularity in polymer backbone is desirable. The present work involves utilization of 3-pentadecyl phenol as a starting material which in turn is obtained from CNSL- a renewable resource material. The monomers were designed in a such way that they possess one or more of the structural features such as: i) presence of flexible ether linkage, ii) non-symmetry in the structure and iii) the naturally gifted pendent pentadecyl chain.[23, 24]

Objective of the Present Thesis

The overall objective of the present thesis is to design and synthesize a series of difunctional monomers using CNSL as a starting material and utilization of these monomers for synthesis of high performance/ thermally stable polymers.

Towards this end, a series of difunctional monomers, *viz,* aromatic diamines, diacid, diphenol, dialdehyde, diacylhydrazide, dibromide and dinitrile containing pendent flexible pentadecyl chain was synthesized starting from CNSL.

Aromatic polyesters, polyimides, poly(1,3,4-oxadiazole)s, poly(arylene ether)s, cyanate ester, bismaleimides and epoxy resins containing pendent pentadecyl chains were synthesized based on the appropriate difunctional monomers based on

CNSL. The effect of pendent pentadecyl chains on polymer properties such as solubility and thermal properties was investigated.

Chapter 1: Introduction and Literature Survey

This chapter summarizes recent advances in field of polymers from renewable resource materials with particular emphasis on monomers and polymers derived from CNSL. A comprehensive review of the literature on high performance polymers, viz., aromatic polyesters, polyimides, poly(1,3,4-oxadiazole)s and poly(arylene ether)s covering method of synthesis, structure property relationship, etc., is also presented.

Chapter 2: Scope and Objectives

This chapter describes scope and the objectives of the thesis work

Chapter 3: Synthesis and Characterization of Condensation Monomers Starting from CNSL

This chapter describes synthesis of difunctional monomers containing pendent pentadecyl chain, *viz.,*

1. 4-(4-Formylphenoxy)-2-pentadecylbenzaldehyde
2. 4-(4-Hydroxyphenoxy)-3-pentadecylphenol
3. 4-(4-(4-(4-Aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline
4. 4-(4-(4-(4-Carboxyphenoxy)-2-pentadecylphenoxy)phenoxy)benzoic acid
5. 4-(4-(4-(4-(Hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy) phenoxy) benzohydrazide
6. 3-Pentadecyl 4,4' biphenol
7. 2, 2-Pentadecyl-[1,1'-biphenyl]-4,4'-diol
8. 4,4’-Dibromo 3-pentadecyl biphenyl
9. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid, and
10. 3-Pentadecyl-[1,1'-biphenyl]-4,4'-dicarbohydrazide

The difiunctional monomers and intermediates involved in their synthesis were characterized by IR, ^{1}HMR, and ^{13}CNMR spectroscopy.

Chapter 4: Synthesis and Characterization of Polyesters Containing Ether linkages and Pendent Pentadecyl Chains

This chapter describes synthesis of aromatic polyesters based on 4-(4-hydroxyphenoxy)-3-pentadecylphenol with aromatic diacid chlorides, viz., isophthalic acid chloride, terephthalic acid chloride and a mixture of isophthalic acid chloride and terephthalic acid chloride and also synthesis of copolyesters from varying composition of 4-(4-hydroxyphenoxy)-3-pentadecylphenol and bisphenol-A with terephthalic acid chloride. (Co)polyester were characterized by inherent viscosity measurements, molecular weight measurements, solubility tests, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis, DSC and dynamic mechanical analysis.

Chapter 5: Synthesis and Characterization of Polyimides Containing Multiple Ether Linkages and Pendent Pentadecyl Chains

This chapter describes synthesis of polyimides based on 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline with commercially available aromatic dianhydrides, viz., 4,4’-oxydiphthalic anhydride (ODPA), 4,4’-(hexafluroisopropylidene) diphthalic anhydride (6-FDA), and 4,4’-biphenyltetracarboxylic dianhydride (BPDA) by one step polycondensation in m-cresol. Polyimides were characterized by inherent viscosity measurements, molecular weight measurements, solubility tests, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC.

