Processable High Performance Polymers: Synthesis, Characterization and Application

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Dedicated To
My Parents
and
Parents-in-law

Certificate of the Guide

Certified that the work incorporated in the thesis entitled **“Processable High Performance Polymers: Synthesis, Characterization and Application”** submitted by Snehalata P. Bapat was carried out under my supervision. Such material as has been obtained from other sources has been duly acknowledged in this thesis.

December, 2007 P. P. Wadgaonkar

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Declaration by the Candidate

I declare that the thesis entitled "**Processable High Performance Polymers: Synthesis, Characterization and Application"** is my own work conducted under the supervision of Dr. P. P. Wadgaonkar, at Polymer Science and Engineering Division, National Chemical Laboratory, Pune. I further declare that to the best of my knowledge, this thesis does not contain any part of work, which has been submitted for the award of any degree either of this University or any other University without proper citation.

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Abstract

High performance / high temperature polymers, such as aromatic polyimides, polyamides and polyesters have received considerable attention as these find applications in various industries, such as aero-space, automobile, electronics industries, etc. due to their excellent mechanical and thermal properties, good chemical resistance and insulating properties. However, due to their structural regularity, rigidity and strong inter chain interactions these polymers generally exhibit low solubility and melting points above their thermal decomposition temperatures, which limits their wide spread applications. The literature reports several approaches to improve processability /solubility of high performance polymers by advising structural modifications within the monomer itself.

The main objective of the present research was to design and synthesize processable high performance polymers such as polyimides, polyamides and polyesters by making use of difunctional monomers containing aromatic pendant groups or cardo groups. Another objective was to study the permeation properties of selected polyimide films

Thus efforts were made to design and synthesize difunctional monomers such as bisphenols containing aromatic pendant groups/cardo groups, new diamines and diacids containing aromatic pendant groups/cardo groups along with flexible ether linkages starting from synthesized bisphenols.

Synthesized bisphenols and diamines are listed below

1) 1,1-Bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane (**NABP)**,
2) 1,1-Bis-[4-hydroxyphenyl-1-(4-phenylsulfonylphenyl)]ethane (**DPSBP**),
3) 1,1-Bis–[4-hydroxyphenyl-(1-biphenyl)]ethane (**BBHPE**),
4) 1,1-Bis-[4-hydroxy-(3,5-dimethylphenyl)]-4-perhydrocumylcyclohexane **(TMPCPBP),**
5) 1,1–Bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane **(PCPBP),**
6) 1,1-Bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene **(DCHBP),**

Synthesized diamines are as follows

1) 1,1-Bis-[4-(4-aminophenoxy)phenyl -1-(2-naphthyl)] ethane **(NABPDA).**
2) 1,1-Bis–[4-(4-aminophenoxy)phenyl-1-biphenyl]ethane **(BBHPDA),**
3) 1,1-Bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (**TMDA),**

4) 1,1-Bis-[4-(4-aminophenoxy)phenyl]octahydro-2(1H)-naphthalene **(DCHDA**),

Synthesized diacids are as follows

1) 1,1-Bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane**(PCPDA),**

2)1,1-Bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (**TMPCPDA)**,

Characterization of the synthesized monomers was carried out with the help of spectroscopic techniques. In case of bisphenols containing cardo groups ^{1}H NMR spectra showed the presence of distereotopic phenyl rings, which are magnetically non-equivalent. Bisphenols containing cardo groups namely PCPBP, TMPCPBP and DCHBP are not symmetrical about a C_2 axis between the two phenolic rings and this results in different environments for aromatic protons present on two different phenyl rings, hence the aromatic rings showed four doublets for aromatic protons in ^{1}H NMR spectra.

This observation was supported by X-ray crystallography. The X-ray crystal structure of 1,1-bis-(4-hydroxy phenyl) octahydro-2(1H) naphthalene (DCHBP) (**Figure 3.51, Chapter 3**) shows that the two phenyl rings attached to carbon C1 are not in the same plane, this gives rise to different environment for protons present on two phenyl rings.

A series of polyimides was synthesized starting from diamines viz 1. NABPDA 2. BBHPDA 3.TMDA and 4. DCHDA and commercially available dianhydrides namely 1. 3,3',4,4'-oxydiphthalic anhydride (ODPA) 2. 3,3',4,4'-hexafluoro isopropylidene diphthalic anhydride (6FDA) 3. 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) 4. 3,3',4,4'-benzophenone tetra carboxylic dianhydride (BTDA) 5. 1,2,4,5 benzene tetra carboxylic dianhydride (PMDA) and 6. 3,3',4,4'-diphenyl sulfone tetra carboxylic dianhydride (DSDA) by conventional two step polymerization reaction, first preparing the soluble amic-acid precursor followed by thermal cyclo dehydration.

Medium to high molecular weight polyimides were obtained with inherent viscosity in the range 0.40-1.62 dL/g. Most of the polyimides were soluble in aprotic polar solvents such as DMF, DMAc and NMP. Tough transparent and flexible films could be cast from the appropriate solvents (chloroform/DMAc). X-Ray diffraction studies of polyimide films showed that all the polyimides obtained were amorphous. The initial decomposition temperature (IDT) and glass transition temperature (Tg) of polyimides were in the range 430-538°C and 244-316 °C respectively.

Mechanical properties of polyimide films based on TMDA and aromatic dianhydrides were tested. Polyimide films possess tensile strength in the range 76-87 MPa, elongation at break in the range 6.02 -11.51 % and initial modulus in the range 1.64 -2.12 GPa indicating that these polyimide films were tough and flexible to be used as strong polymeric materials

Polyimide films derived from TMDA- 6FDA and TMDA-ODPA (PI-IVb, PI-IVa, Chapter 4) were selected for gas permeability studies and the results showed that the replacement of –O- linkage in PI-IVa with $–C(CF_3)_2-$ in PI-IVb increased the permeability of various gases by 2 -3 times in magnitude and the selectivities remained practically similar and slightly increased in case of α (CO_2/ CH_4) (**Table 4.14,Chapter 4**). Only Helium based selectivities [α (He/ N_2) and α (He/ CH_4)] were slightly decreased in case of polyimide containing $–C(CF_3)_2-$ group.

Polyimides synthesized by polycondensation of diamines BBHPDA, TMDA and DCHDA with 6FDA (PI-IIb, PI-IIIb and PI-IVb, Chapter 4) showed dielectric constants in the range 3.5122 – 3.8012

A series of polyamides was synthesized starting from diamines viz 1.NABPDA 2. BBHPDA 3. TMDA 4. DCHDA and commercially available diacids namely 1. isophthalic acid 2. terephthalic acid 3. 4,4'-oxybisbenzoic acid 4. 4,4'-biphenyl dicarboxylic acid 5. 4,4'-hexafluoroisopropylidene bisbenzoic acid, by phosphorylation polycondensation.

Medium to high molecular weight polyamides were obtained with inherent viscosity in the range 0.50-0.82 dl/g. Polyamides containing bulky pendant groups/cardo groups and flexible ether linkages dissolved readily in polar aprotic solvants such as DMAc, NMP. Tough transparent and flexible films of these polyamides could be cast from DMAc. Wide angle X-ray diffraction studies of the polyamide films showed that all polyamides were amorphous in nature.

The initial decomposition temperature (IDT) and the glass transition temperature (Tg) of the polyamides obtained were in the range 378-522°C and 248-301 °C respectively.

Three new polyamides were synthesized starting from diacid PCPDA and commercially available diamines viz. *m*-phenylenediamine, *p*-phenylenediamine and benzidine. Medium molecular weight polyamides were obtained with inherent viscosity 0.51-0.55 dl/g. Polyamides obtained from PCPDA and aromatic diamines were soluble in aprotic polar solvents such as DMAc, NMP and DMF. Tough and flexible films of these polyamides could be cast using DMAc as solvent. Wide angle X-Ray diffraction studies of polyamide films showed that all the polyamides obtained were amorphous in nature. The initial decomposition temperature (IDT) and the glass transition temperature (Tg) of the polyamides obtained from the diacid PCPDA were in the range 382-480^{o}C and 227-305 ^{o}C respectively.

Polyesters were synthesized from bisphenol 1,1-bis-[4-hydroxyphenyl-1-(4-phenylsulfonylphenyl)] ethane (DPSBP), and aromatic diacidchlorides viz. isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC). Since the polyester obtained from bisphenol A (BPA) and TPC is insoluble in common organic solvent efforts were made to obtain soluble copolyesters by incorporating DPSBP as co-monomer.

Inherent viscosity of polyesters was in the range 0.56-1.57 dL/g indicating formation of medium to high molecular weight polymers. Tough transparent and flexible films of polyesters and copolyesters could be cast from their solutions in chloroform. Wide angle X-ray diffraction studies of the polyester films showed that all the polyesters were amorphous in nature. The IDT and Tg of the polyesters and co-polyesters were in the range 462-475^{o}C and 223-260 ^{o}C, respectively.

Overall, the incorporation of bulky pendant group/cardo groups and flexible ether linkages resulted into polyamides and polyimides with improved solubility in polar organic solvents. The solubility for aromatic polyesters in common organic solvents such as chloroform and dichloromethane was achieved by the incorporation of pendant phenyl sulfonyl phenyl groups into polymer backbone. Thus improved solubility combined with retention of thermal properties make these polymers promising high performance polymeric materials.

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Glossary

NABP	1,1-Bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane
DNNABP	1,1-Bis-[4-(4-nitrophenoxy) phenyl]-2-naphthyl)]ethane
NABPDA	1,1- Bis- [4-(4-aminophenoxy) phenyl-2-naphthyl)]ethane
BBHPE	1,1-Bis–[{4-hydroxyphenyl}-1-biphenyl] ethane
DNBBHPE	1,1-Bis- [4-(4-nitrophenoxy) phenyl-1-biphenyl]ethane
BBHPDA	1,1-Bis- [4-(4-aminophenoxy) phenyl-1-biphenyl] ethane
DPSBP	1,1-Bis- [4-hydroxyphenyl-1-(4-phenylsulfonylphenyl)]ethane
PCP	*p*-Cumylphenol
HPCP	Hydrogenated *p*-cumylphenol
HPCP-K	4-(1-Cyclohexyl-1-methyl ethyl) cyclohexanone
PCPBP	1,1-Bis-(4-hydroxyphenyl) -4-perhydrocumyl cyclohexane
TMPCPBP	1,1-Bis-(4-hydroxy-3,5-dimethylphenyl)-4-perhydrocumyl cyclohexane
DNTMPCPBP	1,1-Bis-[4-(4-nitrophenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane
TMDA	1,1-Bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane
DCNPCPBP	1,1-Bis[4-(4-cyanophenoxy) phenyl)]-4-perhydrocumyl cyclohexane
PCPDA	1,1-Bis[4-(4-carboxyphenoxy) phenyl)]-4-perhydrocumyl cyclohexane
DCNTMPCPDA	1,1-Bis[4-(4-cyanophenoxy)3,5dimethylphenyl)]-4-perhydrocumyl cyclohexane
TMPCPDA	1,1-Bis[4-(4-carboxyphenoxy)3,5-dimethyl phenyl)]-4-perhydrocumyl cyclohexane
DCHBP	1,1-Bis- (4- hydroxy phenyl)-octahydro-2(1H)-naphthalene
DNDCHBP	1,1-Bis-[4-(4-nitrophenoxy)phenyl]-octahydro-2(1H)-naphthalene
DCHDA	1,1-Bis-[4-(4-aminophenoxy)phenyl]-octahydro-2(1H)-naphthalene
ODPA	3,3',4,4'-Oxydiphthalic dianhydrides (ODPA),
6-FDA	3,3',4,4-'Hexafluoroisopropylidene diphthalic anhydride

BTDA	3,3’,4,4’-Benzophenonetetracarboxylic dianhydride
PMDA	1,2,4,5-Benzenetetracarboxylic dianhydride
DSDA	3,3’,4,4’-Diphenylsulfonetetracarboxylic dianhydride
TPA	Terephthalic acid
IPA	Isophthalic acid
NMP	N-Methyl-2- pyrrolidone
DMAc	Dimethylacetamide
THF	Tetrahydrofuran
DMF	Dimethylformamide
DCM	Dichloromethane
PCC	Pyridiniumchlorochromate
WAX	Wide angle X-ray diffraction
CTC	Charge transfer complex
FFV	Fractional free volume
COSY	Correlation spectroscopy, two dimensional shift correlation via spin-spin coupling
NOESY	Nuclear overhauser effect spectroscopy
HSQC	Heteronuclear single quantum coherence
HMBC	Heteronuclear multiple bond correlation

1.1 Introduction

High performance polymers (HPPs) can be broadly defined as materials that exhibit properties superior to those of state-of-the-art materials, but the definition changes with the changing context. Many scientists and technologists prefer more specific definition such as the materials which exhibit not only a unique combination of properties (e.g., high strength, high stiffness, high impact resistance along with high chemical resistance, low inflammability etc.) superior to those of state-of- the art materials but also better elevated temperature behavior.

In 1960s the aerospace industry was a significant driving force behind the developments of new materials for demanding environments, and it still remains the major largest user. 1960-1970 was the most prolific decade for high performance polymers (HPPs), where the thermally most stable heterocyclic rings were incorporated within polymer structures and polyimides came in the scenario. The efforts during the early part of this era were directed primarily towards better thermal stability; little attention was paid to processability.

Commercialization of several HPPs took place during 1970s, and soon it was realized that the co-planarity, high structural regularity and strong interchain interactions which make them thermally very stable make these polymers virtually insoluble in common organic solvents hence making them difficult to process.

1980s work focused on exploring ways to produce polymers with enhanced processability and cost effective routes to convert these polymers into various ready to use materials.The research continues in many other areas such as microelectronics (photoresist, interlayer dielectrics), optical fiber waveguides, proton exchange membranes for fuel cells, separation / barrier materials, etc.

Polyimides, polyamides and polyesters are the important classes of high performance polymers. The high regularity and high rigidity of the backbones of HPPs result in strong interchain interactions, high crystallinity, high melting points and low solubility. Thus, processing of HPPs is difficult. In order to increase processability and systematically understand HPPs, a wide variety of modified HPPs have been synthesized. Several approaches have been used (**Figure 1.1**) to modify HPPs including: (1) the insertion of flexible spacers between the rigid units; (2) the insertion of bent or 'crankshaft' units along the aromatic backbone to form random or alternating copolymers; and (3) the appending of bulky side groups or flexible side chains to the aromatic backbone.

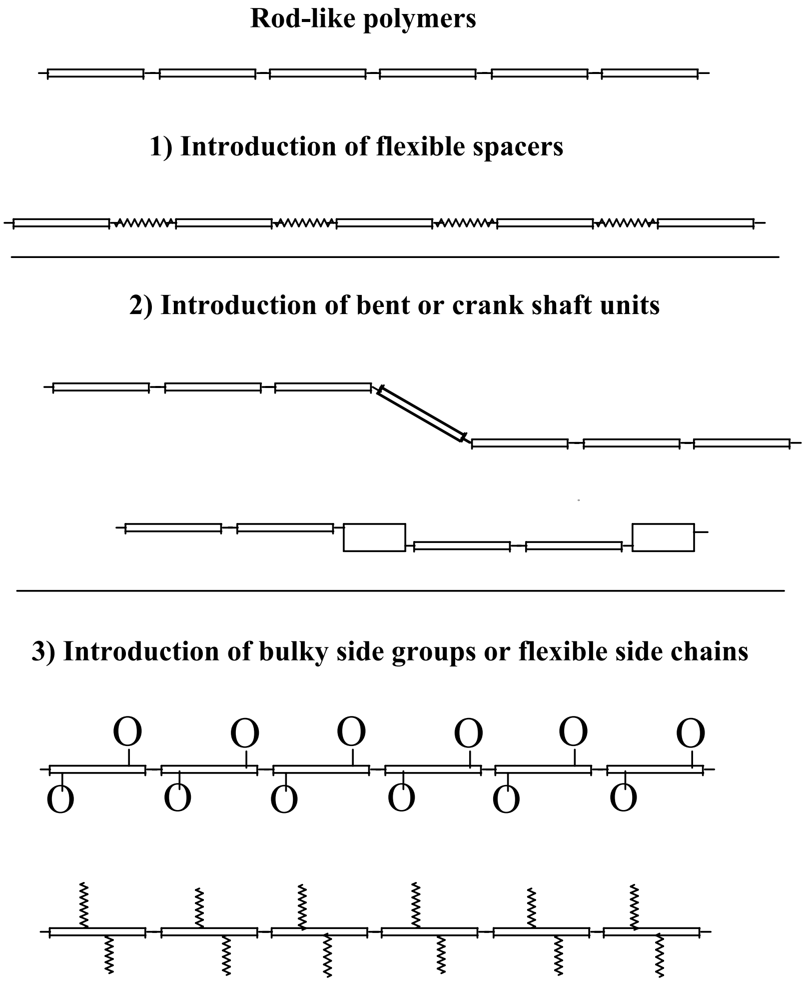
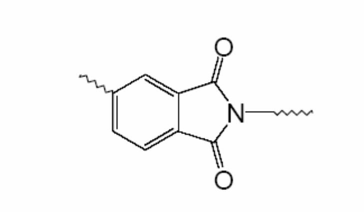


Figure 1.1: Approaches for improving processability of high performance polymers.

This chapter describes some topics including common synthetic chemistry and methods used to prepare polyimides, polyamides and polyesters, important characteristics and their applications.

1.2 Polyimides

Polyimides are a class of polymers containing a heterocyclic imide unit in the polymer backbone.



The first report concerning polyimides was made by Bogert and Renshaw in 1908.[1] However, only in the early 1960s were polyimides successfully introduced as commercial polymeric materials (Kapton) by Du Pont.[2] Since that time, an impressive variety of polyimides have been synthesized and reported in the literature.[3-7]

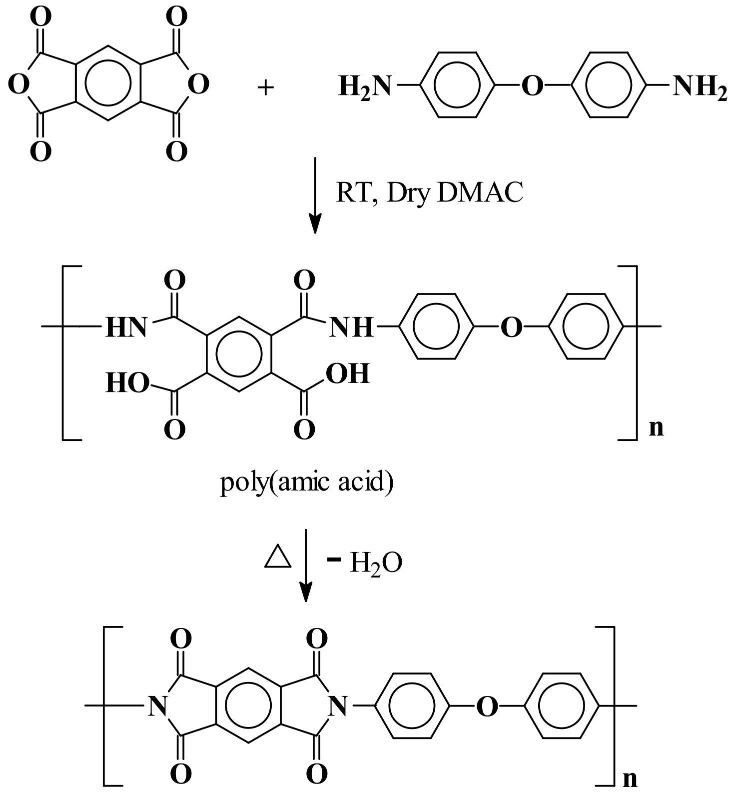
Polyimides are important, both academically and commercially, because of their combination of outstanding key properties, including thermal, thermo-oxidative stability, high mechanical strength, high modulus, excellent electrical properties, and superior chemical resistance. Therefore, in spite of their general difficulty in processing and high cost, polyimides are widely used as matrix resins, adhesives, coatings, printed circuit board and insulators for high performance applications in the aerospace, automotive, electrical, electronics and packaging industries.

1.2.1 Synthesis of polyimides

The structure and the synthetic pathway are important constituents in the development of high performance polyimide materials. Polyimides are generally derived from the step or condensation reaction of organic diamines and tetracarboxylic dianhydrides. In this section, the fundamental aspects and new developments in the chemistry of polyimide synthesis will be discussed.

1.2.1.1 Classical two-step method *via* poly (amic acid)s

The classical synthetic pathway pioneered at Du Pont de Nemours and Co. to cope with the infusibility and insolubility of aromatic polyimides is still the most popular technique for the preparation of polyimides. As shown in **Scheme 1.1**, with the example of Kapton synthesis, this preparative approach consists of the formation of soluble, and thus processable, poly(amic acid) (PAA) precursors from diamines and tetracarboxylic dianhydrides, followed by the conversion of PAAs to the desired polyimides *via* imidization.



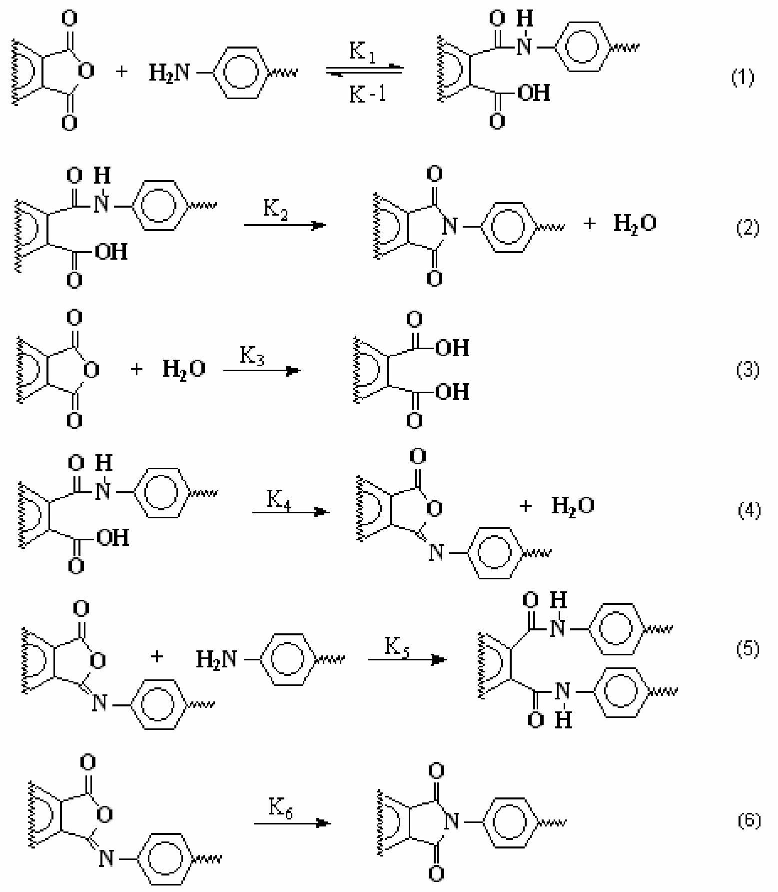
Scheme 1.1: Preparation of Kapton® polyimide.

a) Formation of poly (amic acid)s

The formation of poly (amic acid) is achieved *via* the reaction of a dianhydride and a diamine in a dry aprotic solvent at or below room temperature. The reaction mechanism involves the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group, followed by the opening of the anhydride ring to form an amic acid group. In this equilibrium reaction, the forward reaction is often much faster than the reverse reaction. The acylation reaction of amine is an exothermic reaction.[6] The forward reaction in a dipolar solvent is a second-order reaction and the reverse reaction is a first-order reaction. Therefore, the equilibrium is favored at low temperature and high monomer concentration to form high molecular weight poly(amic acid).[8] The reactivity of the monomers is an important factor governing the rate of amic acid formation. It is expected that the nucleophilicity of the amino nitrogen atom of the diamine and the electrophilicity of the carbonyl group of the dianhydride are important factors in this process. However, structure of the diamine seems to influence the rate of the acylation reaction more than the variation in dianhydride.[9] The high nucleophilicity of the diamine results in high reactivity. The reactivity of diamines correlates well with their basicities (pKa) as expressed by Hammett relation.[10] However, very high basic diamines, e.g. aliphatic diamines, have an unfortunate tendency to form ionic salts with the carboxyl group of the formed amic acid linkage, while the protonation of the amine group prevents its reaction with the anhydride. Recently Ogura and Ueda [11a] have reported synthesis of poly (amic acid) from cyclic trans-1,4 cyclohexane diamine. They successfully synthesized high molecular weight polyamic acids from aromatic dianhydrides such as 3,3',4,4' biphenyl tetra carboxylic dianhydride and alicyclic diamine 1,4 cyclohexyl diamine (CHDA) in presence of monocarboxylic acid such as acetic acid. It has also been reported that acetic acid more than 1 equivalent to CHDA is required to suppress the salt formation from PAA and CHDA. It has been suggested that an optimal diamine should have a pKa of 4.5-6.[11a] Mathew, Kim and Ha have also reported synthesis of aliphatic polyimides from adamantane based aliphatic diamines [11b]. Synthesis of aromatic polyimides with the use of insitu silylated diamines by adding chloro (trimethyl) silane in presence of pyridine has been reported recently [11c]. The use of ionic liquids as solvent for polymerization of aliphatic monomers is also reported [11(d,e,f)]. The effect of the reactivities of anhydrides is manifested by the fact that the reaction rate increases with increasing affinity for the electron by the dianhydride. Earlier investigators[12] quantified electron affinity (Ea) for various dianhydrides by polarographic measurements and demonstrated that the rate of an acylation reaction of 4,4'-diaminodiphenyl ether and a model compound, 4-aminodiphenyl ether, was closely correlated with these Ea values. In addition to the inherent characteristics of the monomers, the properties of the solvent utilized are also critical. For example, the use of polar aprotic solvents that can form strongly hydrogen-bonded complexes with the carboxyl group, play a major role in driving the equilibrium to amic acid. Dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and 1-methyl-2-pyrrolidinone (NMP) are the solvents most generally used. The rate of amic acid formation measured for reaction of phthalic anhydride and 4-phenoxyaniline, increased with solvent in the order of THF <acetonitrile < DMAc.[13]

Several minor, but important, reactions also occur during poly (amic acid) formation. These side reactions may become significant under certain conditions, particularly when the acylation reaction of the diamine is relatively slow because of low monomer reactivity or low monomer concentration. In addition to the amic acid propagation route, five additional potential reaction pathways are possible and are illustrated in **Scheme 1.2** Their relative rate constants are listed in **Table 1.1**.[14] The formation of poly (amic acid) is an equilibrium reaction determined by acylation (k1) and deacylation (k-1) reactions. The latter is also described as an intramolecular acidolysis, forming an anhydride. Poly(amic acid)s are known to undergo hydrolytic degradation even at ambient temperatures. When poly (amic acid)s are in solution, a small amount of the anhydride is always present in an equilibrium concentration. However small, it plays an important role in the hydrolytic degradation of poly(amic acid). In the presence of water, the anhydride group is hydrolyzed to form an *ortho* dicarboxylic group as shown in (3). The reaction is driven by the enhanced nucleophilicity of the water in a dipolar aprotic solvent and by the strong acid-base interaction of the material with the dipolar solvent. The effects of water on the molecular weight of poly(amic acid)s during polymerization, and the effect of added water on the molecular weight of poly(amic acid)s in solution, are well documented.[15] It should be noted that water formed *in situ* by the imidization of amic acid, as shown by equation (2), is important. Even if the rate of imidization, and therefore the formation of water, is relatively low at ambient temperatures, it is still significant enough to cause a gradual decrease in molecular weight over a long period of time. For example, Frost and Kesse[16a] studied aging of a 11% DMAc solution of pyromellitic dianhydride-4,4'-diaminodiphenyl ether (ODA) poly(amic acid) at 35°C. After 21 days, approximately 20% of the amic acid was converted to the imide, generating the corresponding amount of water, which was equivalent to having 0.19% water in the solvent.

When long-term storage is necessary, poly(amic acid) solutions should be kept refrigerated to maintain the properties essential to further processing. Chiefari, etal [16b]has reported the synthesis of polyimides in water. However they have obtained low molecular weight polymers with reduced viscosity in the range 0.2-0.3 dL/g.



Scheme 1.2: Major reaction pathways involved in poly(amic acid) synthesis.[15]

Table 1.1 Relative rate constants for reactions pathways involved in poly (amic acid) synthesis (Scheme1.2).[14]

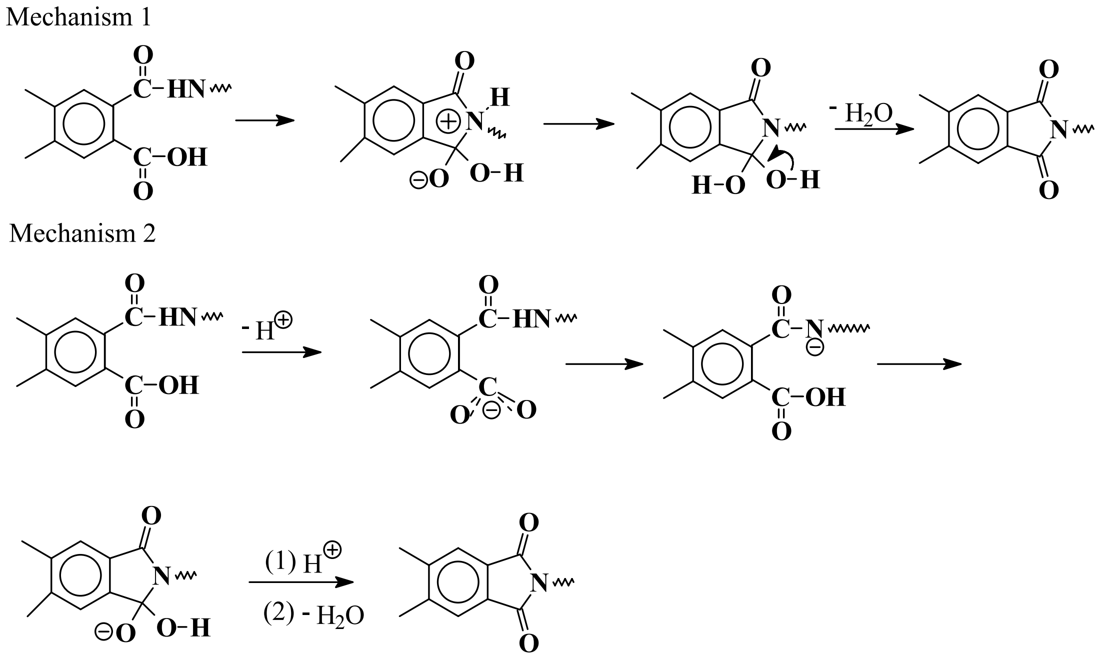
Reaction	Rate constant (s^{-1})*
Propagation (k_1)	0.1-0.5
Depropagation (k_{-1})	10^{-5}-10^{-6}
Spontaneous imidization (k_2)	10^{-8}-10^{-9}
Hydrolysis (k_3)	10^{-1}-10^{-2}
Isoimide formation (k_4)	—
Diamide formation (K_5)	—
Isomerization (k_6)	—

*Rate constants are estimated for a typical polymerization at ca. 10 wt. % concentration, i.e. 0.5M.

b) Thermal imidization of poly (amic acid) s

The first pathway for the cyclization of an amic acid moiety into an imide involves gradual heating of PAA to 250-350°C, depending upon the stability and the glass transition temperature of the polymer. The events occurring during the heating include evolution of solvent and dehydrative cycloimidization. The imidization is accomplished through nucleophilic attack of the amide nitrogen on the acid carbonyl carbon with elimination of water. **Scheme 1.3** shows two amic acid cyclization mechanisms proposed by Harris.[8] The main difference between the two mechanisms is when the loss of the amic acid proton occurs. Harris suggested that mechanism 2 is more likely, since the conjugated base of the amic acid is a more potent nucleophile than the amide. On the other hand, extremely small amide dissociation constants and the demonstrated effectiveness of acid catalyzed reactions tend to support mechanism-1.[9,17,18]

Thermal imidization is particularly effective for the preparation of thin materials such as films, coatings, fibers, and powders because it allows the diffusion of the by-product and the solvent without forming bristles and voids. The problem of film cracking as a result of shrinkage stress can be avoided by carefully controlling the curing profile. A typical heating schedule includes a stage below 150°C, followed by a relatively rapid temperature ramp to a second stage above the Tg of the resulting polyimide. The majority of the solvent is slowly driven off in the first stage, while imidization essentially occurs in the second stage, where curing shrinkage stress is releasable.[14] Such a heating cycle allows the conversion of polyamic acid to polyimide with degree of imidization of about 92-99%, and this is considered to be the maximum that can be achieved *via* thermal imidization. Further heating at 300°C or higher does not result in 100% conversion because of the so-called "kinetic interruption" effect.[6] It should be noted that the hydrolytically unstable residual amic acid units resulting from kinetic interruption are considered as defect sites. Their presence at concentrations of 1-8 % in the resulting polyimide can noticeably reduce hydrolytic stability. This is particularly evident for the rigid-rod like polyimides, for which full imidization is considered the most difficult to achieve.[3]



Scheme 1.3: **Possible imide formation mechanisms.**[6]

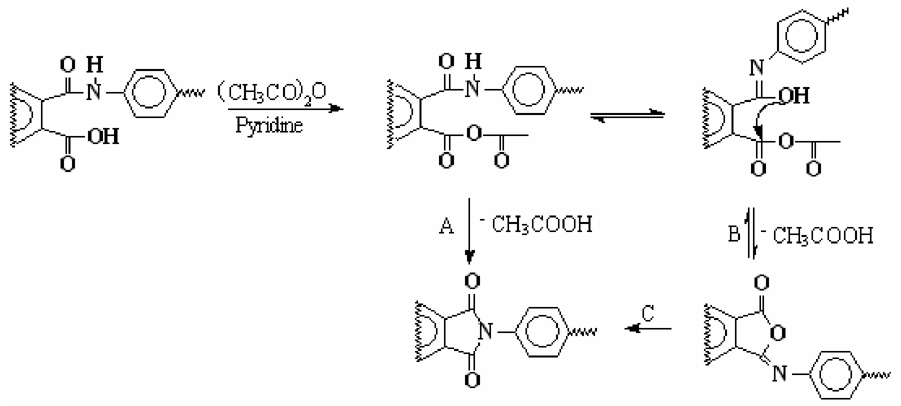
Another important consideration of thermal imidization is the occurrence of side reactions. Compared with polyimides produced from solution imidization, bulk thermal imidization results in polyimides of significantly different properties as a result of these side reactions. A partially reversible decrease in molecular weight in the early stage of imidization was observed as a result of the depolymerization reaction. This effect has been monitored in insoluble polyimide, by both changes in their mechanical properties during imidization and by temporary appearance of the anhydride carbonyl absorption band near 1860 cm^{-1} between 100-250°C.[19-21] Evidence of this effect was later verified by measuring the molecular weight of the soluble polymer at different stages of the thermal imidization.[22] The molecular weight gradually regained at high temperature. The side reactions associated with thermal imidization can also lead to some form of crosslinking.[23] Amine- terminated model imide compounds were monitored by Raman spectroscopy while heating.[24,25] The appearance of Raman absorption at 1665 cm^{-1} (C=N) confirmed that imide-imine conversion was occurring, which was predicted by a proposed crosslink reaction mechanism[26] involving the attack of terminal amino groups to imide carbonyl groups, with the resulting formation of imine. A study by Schulze et.al,[27] however, showed that the imine bond formation is only significant when small amine-terminated species were present. The probability of imine formation decreased with the chain length. Side reactions also include isoimide formation, which thermally isomerizes to the normal imide at later stages.

c) Chemical imidization of poly (amic acid) s

The second pathway of cyclodehydration of amic acid to imide involves the use of a chemical dehydrating agent to promote ring closure reactions in temperature ranges of 20-80°C, which is effective for either soluble or insoluble polyimides.[28,29] Commonly used reagents include acid anhydrides in the presence of tertiary amines. Among the dehydrating agents used were acetic anhydride, propionic anhydride, n-butyric anhydride, benzoic anhydride, as well as others. The amine catalysts used include pyridine, methylpyridine, lutidine, N-methylmorpholine, trialkylamines and others.