Chapter 6: Synthesis and Characterization of Polyhydrazides and Poly(1,3,4-oxadiazole)s Containing Multiple Ether Linkages and Pendent Pentadecyl Chains

This chapter deals with synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s based on 4-(4-(4-(4-(hydrazinocarbonyl)phenoxy)-2-pentadecylphenoxy)phenoxy)benzohydrazide and aromatic diacid chlorides viz., isophthalic acid chloride, terephthalic acid chloride and a mixture of isophthalic acid chloride and terephthalic acid chloride. Polyhydrazides were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC. Poly(1,3,4-oxadiazole)s were characterized by inherent viscosity measurements, molecular weight measurements, solubility tests, IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis, DSC, UV-Visible and fluorescence spectroscopy.

Chapter 7: Synthesis and Characterization of Poly(arylene ether)s Based on 3-Pentadecyl 4,4' Biphenol

This chapter describes synthesis of poly(arylene ether)s based on 3-pentadecyl 4,4' biphenol and commercially available dihalide monomers, *viz*., 4,4’-difluorobenzophenone, 1,3-bis(4–fluorobenzoyl)benzene and bis(4-fluorophenyl)sulfone. Poly(arylene ether)s were characterized by inherent viscosity measurements, molecular weight measurements, solubility tests, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis and DSC. Poly(ether sulfone) containing pendent pentadecyl chains was evaluated as membranes for gas separation studies.

Chapter 8: Synthesis and Characterization of Thermostting Resins Containing Pentadecyl Chains

This chapter is sub-divided into three parts:

a) Synthesis of cyanate ester based on 4-(4-hydroxyphenoxy)-3-pentadecylphenol by reaction with cyanogen bromide.

The cyanate ester was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy and curing kinetics was studied by DSC.

b) Synthesis of bismaleimide based on 4-(4-(4-(4-aminophenoxy)-2-pentadecylphenoxy)phenoxy)aniline by reaction with maleic anhydride. The bismaleimide was characterized FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy and curing kinetics was studied by DSC.

c) Synthesis of epoxy resin based on 4-(4-hydroxyphenoxy)-3-pentadecylphenol by reaction with epichlorohydrin. The epoxy resin was characterized by measurement of epoxy value, FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Chapter 9: Summary and Conclusions

This chapter summarizes the results, salient conclusions and future prospect of the work reported in this thesis.

References:

1. C. K. Williams and M. A. Hillmyer, *Polymer Reviews*, 2008, **48**, 1-10.
2. R. Mülhaupt, *Macromol.Chem. Phys.*, 2013, **214**, 159-174.
3. M. C. Lubi and E. T. Thachil, *Des. Monomers Polym.*, 2000, **3**, 123-153.
4. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem., 2014,* **5**, 3142-3162.
5. G. Mele and G. Vasapollo, *Mini-Rev. Org. Chem.*, 2008, **5**, 243-253.
6. C. K. S. Pillai, *Pure Appl. Chem.*, 1998, **70**, 1249-1252.
7. U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schafer, *Angew. Chem. Int. Ed.*, 2011, **50**, 3854-3871.
8. E. D. Rio, G. Lligadas, J. C. Ronda, M. Galia, M. A. R. Meier and V. Cadiz, *J. Polym. Sci. Part A: Polym. Chem.*, 2011, **49**, 518–525.

9. *Cardolite Corpn., USA:* *http://www.cardolite.com/*.
10. Y. Zhang, M. Li, J. Lian, X. Yang and J. Xi, *Prog. Org. Coat.*, 2012, **74**, 240-247.
11. M. Saminathan, C. Krishna, S. Pillai and C. Pavithran, *Macromolecules*, 1993, **26**, 7103-7105.
12. C. V. Mythili, A. M. Retna and S. Gopalakrishnan, *J. Mater. Sci.*, 2004, **27**, 235-241.
13. C. V. Mythili, A. M. Retna and S. G. . *J. Appl. Polym. Sci.*, 2005, **98**, 284-288.
14. C. K. S. Pillai, *Des. Monomers Polym.*, 2010, **13**, 87-121.
15. P. Blazdell, *Int. Sci. Rev.*, 2000, **28**, 220-226.
16. P. E. Cassidy, *Thermally Stable Polymers, New York: Dekker,*, 1980.
17. M. Arroyo, *Polyarylates, Handbook of Thermoplastics, Olabisi,O., Ed., Marcel Dekker Inc.: New York,*, 1997, 599-608.
18. D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai and C.-S. Ha, *Prog. Polym. Sci.*, **37**, 907-974.
19. S. H. Hsiao and H. W. Chiang, *Eur. Polym. J.*, 2004, **40**, 1691.
20. S. Watanabe, H. Murayama, M. Murata, Y. Masuda, M. Tanabe and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, 1998, **36**, 2229-2235.
21. R. D. Shingte, *Thesis submitted to University of Pune, Pune, India.*, 2006.
22. P. N. Honkhambe, N. S. Bhairamadgi, M. V. Biyani, P. P. Wadgaonkar and M. M. Salunkhe, *Eur. Polym. J.*, 2010, **46**, 709-718.
23. Nair CPR, Mathew D and Ninan KN, *Adv Polym Sci*, 2001, **155**, 1-176.
24. A. D. Kulkarni, B. V. Tawade and P. P. Wadgaonkar, *High Perform. Polym.*, 2014, **25**, 278-286.