The outcome of the reaction can be very different depending on the type of dehydrating agent used, the monomer components of poly (amic acid)s, and the reaction temperature. For example, in the presence of trialkylamines with high pKa (>10.65), high molecular weight polyimides were obtained. On the other hand, the use of a less basic tertiary amine resulted in the formation of polyimides with lower molecular weight. Different results, however, were obtained for heteroaromatic amines. Despite their lower basicity, high molecular weight polymers were formed when pyridine, 2-methylpyridine and isoquinoline ($5.2 < pKa < 5.7$) were used as catalysts.[28] The use of acetyl chloride as a dehydrating agent afforded isoimides.[30] The use of N,N-dicyclohexylcarbodiimde (DCC) also resulted in essentially quantitative conversion of amic acid to isoimides.[31] On the other hand, a mixture of imide and isoimide was formed when pyridine was used as the catalyst.[32] However, when pyridine was replaced with triethylamine, isoimide formation was practically eliminated, which also resulted in a significantly faster reaction rate. In examining the conversion of benzophenone tetracarboxylic dianhydride/9,9- fluorenedianiline based poly(amic acid) to the corresponding soluble polyimide, it was found that the cyclizing agent is most effective when employed in 4-9 moles per repeat unit of the poly(amic acid). Increasing the temperature from 20°C to 100°C decreased the reaction time from 15 h to 2 h to achieve complete imidization.[33]

A kinetic study of chemical imidization process has resulted the mechanism shown in **Scheme 1.4**.[14, 34] A mixed anhydride intermediate is formed by the reaction of the amic acid linkage with acetic anhydride, which is promoted by the presence of a base. The mixed anhydride can further tautomerize from the amide to the iminol form. The amide tautomer cyclizes to the imide (pathway A), the thermodynamically favored product, whereas the iminol tautomer yields the kinetically favored isoimide form (pathway B). Although isoimides are known to thermally isomerize to imides (pathway C), in this case, isomerization occurs *via* the back reaction. This back reaction is apparently initiated by the nucleophilic attack of the acetate ion on the isoimide.[35] Such behavior is consistent with the fact that amines, such as triethylamine, promote acetate formation, and thus increase the back reaction that results in exclusive imide formation.



Scheme 1.4: Mechanism involved in chemical dehydration of amic acid.[14,34]

In contrast to thermal imidization, the chemical imidization of poly (amic acid)s occurs without the depolymerization reaction, and thus the molecular weight of the polymer remains constant.[36] However, chemical imidization is less attractive for commercial applications because of the expense and process complexity.

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

Polyimides resulting from solid state thermal imidization often demonstrate insolubility, infusibility and thus poor processability.[23] To overcome these drawbacks, high temperature solution imidization has been successfully utilized.[9,37,38] Cyclodehydration is conducted by heating a poly(amic acid) solution in a high boiling solvent at temperatures of 160-200°C, in the presence of an azeotropic agent. Compared with bulk thermal imidization, the lower process temperatures and greater mobility in solution ensured the avoidance of degradation and side reactions.

Studies[9,39] were conducted investigating the kinetics and mechanisms of the solution imidization process. Second order kinetics were determined by monitoring amic acid concentrations using non-aqueous titration and an acid-catalyzed imidization mechanism was suggested. It was clearly demonstrated by 2D-^{1}H NMR and intrinsic viscosity measurements that the poly(amic acid) chain cleaved to form anhydride and amine end groups at the initial stage of the reaction. As the reaction proceeded, the end groups recombined or the chains "healed" to form polyimides of higher molecular weight.

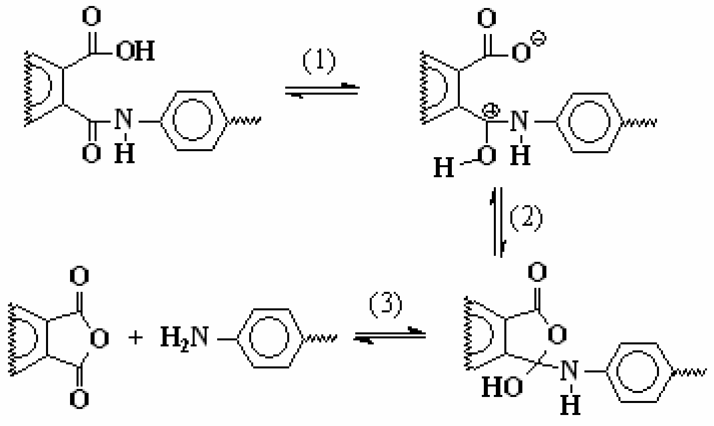
1.2.1.2 One-step high temperature solution polycondensation of polyimides

Soluble polyimides can also be prepared *via* a one-step high temperature solution polycondensation of tetracarboxylic dianhydrides and diamines. In this process, the dianhydride and diamine monomers are heated in a high boiling solvent, or a mixture of solvents, at temperature in excess of 140°C, which permits the imidization reaction to proceed rapidly. Commonly used solvents are dipolar aprotic amide solvents, nitrobenzene, benzonitrile, α-chloronaphthalene, *o*-dichlorobenzene, trichlorobenzenes, and phenolic solvents such as *m*-cresol and chlorophenols. Toluene, *o*-dichlorobenzene, 1-cyclohexyl-2-pyrrolidinone (CHP) are often used as cosolvents to remove the water resulting from condensation *via* azeotroping.[40-43] Unlike the methods described earlier, the preparation of a high molecular weight poly(amic acid) is not required for this procedure. Imidization can still proceed *via* an amic acid intermediate. However, the presence of the amic acid group is relatively small during polymerization because it is short-lived at high temperatures and either rapidly imidizes or converts to amine and anhydride. The kinetic profile consists of second-order amic acid formation and first- or second-order imide formation with amic acid formation as the rate-limiting step.[44,45] Under such conditions, steady-state approximation can be applied to the amic acid formation and the entire process can be expected to follow second-order kinetics. However, this predicted behavior is observed only at low conversions (< 30%) and is likely to be complicated by increased molecular weight at higher conversions. In much of the literature, the reaction was shown to be catalyzed by acid[17,46] Kreuz et al.,[47] however, observed that thermal imidization of poly (amic acid)s could be catalyzed by tertiary amines. High temperature solution polymerization in *m*-cresol could be achieved in the presence of high boiling tertiary amines, e.g., using quinoline as the catalyst. Dialkylaminopyridines and other tertiary amines were effective catalysts in neutral solvent such as o-dichlorobenzene.[48-50] The rate of imidization achieved *via* one-step high temperature solution synthesis was essentially complete, or 100%. No “defect sites,” of either amic acid or isoimide type, were detected in the resulting polymers, which can likely account for the differences in the physical properties observed between polyimides produced by solution synthesis and those obtained by the conventional two-step technique.[40,51] Another advantage of the high temperature solution method is that it allows high molecular weight polyimides to be prepared from monomers with sterically or electronically-hindered groups that would otherwise be hard to successfully polymerize *via* the two-step route. Polyimides whose Tm is ≤ 300°C or whose Tg is ≤ 250°C can be prepared by one-step melt polycondensation using the extrusion molding method.[52]

1.2.1.3 Other synthetic routes to polyimides

1.2.1.3.1 Polyimides *via* derivatized poly (amic acid) precursors

As discussed in Section 1.2.1.1 solutions of poly (amic acid)s are susceptible to hydrolytic degradation. This process breaks down the molecular weight of the amic acid and resulting polyimide.[53] It is believed that hydrolysis occurs through the acid-catalyzed formation of an anhydride, as shown in **Scheme 1.5**[14] rather than through direct hydrolysis of the amide linkage. To prevent this, efforts have been made to derivatize the amic acid to exclude the proton transfer from the acid group.



Scheme 1.5: Postulated mechanism for amic acid back reaction to anhydride and amine.

The simplest way to eliminate the proton transfer step is to neutralize the acid group with a base, such as a tertiary or a secondary amine, to form a polymeric salt.[47] However the viscosity of the solution is very high due to the presence of ionic polymer chains. Alternatively, a more complex approach involves converting the acid group into either an amide or ester moiety. The *ortho*-carboxylic group in poly (amic acid)s can be chemically modified to either an ester or an amide moiety. The ester and amide derivatives of poly(amic acid)s are stable, unable to form caboxylate anion which prevents the creation of degradation intermediate (reaction 1 in **Scheme 1.5**). Poly(amic ester)s can be isolated by precipitation without degradation and can be stored for an indefinite period at ambient temperatures. Such stability is highly desirable for some applications, such as microelectronics. In the preparation of photosensitive polyimides, the photocurable functionality is usually incorporated through derivatizing the poly(amic acid) to poly(amic ester).

The preparation of derivatized poly(amic acid)s can be achieved by one of two general pathways: 1) Formation of the poly(amic acid) followed by derivatization of the *ortho*-carboxylic acid groups along the polymer backbone; and 2) Derivatization of the monomer and subsequent activation to allow the monomer to enter a polymer forming reaction to yield the desired polymer. Conversion of esters of poly(amic acid) to polyimides readily proceeds thermally but at a slower rate and generally requires a temperature significantly higher than 200°C. The increased imidization temperature regime offers a wider processing window.

1.2.1.3.2 Polyimides *via* polyisoimide precursors

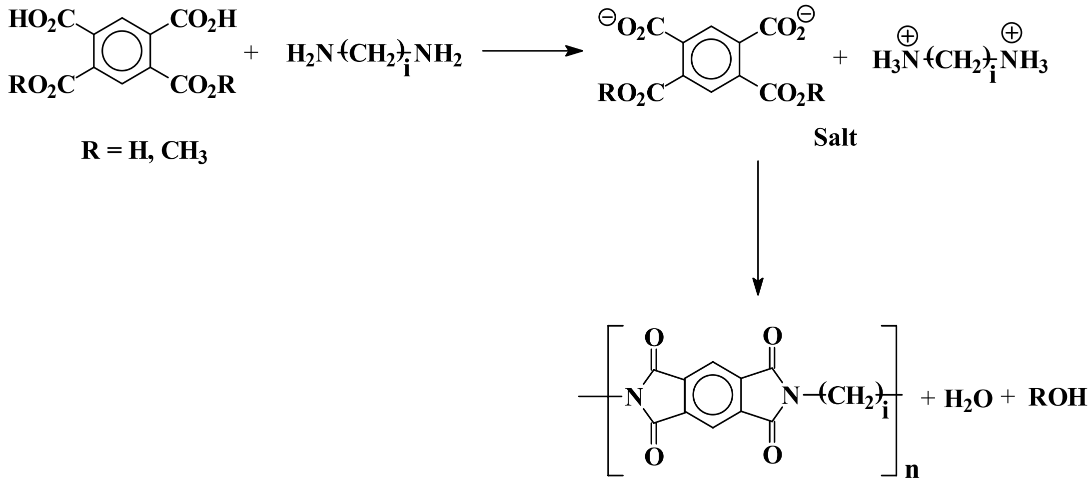
In general, polyisoimides are significantly more soluble and possess lower melt viscosities and lower glass transition temperatures than the corresponding polyimides, mainly because of their lower symmetry and structural irregularity.[54] These features make it possible to prepare rigid rod-like polyimides using soluble and processable polyisoimides.[55] Polyisoimides are formed from the corresponding poly(amic acid), using a dehydrating agent, such as trifluoroacetic anhydride, in conjunction with triethylamine. N, N'-Dicyclohexylcarbodiimide (DCC) and acetyl chloride by themselves were reported to form polyisoimides from poly(amic acid)s in high yield.[30,31,56] A polyisoimide can easily be converted to the corresponding polyimide *via* thermal treatment at >250°C. Alternately, polyisoimides have been reacted with alcohol to produce poly(amic ester)s, which could then be thermally converted to polyimides.[57] On treatment with amines, polyisoimides likewise give poly(amic amide)s quantitatively. Poly(amic amide)s were also thermally converted to polyimides.[58]

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

Synthesizing polyimides *via* the ester-acid route involves derivatizing the anhydride to ester-acid and subsequently allowing the diamine to react, which yields the desired poly(amic acid) and polyimide. Polyimides are frequently synthesized *via* the ester-acid monomer route because this process is relatively tolerant of water in solvents and reactors.[58, 59] In the initial stage of esterification, the dianhydride is simply refluxed in an excess of alcohol. It should be noted that the rate is greatly enhanced by addition of an amine catalyst, e.g., triethylamine, which acts as an acid acceptor. Once the excess alcohol has been evaporated, the resulting diester diacid is then reacted in solution with a suitable diamine to form a poly(amic acid). A polar, aprotic solvent is needed for the similar reason as for poly(amic acid) route. Polyimide is obtained by thermal or high temperature solution imidization described earlier. Previously, it was thought that that the mechanism of amic acid formation from diester-diacid and diamine proceeds by the nucleophilic attack of ester carbonyl by amine resulting in poly(amic acid) with the elimination of alcohol. However, it was later discovered that the anhydride functional group was formed at elevated temperatures *in situ* from the *ortho* ester-acid.[60,61] The anhydride then reacts with the diamine to yield a poly(amic acid).

1.2.1.3.4 Polyimides from tetracarboxylic acids and diamines

This synthetic route for producing aliphatic-aromatic polyimides with high molecular weight involves combining aromatic tetracarboxylic acids and aliphatic diamines to form salts, similar to the synthesis of nylon *via* nylon salts. The salts are thermally imidized under high pressure at temperatures above 200°C to form polyimides (**Scheme 1.6**). It should be pointed out that the intermediate poly(amic acid)s are not detected during the polycondensation stage. Rather, it appears that the imidization and formation of poly(amic acid)s takes place at the same time. This means that the imidization rate is very fast.[62]



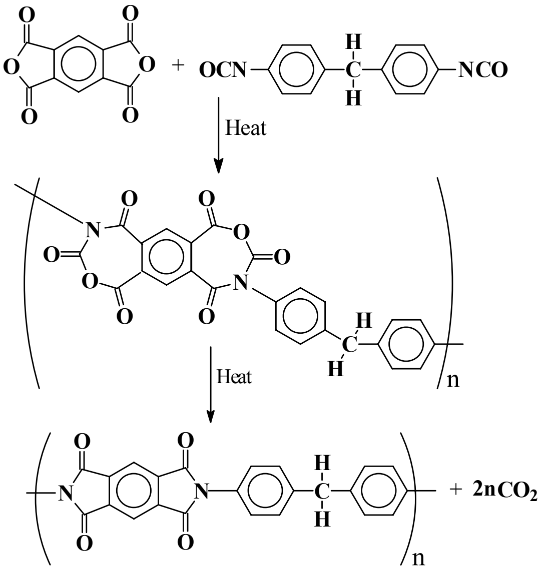
Scheme 1.6: Polyimide synthesis from tetracarboxylic acid-amine salt.

In the one-step melt polymerization of polyimides, it is advantageous to use tetracarboxylic acids because high molecular weight poly(amic acid) intermediates of very high melt viscosities are not formed during the initial heating stage. Another advantage of using tetracarboxylic acids is their stability and ease of purification. Many of them can be readily recrystallized from hot water.

1.2.1.3.5 Polyimides from dianhydrides and diisocyanates.

It has long been known that phthalic anhydride reacts with aromatic and aliphatic isocyanates to give n-aryl - and n-alkylphthalimides,[63] respectively. The reaction of aromatic diisocyanates with dianhydrides has been utilized to synthesize polyimides[64-75] Reaction of isocyanate with anhydride involves formation of a 7-membered cyclic intermediate (**Scheme1.7**).[14, 74a,b] This intermediate is believed to split off carbon dioxide when heated to form 5-memebered imide rings.

High molecular weight polyimides have been synthesized by reacting blocked isocyanates with anhydrides.[76,]

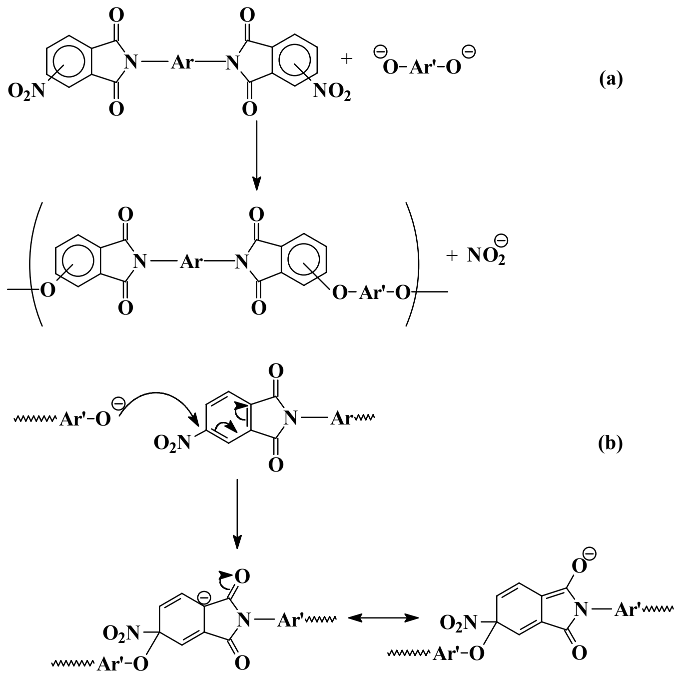


Scheme 1.7: Polyimide synthesis from dianhydrides and diisocyanates *via* an imide-anhydride seven-membered intermediate

1.2.1.3.6 Polyimides *via* nucleophilic aromatic substitution reactions

Aromatic nucleophilic substitution of bishalo- and bisnitro- substituted aromatic ketones and sulfones with bisphenolates can produce polyetherketones[77] and polyethersulfones,[78] respectively. Aromatic halo- and nitro-groups are also strongly activated by imide groups toward nucleophilic aromatic substitution[79-82] with anhydrous bisphenol salts in polar aprotic solvents. The polymer chain is generated by the formation of successive aromatic ether bonds. A general synthetic pathway is depicted in **Scheme 1.8(a)**. Halo- and nitro-substituted imides are more reactive than the corresponding sulfones and ketones. This is due to the fact that the phthalimide ring is not only activated by the additional carbonyl group, but the two carbonyl groups are locked in a coplanar conformation with the phenyl ring, providing more effective resonance. Because of the favorable carbonyl conformation, the Meisenheimer type transition state is stabilized by the effective delocalization of the negative charge as shown in **Scheme 1.8(b).**[83]

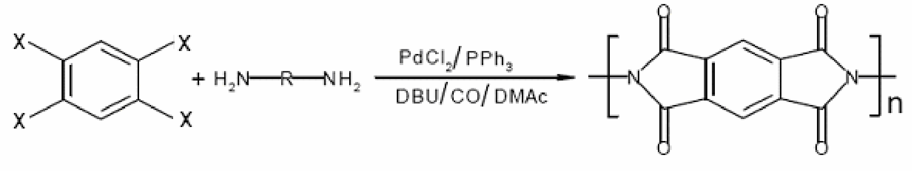
This process is commercially being used by GE, for the production of ULTEM®, a polyetherimide.



Scheme 1.8: Synthesis of polyetherimides by nucleophilic aromatic substitution (a) and delocalization of negative charge in Meisenheimer transition state in imide system (b).[83]

1.2.1.3.7 Other routes to polyimide formation

Many other polyimide preparation methods have been reported in addition to the aforementioned routes. Due to the improved stability and solubility of derivatized poly(amic acid)s, a number of techniques have been developed to form alkyl esters,[84-88] silyl esters,[89,90] and ammonium salts[91,92] of poly(amic acid)s, all of which can be thermally cyclized to form polyimides. The alkyl esters are formed from the reaction of an ester-acid chloride and the silylated esters are formed in the reaction of N,N'-bis(trialkylsilyl) diamines with various dianhydrides. The ammonium salts of PAA's can be formed by reaction with a secondary or tertiary amine. The resulting polyelectrolyte can then be dispersed in an aqueous medium and used to fabricate carbon fiber composites.[92] Polyimides can also be prepared by Diels-Alder[93-96] and Michael[97,98] cycloaddition reactions. Palladium[99-101] (**Scheme 1.9**) and nickel[102,] catalyzed carbon-carbon coupling reactions have also been reported in the literature. Thin films of polyimides for microelectronic applications have been prepared by vapor-phase polymerization of PMDA and ODA[7a,103]. Solventless synthesis of polyimids via a monomeric salt has been carried out with aromatic dianhydrides and aliphatic diamines[104]. Though the polyamic acid, intermediate of polyimide, is moisture sensitive, the reports are available for use of water as a solvent for polyimide synthesis[105 a, b] which might be possible by formation of stable polyamic acid salt, as evidenced by Imai et al.[105c]



Scheme 1.9: Synthesis of polyimides by Pd-catalyzed carbon-carbon coupling reaction.[99]

1.2.2 Structure-property relationship in aromatic polyimides

The properties of polyimides, as for polymers in general, are governed by three fundamental characteristics: chemical structure, average molecular weight and molecular weight distribution.[106] The chemical structure relates to the chemical composition of the repeat unit and the end groups. It also encompasses the composition of any branches, crosslinks or defects in the structural sequence. The average molecular weight describes the average polymer chain size. The molecular weight distribution relates to the degree of regularity in the molecular size.

Extensive literature has been published describing alterations in the structure and the size of the polyimide backbone and how these changes affect the physical and mechanical properties.[107] In this section we will briefly discuss the relationships between structure and properties such as thermal transitions and optical and dielectric properties.

1.2.2.1 Glass transition and solubility

Interchain interactions define the solubility and processability of polymers. In case of polyimides these interactions are basically charge transfer complexes formed between polyimide chains. To address the interchain interactions in polyimides, electron affinity of dianhydrides and ionization potential of diamines should be taken into consideration. Polyimide derived from dianhydride with highest electron affinity and diamine with lowest ionization potential will have strongest interchain interactions. The strongest inetrchain interaction leads to polymers with high Tg and low solubility.[6]

Different methods have been studied to reduce the chain interactions or to promote better interactions between solvent and polymeric chains.

1. Reactants with asymmetric structures (*meta* instead of *para*-catenation).[6, 108a]
2. Reactants with flexible links (O, CH_2, etc) which disrupt conjugation and increase the chain flexibility. [6, 108a]
3. Introduction of polar groups in the repeating units.[108b-c]
4. Introduction of bulky substituents.[4,6,7, 8, 108a]

The general effects of these approaches are summarized in Table 1.2

Table 1.2 Effect of chemical structure on solubility and glass transition

Structure modification	Solubility	Tg	References
***o, m* verses *p* attachment**	↗	↘	**6, 108a**
Flexible links	↗	↘	**6,108a**
Polar groups	↗	↘	**108d,e**
Bulky substituents	↗	↗	**4, 6, 7, 8, 108a**

1.2.2.2 Optical properties

As for the other polymeric materials, amorphous polyimides exhibit a good transparency. Colorless polyimides can be obtained by minimizing the electronic conjugation or formation of charge transfer complexes. Typical approaches include a) use of fluorinated diamines or dianhydrides, b) introduction of bulky “cardo” groups along the polymer backbone, etc. In addition to fluorinated and cardo polyimides, semiaromatic polyimides were synthesized from cycloaliphatic dianhydrides and aromatic diamines. Various cycloaliphatic dianhydrides and diamines have been synthesized to obtain colorless polyimides. UV cutoff of the polyimides derived from cycloaliphatic dianhydrides is around 320 nm with higher transmittance of light.

Controlling the refractive index of colorless polyimides is an important requireminet for optical waveguides. It is performed by the copolymerization of fluorinated dianhydride with a mixture of fluorinated and nonfluorinated diamine. Refractive index of the polymer increases when the molar fraction of nonfluorinated diamine increases, which leads to undesirable optical loss. Use of chlorinated diamines instead of non fluorinated diamines showed increase in refractive index without optical loss. Recently, Ueda et al[108f] have developed polyimides with high refractive index and high transparency by using sulfer containing diamines and dianhydrides.

1.2.2.3 Dielectric properties

Polyimide thin films are used as insulation between wirings in high density electronic packaging such as large scale and very large scale (LSI and VLSI) integrated circuits.[109] For application as an insulator in packaging the material must possess good mechanical properties over the processing temperature range, good adhesion, a glass transition temperature (Tg) higher than the processing temperature, a low thermal expansion coefficient and the dielectric constant as low as possible.[110] Low dielectric materials minimize crosstalks and maximize signal propogation speed in devices. Hence the development of polyimides with increasingly lower dielectric constants has been the focus of several recent investigations.[111]

Among the stratagies used to lower the dielectric constant in polyimides are:

1). Incorporating diamine and dianhydride reactants which minimize polarizabiliy,

2). Incorporating diamines and dianhydrides which impart a high degree of free volume and

3).Incorporating fluorine atoms into the molecular structure of the polyimide.[112a]

a) Polarizability

The dielectric constant of polyimides are known to decrease gradually with increasing frequency. For example, Kapton H film (25.4 μm) has a dielectric constant of approximately 3.5 at 1 kHz and 3.3 at 10 MHz.[112b] This variation in dielectric constant is attributed to the frequency dependence of the polarization mechanism which comprise the dielectric constant. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units in a polymer to orient fast enough to keep up with the oscillations of an alternating electric field. As shown in Figure 1.2, the polarizable units are electronic, atomic and dipolar.

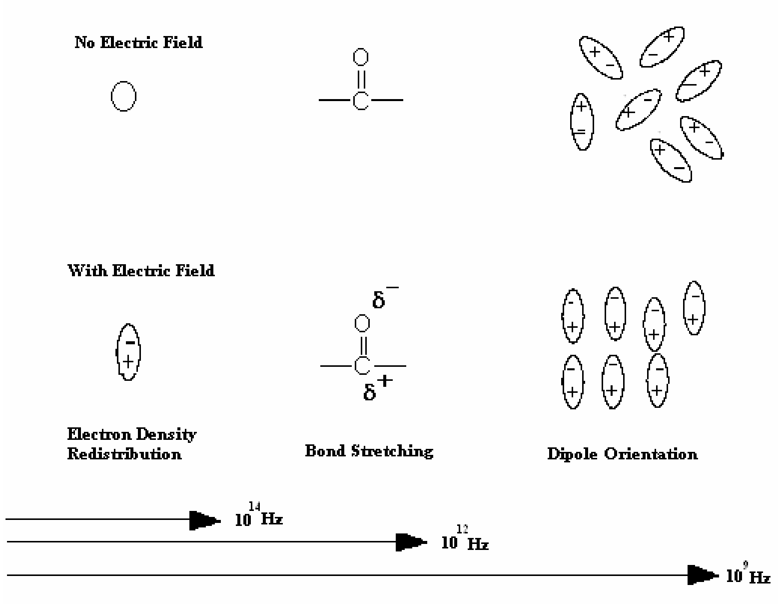


Figure 1.2 Induced atomic polarization

At optical frequencies (10^{14} Hz), only the lowest mass species, electrons are efficiently polarized. At lower frequencies, atomic polarization of heavier , more slowly moving nuclei also contribute to the dielectric constant.Atomic polarization of induced dipoles such as a carbonyl group can occur in the infrared (10^{12} Hz) or lower frequency regimes. Dipole polarization is the redistribution of charge when a group of atoms with a permanent dipole align in response to the electric field. In the solid state alignment of permanent dipoles requires considerably more time than electronic or atomic polarization, occurring at microwave (10^9 Hz) or lower frequencies.

The polarizability (α) of each species is generally additive (i.e. $\alpha = \alpha_{\text{electronic}} + \alpha_{\text{atomic}} + \alpha_{\text{dipolar}}$) and can be combined with the Clausius-Mossotti relationship to estimate the contribution of each polarization mode to the dielectric constant (ε) as shown in equation[113] (1).

$$\varepsilon = \varepsilon_{\text{electronic}} + \varepsilon_{\text{atomic}} + \varepsilon_{\text{dipolar}} \qquad \text{……….(1)}$$

At optical frequencies, where only electronic polarization occurs, the dielectric constant, ε_∞ , is related to the refrective index, η_{ref}, by Maxwell’s identity.

$$\varepsilon_\infty = (\eta_{\text{ref}})^2 \qquad \text{… ……….(2)}$$

A comparison of the ε_∞ and the dielectric constant measured at frequencies lower than optical frequency can lead to a basic understanding of the influence of molecular structure on dielectric properties in polyimides

b) Free volume

A correlation of high free volume and low dielectric constant has been reported for polyimides.[114,115] The free volume fractions can be determined by either positron lifetime spectroscopy or by group additivity methods. The introduction of free volume in a polymer decreases the number of polarizable groups per unit volume resulting in lower values of ε_{atomic} and $\varepsilon_{dipolar}$. The addition of pendent groups, flexible bridging groups, and bulky groups which limit chain packing density have all been used to enhance free volume in polyimides.[116]

c) Fluorine content

Although incorporation of fluorine into polyimides has been shown to lower dielectric constants, but nonsymmetric substitution of fluorine atom increases the average magnitude of the dielectric constant by approximately 0.05 per substituted ring.[113a] Symmetric substitution of fluorine does not increase the net dipole moment of the polymer and hence does not increase the dielectric constant. Houghman et.al[113a] have also shown that the dielectric constant decreases with symmetrical fluorine substitution by a combination of lower electronic polarizability and larger free volume.

1.2.2.4 Applications of polyimides in microelectronics

Polyimides find application as alignment layers in liquid crystal displays. Polyimide films are used as stress buffers or as protective coatings for semiconducters. Polyimide films are also used as photoresists in microlithography. Fluorinated polyimides find applications in optical wave guides since they are highly transparent and stand better for soldering temperatures and various circumstances than PMMA or polycarbonate.[113 b] Fluorinated polyimides also serve as an interlayer dielectrics in both semiconducters and thin film multichip modules. The applications of polyimides in miroelectronics are unlimited. The low dielectric constant, low residual stress, high modulus and thermal stability make them well suited for these multiple applications. A summary of literature on application of polyimides as interlayer dielectrics is presented here briefly.

a) Need for low dielectric constant material

In microelectronics as the size of the device becomes smaller the distance of the electrically interconnected lines also decreases .Below a certain distance, these lines start to influence each other, when voltage and current are applied. Inductive and capacitive effects increase. A change of electrical current in one line induces a current in the neighbouring line through a change of electrical field. Hence, inductive cross talk decreases the reliability of data transport. Equation (3)[116] shows the dependence of the signal delay on the size of the transistor.

The interconnect delay can be caculated by Equation (3)

$T = RC = 2\,\rho\,\varepsilon\,\varepsilon_0\,[\,4L^2/D^2 + L^2/T^2]$ where T is the signal delay time ………(3)

R is the resistance

C is the capacitance

ε is the dielectric constant

ε_0 is the dielectric constant of vacuum

L is the length of the conducter

T is the thickness of the conducter.

Based on Eq (3) increased signal speed can be obtained in three ways 1. changing the lay out i.e. changing the ratio of width to thickness of the metal lines. 2. by decreasing the specific resistance ρ of the interconnecting metal 3. by decreasing the dielectric constant of the insulating material (inter metal dielectric).

Presently state-of- the-art is the use of SiO_2 as insulating material (inter layer dielectric (ILD); and inter metal dielectrics (IMD).and its dielectric constant is $\varepsilon = 4$ [117a].

In addition to dielectric constant and thermal stability, many other properties are to be considered before a new material can be used as intermetal dielectric. Important once are moisture uptake, adhesion to Al, Cu, SiO_2, and other inorganic materials, planarization behavior, plasma etching behavior etc.

From early1970-to-late 1980s the polyimides were already used as intermetal dilectrics.[117b,c,d] At that time the driving factor was cost rather than low dielectric constant, but now the performance and speed, the minimum size of the device and hence the low dielectric constants of ILD and IMD are of much focus.

b) Fluorinated polyimides

It is well known that the incorporation of fluorinated substituents into polymers decreases the dielectric constant. Fluorinated dianhydride and diamine monomers reported in the literature for the preparation of polyimides for use as ILD/IMD materials are given in **Table1.3** [118-138].

Table 1.3 Fluorine containing dianhydrides and diamines for the synthesis of polyimides[118-138].

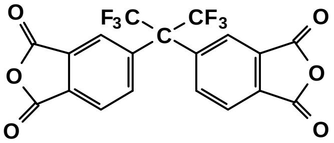
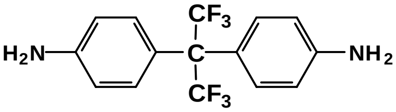
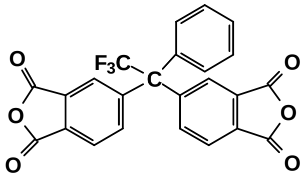
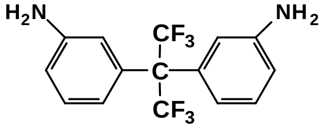
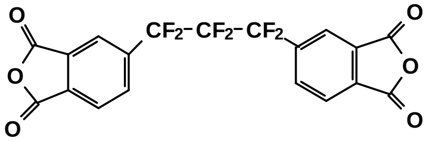
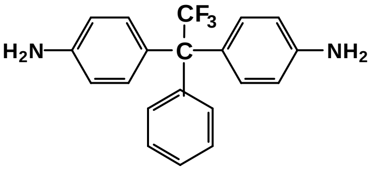
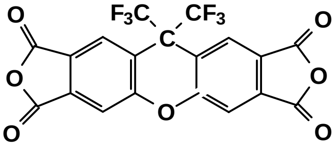
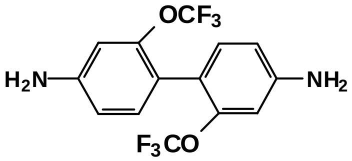
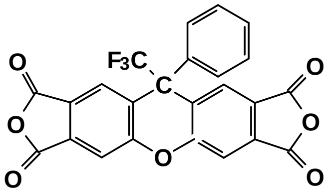
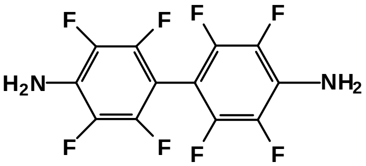
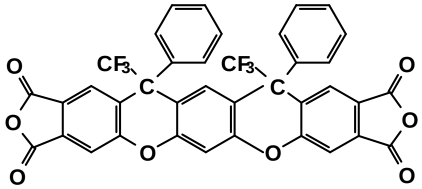
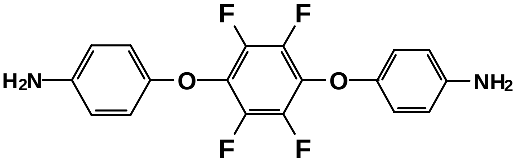
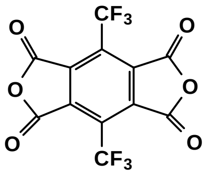
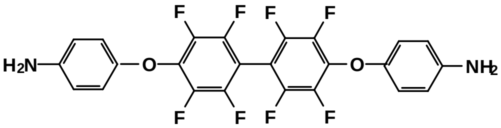
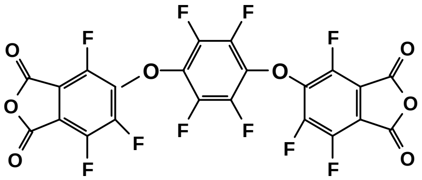
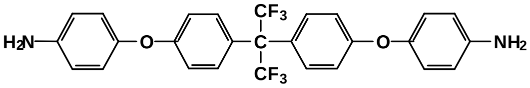
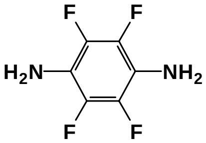
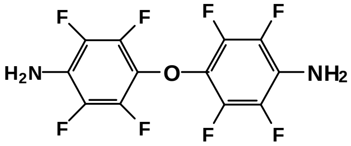
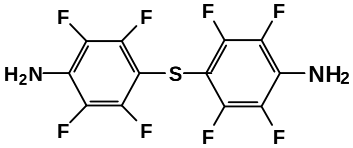
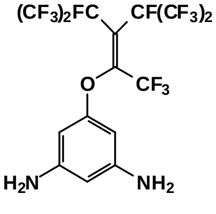
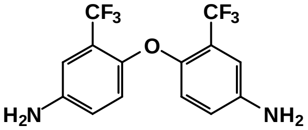
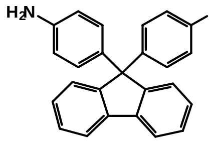
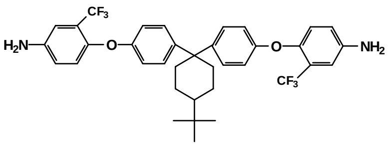
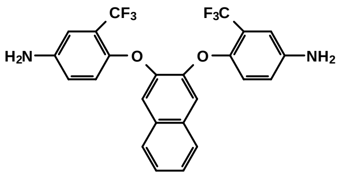
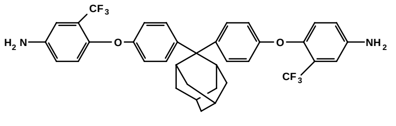
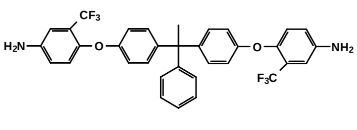
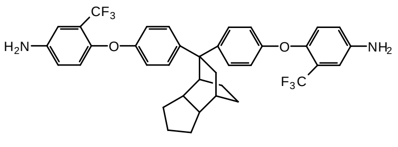
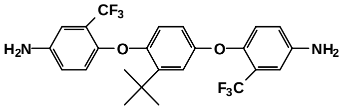
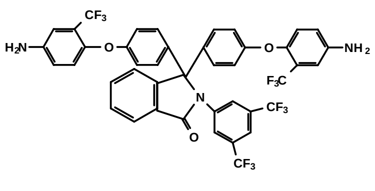
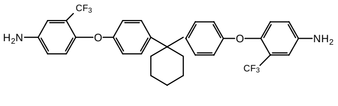
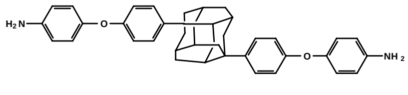
Sr.No.	Dianhydrides	Sr.No.	Diamines
1.		1.	
2.		2.	
3.		3.	
4.		4.	
5.		5.	
6.		6.	