Bhausaheb V. Tawade	**Prakash P. Wadgaonkar**
(Ph.D. Candidate)	**(Research supervisor)**

List of Publications

1) *Processable Aromatic Polyesters Based on Bisphenol Derived from Cashew Nut Shell Liquid: Synthesis and Characterization*

   Bhausaheb V. Tawade, Jagadish K. Salunke, Prakash S. Sane, Prakash P. Wadgaonkar

   J. Polym. Res. 21 (**2014**): 617

2) *Functionalization of Cardanol: Towards Biobased Polymers and Additives*

   Coline Voirin, Sylvain Caillol, Nilakshi V. Sadavarte**, Bhausaheb V. Tawade**, Bernard Boutevin, Prakash P. Wadgaonkar,

   Polym. Chem. 5, (**2014**) 3142-3162

3) *Synthesis and Characterization of Polyetherimides Containing Pendent Pentadecyl Chains*

   Bhausaheb V Tawade, Prakash P. Wadgaonkar (Manuscript under preparation)

4) *Poly(arylene ether) containing biphenylene units in the main chain and pendent pentadecyl chains*

   Bhausaheb V Tawade, Prakash P. Wadgaonkar (Manuscript under preparation)

5) *Synthesis, characterisation and opto-electronic properties of poly(1,3,4-oxadiazole)s containing multiple ether linkages and pendent pentadecyl chains*

   Bhausaheb V Tawade, Prakash P. Wadgaonkar (Manuscript under preparation)

6) *A Facile Strategy for Synthesis of α, α'-Heterobifunctionalized Poly ε-caprolactones and Poly(Methyl methacrylate)s Containing "Clickable" Aldehyde and Allyloxy Functional Groups Using Initiator Approach*

   Prakash S. Sane, **Bhausaheb V. Tawade**, Indravadan Parmar, Savita Kumari, Samadhan Nagane, Prakash P. Wadgaonkar,

   J. Polym Sci Part A: Polym Chem. 51, (**2013**), 2091-2103

7) *Synthesis and Characterization of Poly(ether ether ketone)s and Poly(ether ether ketone ketone)s Containing Pendant Biphenyl and Naphthyl Groups*

   Pandurang N. Honkhambe, Neelam A. Dhamdhere, **Bhausaheb V. Tawade**, Manikrao M. Salunkhe, Prakash P. Wadgaonkar

   High Perform. Polym. 25, (**2013**), 260-267

8) *Cyanate Ester Resins Containing (Pentadecyl Substituted) Cyclohexyl Moiety: Synthesis, Curing and Structure-Property Relationship*
   Arun D. Kulkarni, **Bhausaheb V. Tawade**, Prakash P. Wadgaonkar
   High Perform. Polym. 25, (**2013**), 278-286
9) *Aromatic Aldehyde Functionalized Polycaprolactone and Polystyrene Macromonomers: Synthesis, Characterization and Aldehyde-Aminooxy Click Reaction*
   Prakash S. Sane, **Bhausaheb V. Tawade**, Dnyaneshwar V. Palaskar, Prakash P. Wadgaonkar
   React. Funct. Polym. 72, (**2012**), 713-721

List of Patents

1) Prakash P. Wadgaonkar, Bhimrao D. Sarwade, **Bhausaheb V. Tawade**,
   Process for preparing a cross linking catalyst from cashew nut shell liquid
   US 20140357891 A1
2) Samadhan S Nagane, Prakash S Sane, **Bhausaheb V. Tawade**, Prakash P. Wadgaonkar
   2,2’-Bis(4-hydroxyphenyl) alkyl azides and process for the preparation thereof
   WO2014073001 A1