Table1.3 Fluorine containing dianhydrides and diamines for the synthesis of polyimides[118-138] continued….

Sr.No.	Dianhydrides	Sr.No.	Diamines
7.		7.	
8.		8.	
		9.	
		10.	
		11.	
		12.	
		13.	

Presence of bulky groups and flexibilizing links with in the polymer backbone may result in polyimides which are soluble even in the fully imidized form. This is especially so when cardo structures such as 1,6 bis[4-(4 aminophenoxy)phenyl] diamentane (DAPF) are used [146]. Such polyimides have reduced sovent resistance and sometimes increased moisture uptake due to increased free volume. Diamine monomers containing bulky groups with fluorine atoms and cardo groups with flexible ether linkages that have been used for synthesis of polyimides which have potential application as ILD/IMD materials [139-146]are given in **Table1.4**

Table 1.4 Diamines monomers for the synthesis of polyimides in application as ILD/IMD materials

No.	**Diamine**	Ref.	No.	**Diamine**	Ref.
1.		139	6.		144
2.		140	7.		144
3.		141	8.		144
4.		142	9.		145
5.		143	10.	 DAPF	146

1.2.2.5 Gas separation

Gas separation using polymeric membranes was first reported by Mitchell in a study with hydrogen and carbon dioxide mixture in 1831.[147]Thomas Graham, in 1866, made next important step in understanding the permeation process. He postulated that permeation is a three step process: the solution of the gas flows onto the upstream (high-pressure) surface of the membrane, gas diffuses through the membrane and finally, gas evaporates from the downstream (low-pressure) surface of the membrane.[148] This early description of gaseous transport is considered to be the basis for today's "solution-diffusion model", which is used to explain many membrane separations.

The separation of oxygen and nitrogen from air, and hydrogen from carbon monoxide, methane or nitrogen are large consumers of energy in the chemical processing industry. In general, purified gases are more valuable than arbitrary mixtures of two or more components since pure components provide the option of formulating an optimum mixture for particular applications.

Energy-intensive compression of feed system is often needed to provide the driving force for permeation in membrane-based separations. In their simplest ideal forms, membranes appear to act as molecular scale filters that take a mixture of two gases, A and B, into the feed port of the module and produce a pure permeate containing pure A and a nonpermeate containing pure B (**Figure 1.3**). Real membranes can approach the simplicity and separation efficiency of such idealized devices, but generally complex recycling of some of the permeate or nonpermeate stream may be needed because perfect selection of A and B molecules cannot be achieved in a single pass.

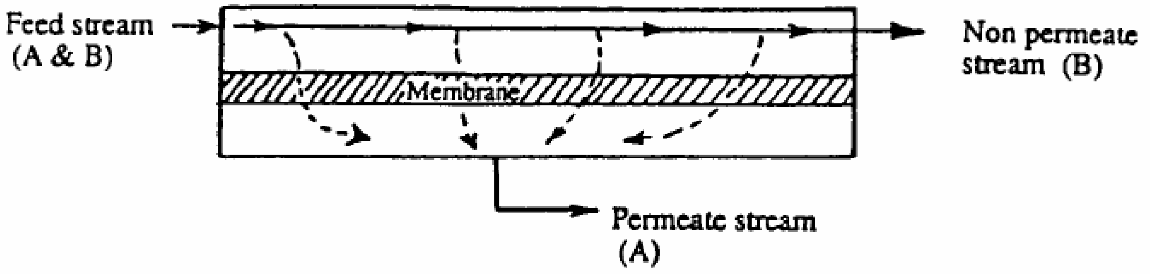


Figure 1.3: Generalized representation of an ideal membrane separation process.

Solution-diffusion membranes rely on the thermally agitated motion of chain segments comprising the polymer matrix to generate transient penetrant-scale gaps that allows diffusion from upstream to the downstream face of the membrane. By varying the chemical nature of the polymer one can change the size distribution of the randomly occurring gaps to retard the movement of one species while allowing the movement of the other. If one could perfectly control this distribution, a true molecular sieving process would occur and infinite selectivity would be achieved. The essential impossibility of such a situation is suggested by kinetic diameter data of various important penetrants (**Table 1.5**). The ability to regulate the distribution of transient-gap sizes in solution diffusion membrane is achieved by the use of molecules with highly hindered segmental motions and packing. Typically these materials are amorphous and are referred to as glassy polymers.

Table 1.5 Minimum kinetic diameter of various penetrants.[149]

Penetrant	He	H_2	NO	CO_2	O_2	N_2	CO	CH_4	C_2H_4	Xe	C_3H_8
Kinetic diameter (Å)	2.6	2.89	3.17	3.3	3.46	3.64	3.76	3.8	3.9	3.96	4.3

Permeation is a function of two parameters: the solubility constant, S, and the diffusion coefficient, D. The solubility constant is a thermodynamic term based on specific polymer-penetrant interactions and condensability of the penetrant. The diffusion coefficient is a kinetic term referring to the movement of gas molecules inside the polymer matrix.[150] The diffusion coefficient determines "how frequently, on a time-averaged basis, a hole of sufficient volume appears next to the gas penetrant, enabling it to jump further through the membrane".[151]

The permeability coefficient of penetrant molecule A (P_A) can be expressed in terms of the mean diffusion coefficient (D_A) and the solubility coefficient (S_A)[152, 153]

$$P_A = D_A \times S_A$$

The permeability coefficient of penetrant molecule A (P_A) through a dense polymer membrane, having an effective membrane thickness of *l*, can be derived from the steady state flux, F_A

$$P_A = F_A \times {}^{l}\!/\!_{\Delta\ p}$$

where Δ_P is the partial pressure difference between the upstream and downstream pressure of penetrant molecules A across the membrane. Several methods have been devised to determine the permeability coefficient of gases through membranes and, thus, a number of different units have been used to express the permeability coefficient. The permeability coefficient is expressed in units of Barrers, where 1 Barrer is $10^{-10} \bullet [\ \mathrm{cm}^3\ (\mathrm{STP}) \bullet \mathrm{cm/cm}^2 \bullet \mathrm{s} \bullet \mathrm{cmHg}\ ]$.

The selectivity, $\alpha(A/B)$ or the so-called separation factor, of a dense polymer membrane between two penetrant gas molecules A and B is the ratio of the permeability coefficients of both penetrant gases. When the downstream pressure is negligible relative to the upstream pressure and when strong interactions between the polymer and both penetrant molecules are not observed, $\alpha(A/B)$ is almost equal to the "ideal" separation factor, $\alpha(A/B)^*$. This ideal separation factor can be decomposed into contributions of solubility selectivities (S_A/S_B) and diffusivity selectivities (D_A/D_B). Therefore,

$$\alpha = \frac{PA}{PB} = \left(\frac{DA}{DB}\right)\left(\frac{SA}{SB}\right)$$

The solubility selectivity (S_A/S_B) is determined primarily by the difference in inherent condensability between both penetrant molecules A and B and by their interactions with the membrane boundary. The diffusivity selectivity (D_A/D_B) is determined by the ability of the polymer matrix to function as size and shape selective media through segmental mobility and intersegmental packing factors. In the absence of strong polymer-penetrant interactions, the diffusivity selectivity tends to be the major factor in the separation process. For commonly available polymers, it has been found that the permeability coefficient and the selectivity are interdependent. Higher gas permeability coefficients are usually accompanied by lower selectivities, and vice versa.

Usually the gas transport properties behavior is analyzed and correlated to the polymer properties such as glass transition temperature (T_g), *d*-spacing and fractional free volume (FFV). The d-spacing, the average distance between adjacent segmental backbones is determined by X-ray diffraction analysis and can be used as an index of "openness" of polymer matrix. The FFV takes into account the specific and occupied volumes and generally seems to give better representation of the "non-occupied space" in the polymer available for transport than does the *d*-spacing.

1.2.2.5.1 Aromatic polyimides as gas separation membranes.

The structure / permeability relationship of polyimides have been investigated extensively since the pioneering work of Hoehn[154,155]because some of these polymers exhibit a markedly higher gas selectivity as well as a higher permeability than many other glassy polymers. Koros and co-workers[156,157] were among the first to study systematically the effects of subtle modifications in the structures of aromatic polyimides on their gas permeability and selectivity. They attributed the higher permeability and selectivity of the 6FDA polyimides when compared to PMDA polyimides, to the presence of the bulky –$C(CF_3)_2$– groups in their dianhydride moiety, such groups hinder intersegmental mobility, and thereby stiffen the backbone chains and also inhibit intersegmental chain packing .

The substitution of increasingly bulkier diamine moieties in polyimides with the same dianhydride moiety has the effect of enhancing the permeability and decreasing the selectivity[156-161].

Representative examples of polyimides used for gas separation are given in **Table 1.6**.

Table 1.6 Polyimides studied for gas separation

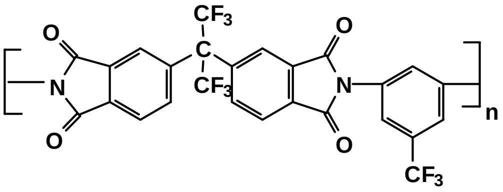
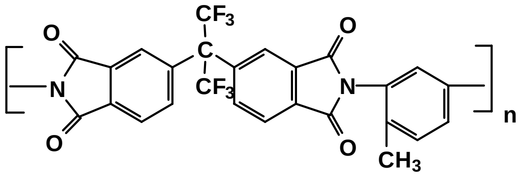
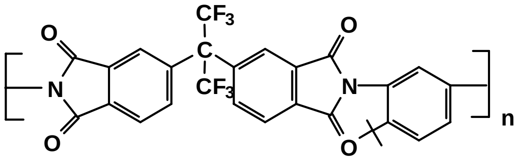
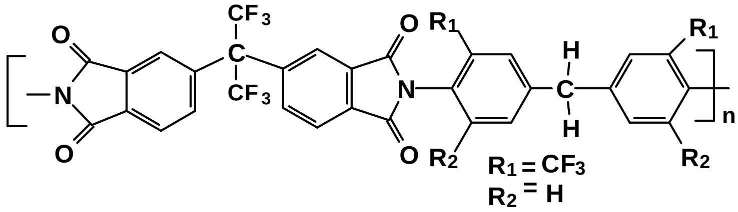
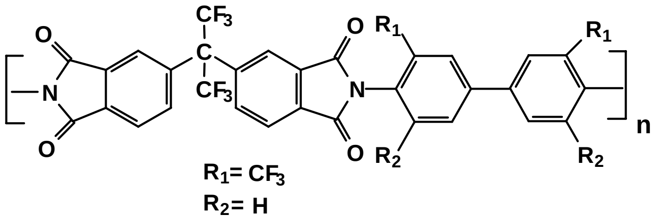
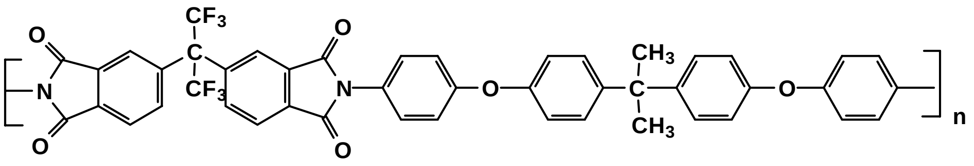
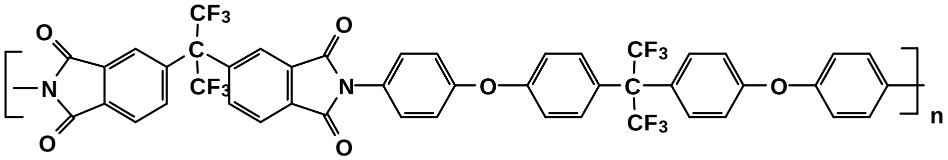
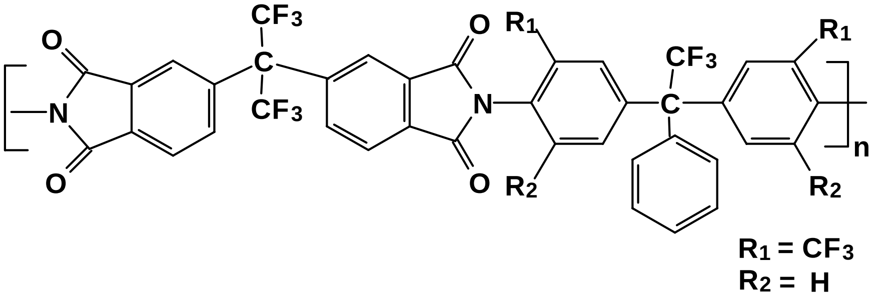
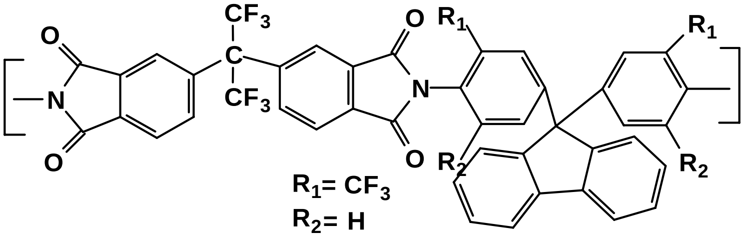
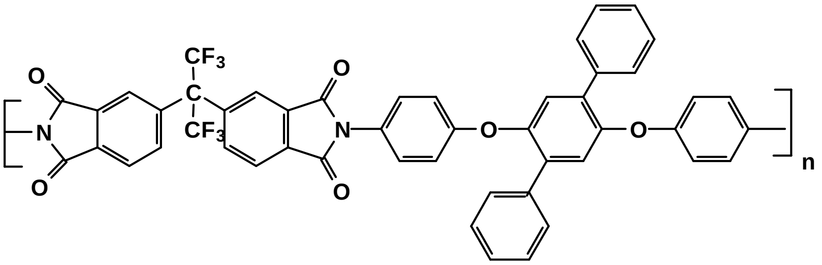
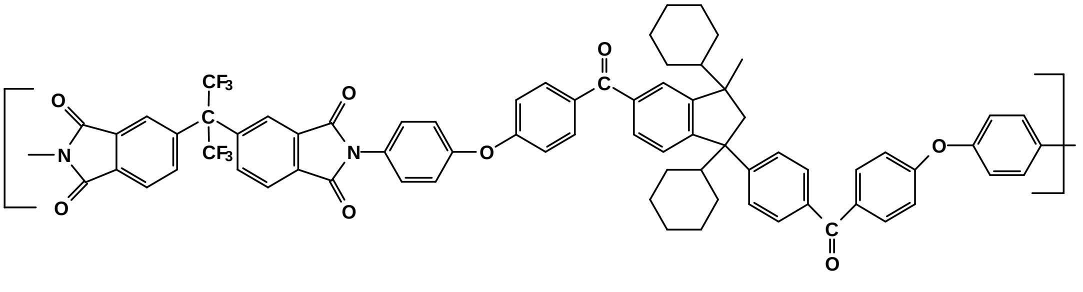
No.	Polyimides	Ref
1.		162
2.		162
3.		164
4.		163
5.		163
6.		165

Table 1.6 Polyimides studied for gas separation…… continued.

No.	Polyimides	Ref
7.		165
8.	 $R_1 = CF_3$ $R_2 = H$	163
9.	 $R_1 = CF_3$ $R_2 = H$	163
11.		166
13.		167

1.3 Polyamides

The first synthetic aromatic polyamide, polybenzamide was obtained by Harbordt in 1862 [168]. In 1974 aliphatic and aromatic polyamides were given separate generic nomenclature by Federal Trade Commission. Polyamides are generally classified as aliphatic polyamides or ‘Nylons’ and aromatic polyamides or ‘Aramids’. Aromatic polyamides are among the oldest members of the class of thermally stable polymers and the first commercially produced aromatic polyamide was poly (m-phenyleneisophthalamide) (Nomex, Du pont)[169]. Some years later, development of method of the preparation of poly(p-phenyleneterephthalamide) led to the commercialization of the *para* product Kevlar (Du Pont) in the early seventies.[170,171]

A number of excellent review articles on aramids have been published[172]. However, intractability of aromatic polyamides limits their applications [173]. Structural modifications such as the introduction of (1) bulky pendant substituent [174-176] (2) non coplanar moieties[177] and (3) flexible alkyl spacers have been reported to enhance the solubility and to lower the transition temperatures.

1.3.1 Synthesis of polyamides

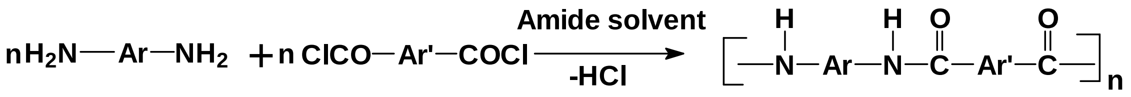
Aromatic polyamides have been prepared by several methods.[172c]

1.3.1.1 Low temperature polycondensation of diamines and diacid chlorides

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

1.3.1.1.1 Solution polycondensation of diamine and diacid chloride

Solution polycondensation involves a diamine and a diacid chloride reacting in an amide solvent such as NMP, HMPA, DMAc[178,179] or tetramethylurea (TMU) (**Scheme 1.10**).



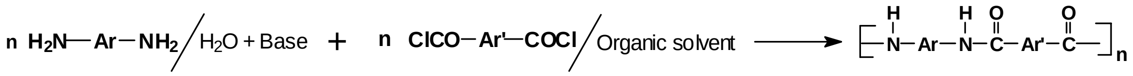
$$n\,H_2N{-}Ar{-}NH_2 + n\,ClCO{-}Ar'{-}COCl \xrightarrow[\text{-HCl}]{\text{Amide solvent}} \left[{-}\overset{H}{\overset{|}{N}}{-}Ar{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}Ar'{-}\overset{O}{\overset{\|}{C}}{-}\right]_n$$

Scheme 1.10: Solution polycondensation of a diamine and a diacid chloride.

The amide solvent serves also as an acid acceptor for the hydrogen chloride produced in the reaction. Other polar aprotic solvents such as dimethylformamide and dimethylsulfoxide cannot be used because they react significantly with acid chlorides. The solvent should allow maximum solubility (swellability) of the polymer formed at the early stage of polycondensation, and the solvation properties of amide solvents can usually be increased by the addition of salts such as LiCl or $CaCl_2$.[180, 181]

1.3.1.1.2 Interfacial polycondensation of diamine and diacid chloride

As described above, in low temperature solution methods, the monomers are dissolved and reacted in a single solvent phase. Monomers can also be brought to react at the interface of two phases. The so-called interfacial polycondensation method is an adaptation of the well known Schotten-Baumann reaction. In this method, two fast reacting intermediates are dissolved in a pair of immiscible liquids, one of which is preferably water. The water phase generally contains the diamine and usually an inorganic base to neutralize the byproduct acid. The other phase contains the acid chloride in an organic solvent such as dichloromethane, toluene or hexane (**Scheme 1.11**).

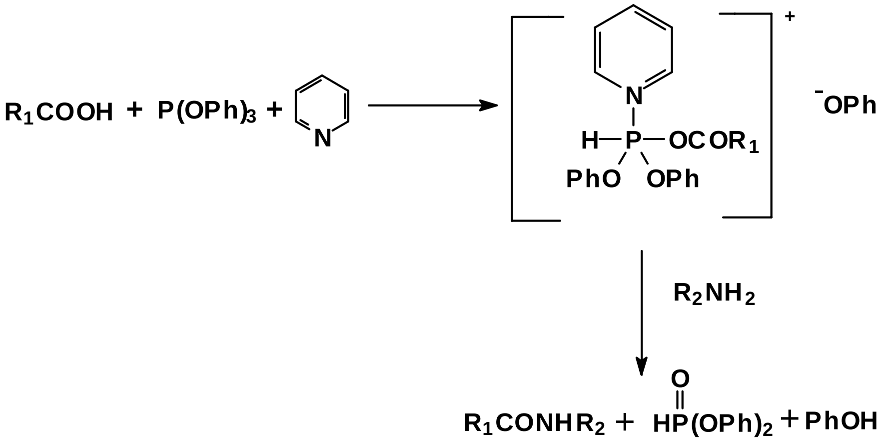


Scheme 1.11: Interfacial polycondensation of diamine and diacid chloride.

The two-phase system is stirred vigorously to obtain high molecular weight polymers. The difference between conventional step polymerization and interfacial polymerization is that in the interfacial polymerization the monomer diffusing to the interface reacts only with the end of the polymer chain resulting in high molecular weight polymer. The key factors that influence this type of polycondensation have been studied in detail by Morgan.[182] Since the temperatures needed are low, the side reactions are minimized and also the polymers, which are unstable at high temperatures, can be synthesized.

1.3.1.2 High temperature solution polycondensation of dicarboxylic acids and diamines

In the beginning of 1970's two Japanese groups Ogata and co-workers[183,184] and Yamazaki and Higashi[185,186] published a series of papers on the successful use of phosphorus compounds as condensing agent for the direct polycondensation of dicarboxylic acids and diamines to form polyamides. This reaction involves the formation of a complex of the acid with triphenylphosphite in NMP and pyridine, which further reacts with diamine to give the product (**Scheme 1.12**).



Scheme 1.12 Condensation reaction involving acid and amine to form amide in the presence of triphenylphosphite.

$CaCl_2$ and LiCl were used along with NMP to improve the molecular weight of polymers. The role of $CaCl_2$ and LiCl is quite complicated. They can form complexes with pyridine which are more soluble than the salts alone, and NMP with a higher content of metal salt can solubilize polyamide formed in the reaction medium more effectively, leading to high molecular weight products. Several key factors can considerably influence the molecular weight of the final polymer such as:

a) Concentration of monomers

b) Ratio of triphenylphosphite to monomer

c) Reaction temperature and time

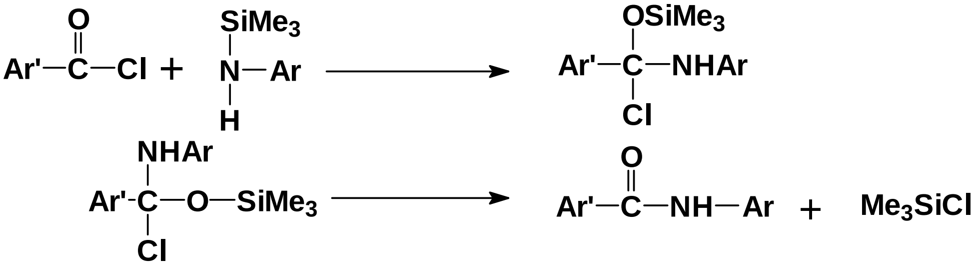
d) Concentration of LiCl or $CaCl_2$

e) Solvent and amount of pyridine relative to the metal salt.

Eventually, Krigbaum etal.[186 b,c] optimized the conditiones successfully for polyphenyleneterephthalamide with $\eta_{inh} = 6.2$ dl/g (9).

1.3.1.3 Polycondensation of N-silylated diamines and diacid chlorides

While most of the efforts in the synthesis of high molecular weight polyamides have been oriented towards the activation of the diacids, there are some reports on the activation of diamine component by reacting it with trimethylsilyl chloride. Indeed, high molecular weight polyamides have been synthesized by low temperature polycondensation of an N-silylated aromatic diamine with aromatic diacid chloride.[187-189] The following nucleophilic addition-elimination two-step mechanism has been proposed for the acyl substitution of an acid chloride with an N-silylated amine (**Scheme 1.13**).



Scheme 1.13: Condensation reaction of N-silylated amine and acid chloride.

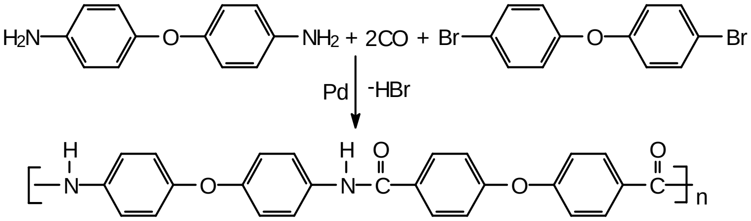
Lozano et.al[190] have reported the formation of silylated diamines *in situ* by adding trimethylchlorosilane to the diamine solution that, on addition of diacid chloride gives polyamides. This method is especially useful for the preparation of polyamides from aromatic diamines having low reactivity.

1.3.1.4 Polycondensation of diisocyanates and dicarboxylic acids

Another promising route for the preparation of aromatic-aliphatic copolyamides has been developed by Simioneseu et al[191] and Onder et al[192,193] from a combination of aromatic diisocyanates and dicarboxylic acids. This route leads to the direct formation of polyamides with the elimination of CO_2 without the use of any condensing agents. Several polyamides and copolyamides have been prepared by this method.[194-195] A commercial scale preparation of aromatic polyamides from 1,3-phenylene diisocyanate and isophthalic acid in the presence of a catalyst has been reported.[196] Polyamides have also been prepared by the reaction of aromatic diisocyanates with aromatic hydrocarbons in the presence of Friedel-Crafts catalyst.[68,197]

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

Polyamides can also be synthesized by palladium-catalyzed carbonylative coupling of diamines and dihalides (**Scheme 1.14**).[198-203]



Scheme 1.14: Transition metal catalyzed carbonylative coupling of aromatic diamines and dihalides.

1.3.2 Effect of structure on properties of polyamides.

1.3.2.1 Solubility and thermalstability

The high thermal stability and excellent mechanical properties of aromatic polyamids have been recognized for a long time. Attempts made to improve solubility of polyamides have been numerous and a number of srategies have been adapted such as[172c] (1) introduction of flexible bonds in the backbone (2) introduction of bulky pendent group in the diamine or diacid monomer and (3) use of noncoplanar structures and (4) the use of heterocyclic monomers.

1.3.2.1.1 Halogen substituents

The solubility of polyamide increased when the number of halogen substituents is increased. The effect of different halogen substituents on polymer properties is well documented[172].The incorporation of halogen substituents along the polymer backbone leades to flame resistant polymers. The thermostability of halogen substituted polyamides decreases in the order H> F> Cl>Br. This order corresponds to the bond dissociation energy. Increase of halogen content generally leads to a decrease in decomposition temperature.

Fluorinated polyamides have shown outstanding mechanical properties, film forming properties, improved melt flow, increased solubility, flame resistance and chemical resistance. Low reactivity of tetrafluoro isophthaloyl chloride, and tetrafluoro terephthaloyl chloride was attributed to steric hindrance of the adjacent fluorene atoms[204]. The reaction of these halogenated acid chloides can be carried out with N-silylated diamines as they are far more reactive than the corresponding unsubstituted diamines.[205, 206].

1.3.2.1.2 Other substituents

Chaudhari et al.[207a] in their study of thermostability of aromatic polyamides have introduced various polar groups onto the polymer e.g. -NO_2, -COOH, -OH, -SO_3H. They reported that the thermostability decreased in the following order -NO2 > -COOH, and OH >SO_3H. Use of isophthalic acid containing –NHCOPh, and –OCOPh groups and use of *m*-phenylene diamine containing –CONHPh group **(Figure 1.4)** is also reported[207b,c,d] to impart solubility in highly polar solvents, and some are soluble or swellable in m-cresol

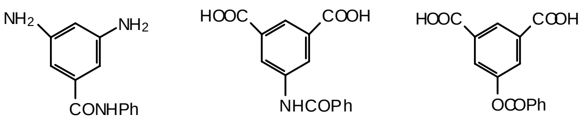


Figure 1.4: Substituted monomers for polyamide synthesis

1.3.2.2 Pendant alkyl/aryl group containing polyamides.

Pendant groups were introduced in the main chain [206-209], as an effective means of enhancing solubility with retention of good thermal stability.[210-215] Cimecioglu and weiss[216] prepared polyisophthlamides using 5-benzamidoisophthalic acid by direct polyamidation, leading to soluble polymers without sacrificing thermal properties. Polyamides based on substituted bulky monomers containing 3,3-substituted binaphthyl and biphenyl groups have also been reported. [217]

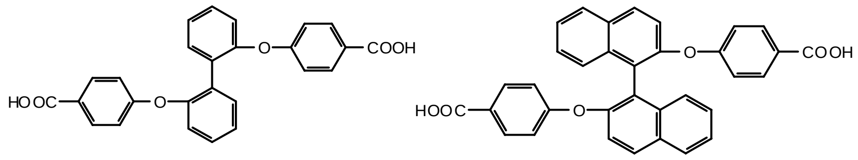


Figure 1.5 Monomers containing benzene rings for polyamide synthesis

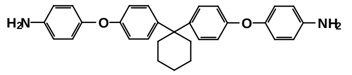
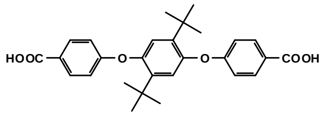
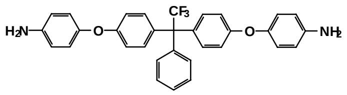
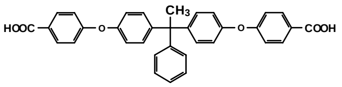
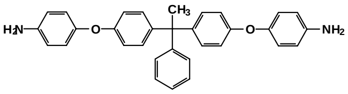
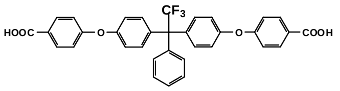
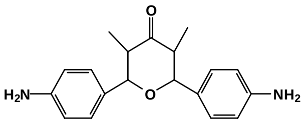
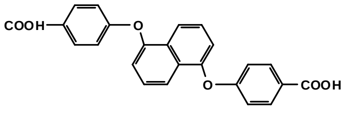
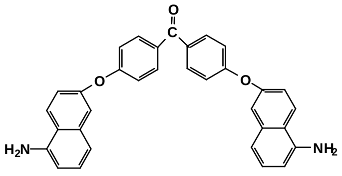
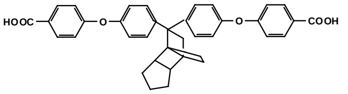
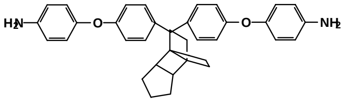
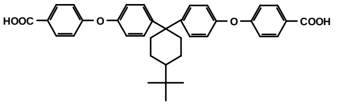
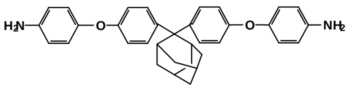
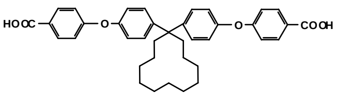
As shown in **Figure 1.5** biphenyl-2,2’-diyl and 1,1’-binaphthyl-2,2-diyl containing aramids can be synthesized by reacting diacid chlorides of 2,2’-bis(*p*-carboxy phenoxy)biphenyl and 2,2’-bis(*p*-carboxy phenoxy)-1,1’-binaphthyl with aromatic diamines by low-temperature solution polymerization [218].They had excellent solubility and high Tg.

Phenylated heterocyclic diamine such as 2,5-bis(4-aminophenyl)-3,4-diphenylhiophene etc. and diacid chlorides have been used to synthesize polyamides with high solubility retaining thermal stabiliy [219-245].

1.3.2.3 Polyamides containing flexible linkages.

Introduction of polar and flexible linkages into the polymer backbone is one of the approaches towards improving solubility without appreciable loss of thermal stability. Aromatic polyamides containing sulfide, sulfone, and ketone groups have been synthesized. Direct polycondensation of bis (*p*-phenylthio) dibenzoic acid, 4,4’-sulphonyl bis(*p*-phenylthio) dibenzoic acid and 4,4’-[carbonyl bis (*p*-phenylthio) dibenzoic acid with various aromatic diamines has been reported by Joseph et al [230].Now a days one of the most common approaches to increase solubility retaining the thermal properties is the introduction of flexible bonds in the polymer backbone alongwith the incorporation of bulky pendent groups along the main chain. The representative examples of this kind of monomers (diamines/dicarboxylic acids) having flexible ether linkages with bulky groups for the synthesis of polyamides are given in **Table 1.7.**

Table 1.7 Diamines/Dicarboxylic acids containing flexible ether linkages with bulky groups for the synthesis of polyamides

No.	Diamines	Ref.	No.	Dicarboxylic acids	Ref.
1.		231	1.		240
2.		232	2.		232
3.		233	3.		233
4.		234	4.		241
6.		236	5.		242
7.		238	6.		243
8.		238	7.		244

1.3.3 Applications of polyamides

Aromatic polyamides are resistant to alkali and have good hydrolytic stability as compared to nylons and polyesters, these properties make aromatic polyamides suitable to be used as filter bags for hot stake gases, press cloths for industrial presses and sewing threads for high speed sewing [245].

Aramids have good permselective properties and are used as hollow-fiber permeation membranes to purify sea and brackish water or for removal of numerous types of salts from water[246]. Polyamides are also used as high performance gas separation membranes [247].

'Nomex' fibers are used as tyre cord in car cases and as belts in biased belted and radial belted tyres.They are also used as cables, parachutes, body armour in rigid re-enforced plastics. Aromatic polyamides exhibit high volume resistivity and high dielectric strength. At elevated temperatures they retain these properties and possess high potential to be used as high temperature dielectrics particularly in motors and transformers[247]. Aromatic polyamide fibers possess flame retardence hence they are used as industrial protective clothings ,welder clothing and protective shields.

Polyamides containing pendant alkyl groups [248a,b,c] have been used as liquid crystal alignment layers. Polyamides have also found application as light emmiting polymers[248 d]. Hsiao et al[248 d] have studied polyamide films based on 4,4'-dicarboxy-4''-N-carbazoyltriphenyl amine and different aromatic diamines. These films exhibited multicolor electrochromic behaviour from original pale yellow to green and then to blue colors when various different potentials were applied.

1.4 Polyesters

The reaction of aromatic dicarboxylic acids and diphenols was first noted by Conix [249] in 1957. The literature on polyarylates based on diphenols is extensive. Before the production of first commercial aromatic polyester, U-polymer (a polyarylate based on bisphenol A and tere/iso phthalates) by Unitica, in 1974, 140 different chemical compositions of polyarylates were listed.[250]

Polyarylates exhibit good thermal stability, solvent resistance and good mechanical properties, and are, therefore, applied widely in the aviation, automobile and electronic industries.[251-253] However, most polyarylates encounter processing difficulties due to their high glass transition or melting temperatures coupled with insolubility in common organic solvents. Copolymerization and use of unsymmetrically substituted monomers are the two most commonly used synthetic approaches in obtaining compositions whose transition temperatures lie in a manageable temperature range either for processing or for characterization.[254,255] In other methods for improving solubility of aromatic polyesters, several approaches have been taken: introducing kinks of flexible units in the main chain[256-258] or replacing the conventional monomers with ones containing bulky pendant groups.[259-269] The latter approach is of particular interest and has been exploited in the past. Depending upon the bulkiness and position of the substituent, the resulting polyarylates, in some cases, are amorphous with improved solubility in organic solvents.

1.4.1 Synthesis of Polyesters

High molecular weight polyarylates are prepared by two routes.

1. Acid chloride route
2. Transesterification route

1.4.1.1 Acid chloride route

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

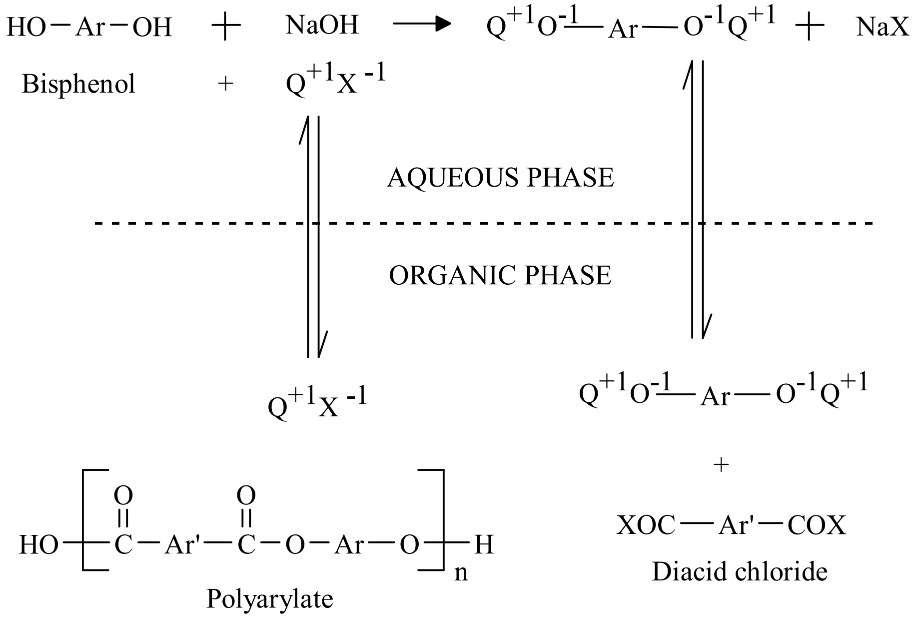
1.4.1.1.1 Interfacial polycondensation

The interfacial process for the preparation of polyarylates was first described by Eareckson[270] and Conix[249]. Basically, the interfacial polymerization involves the reaction of an aqueous solution of the dialkali metal salt of a diphenol with a solution of the acid chloride(s) in a water immiscible solvent which is inert under the reaction condition. The water immiscible solvents used for the interfacial polycondensation are methylene chloride, chloroform, 1,2-dichloroethane, chlorobenzene, nitrobenzene, cyclohexane, etc.

As the two starting immiscible solutions are brought into contact, the polymerization occurs at the interface where a film of the polymer is formed. Diffusion through this film, affected by the extent to which the solvent can swell or dissolve the polyarylate, is an important factor to achieve high molecular weight polyesters.

The two phase reaction can be accelerated by the use of small amount of phase transfer catalyst (PTC) such as tertiary amines as well as quaternary ammonium or phosphonium salts or crown ethers.

A typical phase-transfer catalyzed interfacial polycondensation is shown in **Scheme 1.15.**



Scheme 1.15: Schematic of interfacial polycondensation.

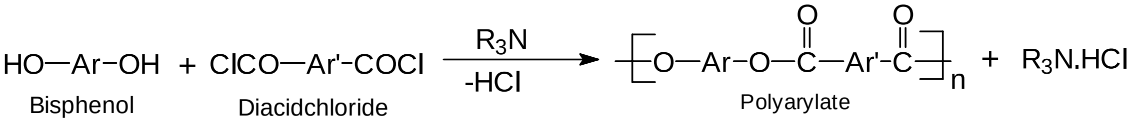
The basic function of PTC is to transfer the anions of the reacting salt into the organic medium in the form of ion pairs. These ion pairs react with chloride ions in the organic phase producing the desired product. The regenerated PTC is transferred back into the aqueous medium.[271,272] The most commonly used PTC's are benzyltriethyl-ammonium chloride (BTEAC), tetraethylammonium chloride (TEAC), tetramethylammonium chloride (TMAC), benzyltriphenyl phosphonium chloride (BTPPC), 15-crown-5 (15-C-15), and 18-crown-6 (18-C-6).

The choice of organic solvent is very important in interfacial polycondensation. It is advantageous that the polyarylate formed during the polymerization should remain in the solution form to obtain the high molecular weight polymers. The precipitation of polymer lowers the reaction rates, hence, low molecular weight polymers are obtained.

An interfacial synthesis of polyarylates using acid chlorides that were prepared *via* the chlorination of the corresponding dimethyl esters was described.[273] The process reportedly yields materials having excellent color, as well as improved thermal and hydrolytic stability.

1.4.1.1.2 Low temperature solution polycondensation

Low temperature solution polycondensations are generally run at room temperature or between -10^{0}C to +30^{0}C. Polyarylates are synthesized by the reaction of equivalent amounts of a diacid chloride and a dihydroxy compound in an inert solvent in the presence of an acid acceptor. The reaction is typically conducted in solvents such as dichloromethane, in the presence of acid acceptor such as pyridine or triethylamine (**Scheme1.16**).



Scheme 1.16: Solution polycondensation of bisphenol and diacid chloride.

High molecular weight polyarylates are successfully synthesized in pyridine alone or in combination with a tertiary amine in an inert organic solvent.[249, 270, 274-276]

1.4.1.1.3 High temperature solution polycondensation

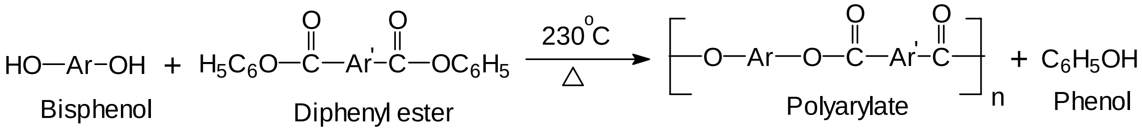
The polycondensation of a diacid chloride with a bisphenol without an acid acceptor is slow at room temperature. The rate of polycondensation increases with increasing temperature. The high temperature solution polycondensation is carried out at elevated temperatures (~200^{0}C) in an inert high boiling solvent. The high boiling solvents used are nitrobenzene and o-dichlorobenzene.[277] The *O*-dichlorobenzene and pyridine system is the most effective one to produce the polymer with high molecular weight.[278] Polyarylates are also prepared in good yields at 215-220^{0}C in dichloroethylbenzene.[279, 280] No acid acceptor is needed because the evolved hydrogen chloride is continuously removed from the system with the aid of an inert gas. A wide variety of other solvents are useful and include chlorinated benzenes (tetrachlorobenzene), chlorinated biphenyls or diphenylethers, chlorinated naphthalenes, as well as non-chlorinated aromatics such as terphenyl, benzophenones, dibenzylbenzenes,and the like.

1.4.1.2 Transesterification route

Transesterification reactions are carried out by three different routes.

1.4.1.2.1 Phenyl ester route

The reaction between a diarylester of an aromatic dicarboxylic acid and an aromatic diphenol results in high molecular weight polyesters (**Scheme 1.19**). This method was successfully employed for the first time by Blaschke and Ludwing[281] for the synthesis of polyarylates. The diphenylesters are less reactive as compared to the corresponding acid chlorides, hence, higher reaction temperatures and longer reaction times are necessary to obtain high molecular weight polyarylates.



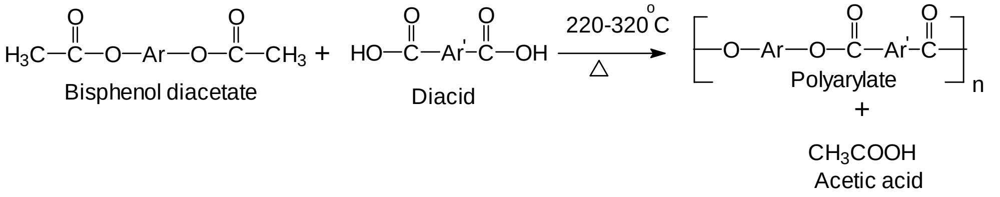
Scheme 1.17: Polyester synthesis *via* diphenylester route.

In this process the ester interchange reaction proceeds without catalysts, but the rate enhancement can be achieved in the presence of catalyst.[282-285] Lithium phenoxide, sodium phenoxide and potassium borophenoxide are the preferred catalysts. This is a reversible reaction; hence, removal of phenol, a by-product from the reaction system is essential to obtain high molecular weight polyarylates. This route compares favorably with the diacetate route.

1.4.1.2.2 Phenol acetate route

In this process, polyarylates are synthesized by the reaction of stoichiometric amounts of an aromatic dicarboxylic acid and the diacetate derivative of an aromatic diphenol at high temperature under inert atmosphere (**Scheme 1.20**).

Phenol acetate route, first described by Conix[249] and Levine and Temin[286] is essentially a reversible melt process which requires continuous removal of acetic acid-a by-product in order to achieve high molecular weight polyesters. It was postulated that the aromatic ester formation occurs by the reaction of a phenol end group and mixed anhydride with elimination of acetic acid[287.]



Scheme 1.18: Polyester synthesis *via* phenol acetate route.

Generally, the polycondensation is carried out in the melt or solid state at a temperature ranging from 220-320^{0}C under nitrogen atmosphere with or without catalyst.[288] The color and the thermal stability of polyarylate is affected by the presence of residual quantity of catalyst in the product, hence, polycondensation reaction without a catalyst is preferred. Catalyst most often cited for the phenol acetate route are based on antimony, titanium, magnesium, manganese and zinc. The choice and use of catalyst is such that there should not be deleterious effects on the color and hydrolytic stability of the polyarylates.

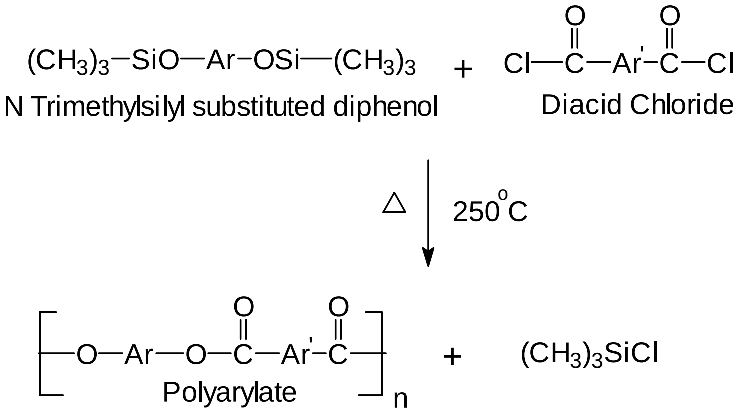
1.4.1.2.3 Phenyl ester and phenol acetate route

One variation of the diacetate route involves the reaction of bisphenol-A diacetate with dimethyl ester of aromatic dicarboxylic acids i.e. dimethyl tere/ isophthalates. In this sequence, condensation would occur with the liberation of methylacetate; however, the reactions proceeds only to very low molecular weights (catalyzed or uncatalyzed).[251] German group around 1990 has claimed that high molecular weight polyarylates can be prepared from bisphenol-A diacetate, dimethylterephthalate, and dimethylisophthalate.[289] An improved process for preparation of aromatic polyesters using simple alkylester of aromatic dicarboxylic acids and dihydric phenols by melt polycondensation has been reported.[290]

1.4.1.3 Other routes for polyester synthesis

1.4.1.3.1 Phenol silyl ether route

Phenol silyl ether route for the synthesis of polyarylates was first demonstrated by Kricheldorf[291] in 1979. The condensation of bisphenol disilylethers with dicarboxylic acid chlorides at elevated temperature yields high molecular weight polyarylates (**Scheme 1.19**). Various polyarylates with high molecular weight have been produced by this method.[292-294]

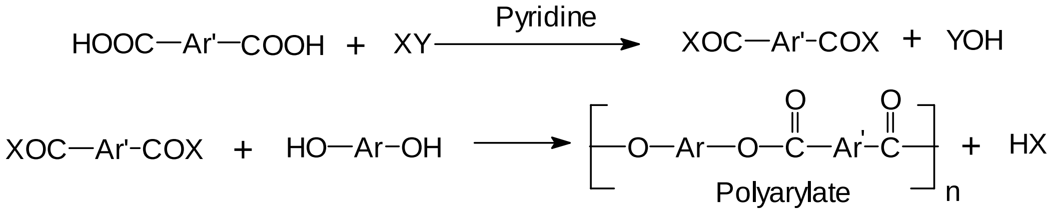


Scheme 1.19: Polyester synthesis *via* phenyl silyl ether route.

There are several advantages of this method. Silylated monomers are obtained in pure form by simple distillation. The volatile halosilanes obtained as a byproduct during the polycondensation are less harmful compared with hydrogen fluoride and hydrogen chloride which are generated in the absence of silyl groups.

1.4.1.3.2 Direct esterification route

Polyesterification of an aromatic dicarboxylic acid and an aromatic diol is very sluggish even at high temperature because of low reactivity of monomers. However, polyarylates have been synthesized by direct polycondensation of a dicarboxylic acid and a diphenol in the presence of a condensing agent, The condensing agent acts as an activating agent for dicarboxylic acid. The activated diacid intermediate formed condenses with bisphenol to form polyarylates (**Scheme 1.20**).



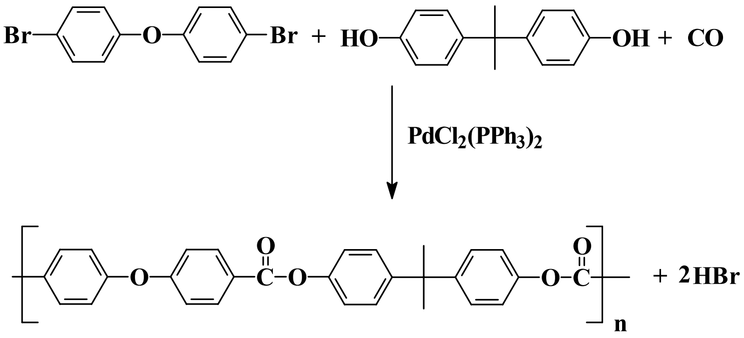
Scheme 1.20: Polyester synthesis *via* activated polycondensation.

This method has been extensively studied by Higashi.[295] A dicarboxylic acid is reacted with a condensing agent in a solvent such as pyridine. The resulting activated diacid intermediate is then condensed with bisphenol in the solution under relatively mild conditions. Mixed polymerization solvent were used to obtain high molecular weight polyarylates.[296] The effective condensing agents investigated so far for the preparation of polyarylates are triphenylphosphine chloride,[297] aryl sulfonyl chloride,[298] diphenyl chlorophosphate with metal salts,[299,300] phosphorous oxychloride with metal salts,[301] thionyl chloride[302] and p-toluenesulfonyl chloride with dimethylformamide.[296,303,304] The condensing agents afford highly reactive diacid derivatives such as acyloxyphosphonium salts or mixed anhydrides by the *insitu* reaction with dicarboxylic acids.

Direct polycondensation reactions are sensitive to reaction medium, aging conditions and reaction temperature. The direct polyesterification method is useful for the laboratory scale preparation of polyarylates.

1.4.1.3.3 Palladium-catalyzed carbonylation of aromatic dibromides and bisphenols

Heck[305]and Stille[306] reported the palladium-catalyzed carbonylation of aromatic dibromides with dihydroxyl compounds. However, the resulting polyesters were low molecular weight polymers. This ester forming reaction was extended by Imai et al[307] for the synthesis of polyesters based on aromatic dibromide, bisphenol-A and carbon monoxide using $PdCl_2$ $(PPh_3)_2$ and 1,8- diazabicyclo[5,4,0]-7-undecene (DBU) in chlorobenzene at 115°C (**Scheme 1.21**).



Scheme 1.21: Polyester synthesis *via* metal catalyzed reaction

The effects of reaction variables, such as type and amount of base, catalyst, reaction medium and reaction temperature have been studied in detail. Synthesis of high molecular weight polyarylates were reported using diiodide monomers such as p-diiodbenzene and 2,5-diiodo-p-dodecyloxybenzene.[308]

1.4.2 Structure-property relationship in aromatic polyesters

According to definition, polyarylates are polyesters from diphenols and aromatic dicarboxylic acids. Various efforts have been made to clarify the structure property relationship in polyarylates[250, 270].

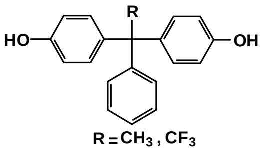
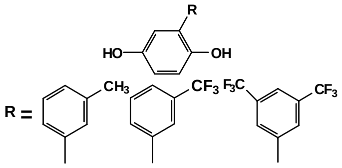
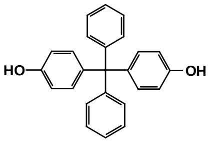
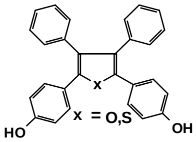
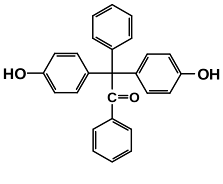
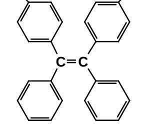
The properties of these polyesters depend on the kind of substitution present at the central carbon atom between the two phenyl rings. Polyesters bearing phenyl rings or large cross planar substituents show higher thermal properties, they are soluble in common organic solvents and do not show a tendency to crystallize[309]. Also the inclusion of -CF_3 group into the polyester backbone improves the solubility and thermal stability of the resulting polymers.[310, 311 a] Introduction of cardo groups (pendent loops) along the polymer backbone has been shown to impart greater solubility as well as better mechanical and thermal properties.[311b]

Use of *meta*- substituted aromatic monomers such as substituted isophthalic acid or resorcinol results in the formation of kinks in the polymer chain, which disrupt lateral interactions.

Substituted terephthalic acid with pendent functional groups also lead to polyesters with improved solubility. 2-Sulfomethylterephthalic acid and 2-phosphonoterephthalic acid have been employed in the preparation of rigid-rod polymers with enhanced solubility.[312]

Thermally stable polyarylate derived from isophthalic acid and terephthalic acid with bisphenol A has been commercialized [313]. There are studies on different co-polyesters, in which composition of the co-polyester is varied in the diol structures rather than in the diacid chloride structures[314,315] to control the final properties of the polymers. Introduction of bulky pendent substituents along the polymer backbone is one of the approach to obtain processable/ soluble polymer. A number of bisphenols containing bulky pendent groups have been synthesized for the synthesis of polyesters. Representative examples of such bisphenols are presented in **Table 1.8**.

Table 1.8 Representative bisphenols containing bulky pendant groups

No.	Bisphenols	Ref.
1.	 R = CH_3 , CF_3	265,250
2.		316
3.		260
4.	 X = O,S	317,262
5.		318
6.		319

1.4.3 Applications of polyarylates

Polyarylates are excellent in their UV stability and suggests utility in exterior glazing, solar energy collectors, transparent signs, automotive lenses, lighting housing, transparent lamp diffusers, traffic lights, etc.

Liquid crystalline polyesters are among the first industrially used polymers for liquid crystal display applications and continue to be the most suitable polymer for such kind of application [320].

Polyesters are used to make dielectric films for capacitor, film insulations for wire and insulating tapes. They also find applications in the field of electronics as electrical connectors and capacitors. Additional suggested applications include bearings, bushings, high temperature valves, and ball joint seals in automotive industry.

The foregoing description reveals that polyimides, polyamides and polyesters constitute promising examples of high performance polymers, which have been successfully put to use in many branches of emerging technologies where properties such as high heat resistance, mechanical strength, photostability, electrical insulation, barrier properties, etc. are needed.

The knowledge of characteristic features of the formation of polyimides, polyamides and aromatic polyesters and the relation between their structure and properties has led to enormous prospects for specific design of the polymer chain and hence for imparting a set of desired properties to such polymers.

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Chapter 3 Synthesis and Characterization of Difunctional Monomers

3.1 Introduction

Aromatic polyimides, polyamides and polyesters are important classes of high performance polymers. Although their excellent thermal stability is complimented by excellent chemical resistance, mechanical and electrical performance, their insolubility in common organic solvents and high glass transition and softening temperatures limit their widespread applications.

As mentioned in Chapter 1, there are several approaches to modify the properties of these polymers so as to make them processable. One of the promising strategies is the incorporation of bulky pendent groups or cardo groups via monomer molecule, which consequently becomes a part of repeat unit of the polymer chain. This modification increases interchain distance, disrupt the geometrical regularity of the chains thus reducing the interchain interactions and thereby enhancing the solubility / processability.

A variety of difunctional monomers containing bulky pendant groups/ cardo groups have been reported in the literature [1-32]. Tables 3.1, 3.2, 3.3, 3.4 and 3.5 present a catalogue of representative monomers containing bulky pendant /cardo groups.

Table 3.1 : Representative bisphenols containing bulky pendant groups

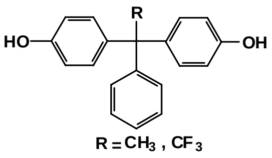
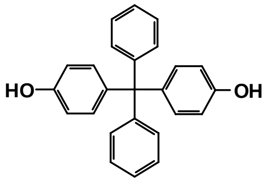
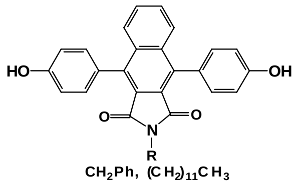
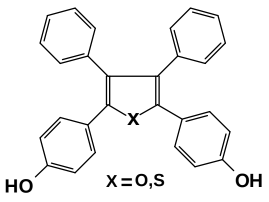
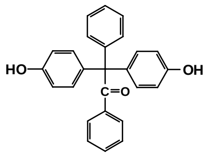
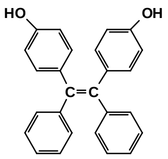
Sr.No.	Bisphenol	Polymers Synthesized	References
1		Polyesters Poly(arylene ether sulfone)s	1,2 3
2		Polyesters Poly(arylene ether sulfone)s Poly(ether ether ketone)s	4 5 5
3		Poly(arylene ether sulfone)s Poly(ether ether ketone)s	6 6
4		Polyesters Poly(arylene ether sulfone)s Poly(ether ether ketone)s	7,8 9 9
5		Polyesters	10
6		Polyesters Poly(arylene ether sulfone)s Poly(ether ether ketone)s	11 11 11

Table 3.2: Representative bisphenols containing cardo groups

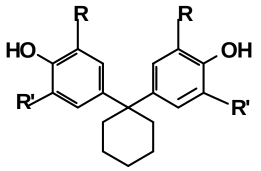
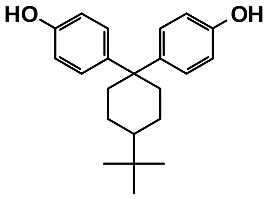
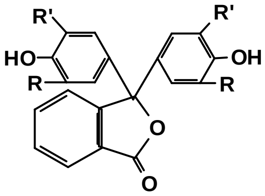
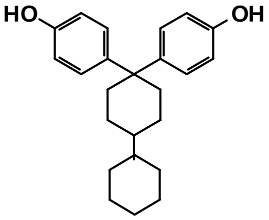
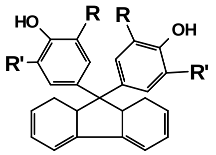
Sr.No.	Bisphenol	Polymers Synthesized	References.
1	 R = R' = H R = R' = CH_3 R = H, R' = CH_3	Polyesters Poly(arylene ether sulfone)s Poly(ether ether ketones)s	12 13 13
2		Polyesters	4
3	 R = R' = H R = R' = CH_3 R = H, R' = CH_3	Polyesters Poly(arylene ether sulfone)s Poly(ether ether ketone)s	14 15a 16
4		Polyesters	4
5	 R = R' = H R = R' = CH_3 R = H, R' = CH_3	Polyesters Poly(arylene ether sulfone)s Poly(ether ether ketone)s	17 18 18

Table 3.2: Representative bisphenols containing cardo groups continued……..

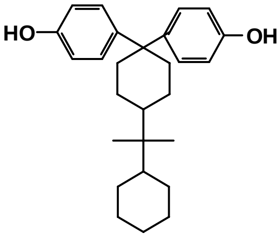
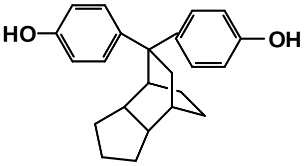
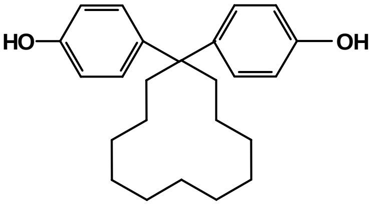
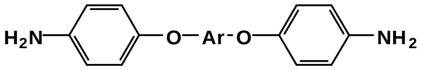
Sr.No.	Bisphenol	Polymers Synthesized	References
6		Polyesters	19
7		Polyesters	4
8		Polyesters	4

Table 3.3: Representative diamine monomers containing cardo groups and ether linkages



Where ‘Ar’ is

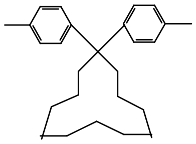
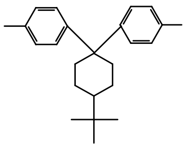
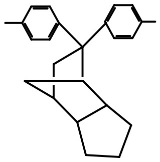
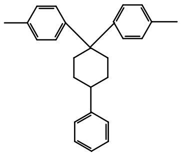
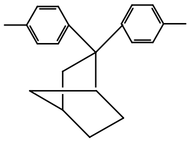
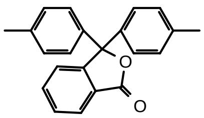
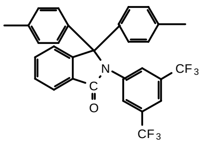
Sr.No.	Diamine ‘Ar’=	Polymers Synthesized	References
1		Polyimides	20
2		Polyimides	20
3		Polyimides	20
4		Polyimides	20
5		Polyimides	20
6		Polyimides	21
7		Polyimides	22

Table 3.4: Representative diamine monomers containing bulky pendent groups and ether linkages

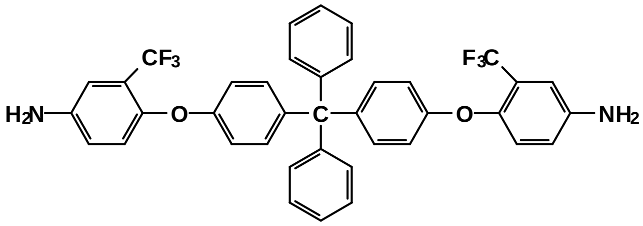
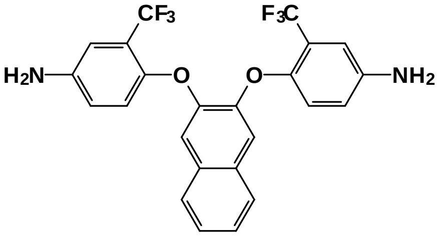
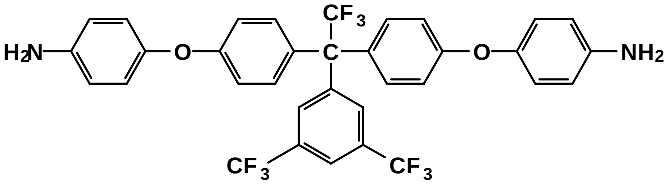
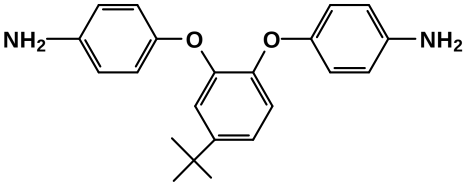
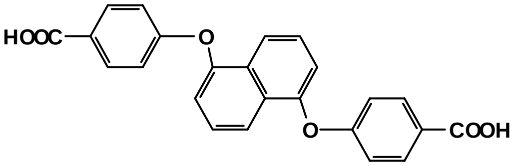
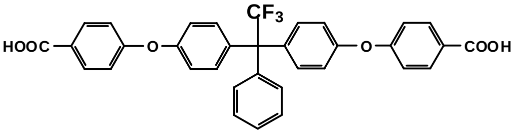
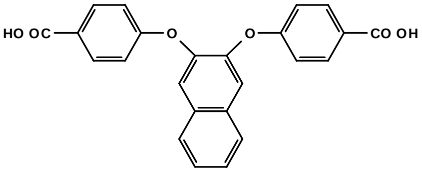
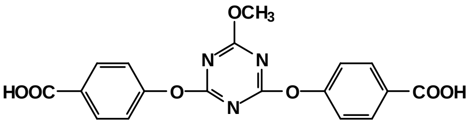
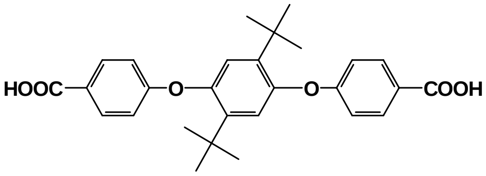
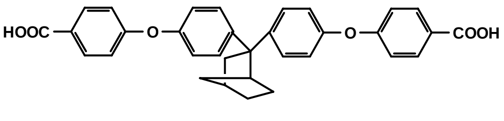
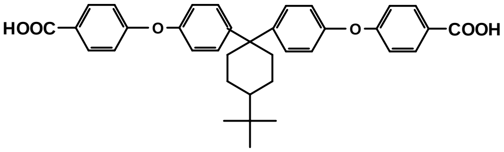
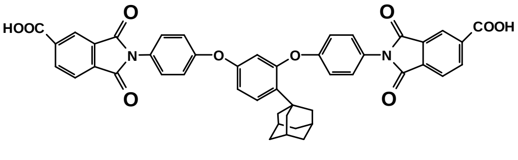
Sr.No.	Diamine	Polymers Synthesized	References
1		Polyamides	23
2		Polyimides	24
3		Polyimides	25
4		Polyimides	26

Table 3.5: Representative diacid monomers containing bulky groups / cardo groups and ether linkages

Sr. No.	Diacid	Polymer Synthesized	References.
1.		Polyamides	27
2.		Polyamides	28
3		Polyamides Polyoxadiazoles	29
4		Polyamides	30
5		Polyamides	31
6		Polyamides	32
7		Polyamides	33b
8		Polyamides	33c

This chapter deals with synthesis and characterization of the following monomers

A. Bisphenols and diamines containing bulky pendent groups

1. 1,1-Bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane (NABP),
2. 1,1-Bis-[4-hydroxyphenyl-(4-phenylsulfonyl phenyl)]ethane (DPSBP),
3. 1,1-Bis-[4-hydroxyphenyl-(1-biphenyl)] ethane (BBHPE),
4. 1,1-Bis-[4-(4-aminophenoxy) phenyl-1-(2-naphthyl)]ethane (NABPDA),
5. 1,1-Bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane (BBHPDA),

B. Bisphenols and diamines containing cardo groups

1. 1,1-Bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP),
2. 1,1-Bis-[4-hydroxy-(3,5-dimethyl phenyl)]-4-perhydrocumylcyclohexane (TMPCPBP),
3. 1,1-Bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP),
4. 1,1-Bis-[4-(4-aminophenoxy)3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA)
5. 1,1-Bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene (DCHDA),

C. Diacids containing cardo groups

1. 1,1-Bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane (PCPDA).
2. 1,1-Bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMPCPDA)

3.2 Experimental

3.2.1 Materials

p-Cumylphenol (Herdilia Chemicals Ltd., India), *p*-chloronitrobenzene, *p*-fluorocyanobenzene, 2,6-dimethylphenol, 10% Pd/C, 5% Ru/C, 3-mercaptopropionic acid (3-MPA), CaH_2, decahydro-2-naphthol, 2-acetonaphthone and diphenyl sulfide (from Aldrich Chemicals) were used as received. Sodium sulfate, sodium bicarbonate, potassium carbonate, potassium hydroxide, sodium hydroxide, hydrazine hydrate, acetic acid, hydrochloric acid, sulphuric acid and nitric acid (S.D. Fine Chem., India) were used as received. *m*-Cresol, tetrahydrofuran, methanol, ethanol, 2-propanol, dichloromethane, chloroform, ethyl acetate, hexane, toluene, N,N-dimethylformamide (DMF) and N- methyl 2-pyrrolidone (NMP) (from S.D. Fine Chem., India) were of reagent grade and were purified prior to use according to reported procedures.[33a] Biphenyl and phenol crystals (from Merck) were used as received. Acetyl chloride and carbon disulfide (from Merck) were distilled prior to use. Pyridiniumchlorochromate (PCC) was prepared according to the procedure reported in the literature.[34]

3.2.2 Measurements

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

FTIR spectra were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer in chloroform or in KBr pellet.

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.

Mass spectra were recorded on GC-MS, QP-2010 spectrometer from Shimadzu Company. (Column: DP; Length: 30 meters). For DI the instrument programming was: Initial temperature was room temperature and then every 10 °C rise per minute till 350 °C and at the maximum temperature the hold time was 10 minute.

HPLC analysis was performed on Waters Modular System consisting of three 515 pumps, 717 auto sampler, 996-photodiode array detector, 2410 RI detector controlled by *Millenium 32* software. Column used was *Zorbax* RP-C8.

Single crystal X-ray diffraction measurements were carried out on *Bruker SMART APEX* CCD diffractometer with Mo K_α radiation at room temperature and fine focus tube with 50kV and 30 mA. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (Shelx TL)[15b] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model.

3.3 Synthesis

3.3.1 Synthesis of bisphenols and diamines containing bulky pendant group

3.3.1.1 Synthesis of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane

Into a 500 mL three necked round bottom flask equipped with a magnetic stirrer and a HCl gas inlet, 2-acetonaphthone (10 g, 0.058 mol), phenol (37 g, 0.39 mol) and 3-

mercaptopropionic acid (0.63g, 0.006 mol) were taken and the reaction mixture was heated at 60°C. Anhydrous HCl gas was bubbled through the reaction mixture for a period of 3 days till the reaction mixture solidified. The solid obtained was dissolved in ethyl acetate and the solution was washed with aqueous sodium bicarbonate, brine and water, dried over anhydrous sodium sulfate and filtered. Ethyl acetate was evaporated off to give brown viscous liquid. Excess phenol was distilled off under reduced pressure. The solid mass obtained was purified by recrystallization from toluene to obtain a white solid.

Yield = 7.20 g (35 %)
m.p. = 190 ^{o}C
Purity (HPLC) = 99.8%

3.3.1.2 Synthesis of 1,1-bis-[4-hydroxyphenyl-1-(4-phenylsulfonylphenyl)] ethane

3.3.1.2.1 Synthesis of 4-acetyl diphenyl sulphide

Into a 250 mL three-necked round-bottom flask equipped with a magnetic stirring bar, a reflux condenser and two dropping funnels, aluminium chloride (8 g, 0.06 mol) and carbon disulphide (70 mL) were added and the reaction mixture was cooled to 10^{o}C. Diphenyl sulphide (9.30g, 0.05 mol in 40 mL carbon disulfide) was taken in one dropping funnel and acetyl chloride (3.5 mL, 0.05 mol in 20 mL carbon disulfide) in the other dropping funnel. The solutions were added simultaneously to the reaction mixture at 10^{o}C over a period of 30 min. After completion of addition, reaction mixture was stirred at room temperature for 3 h. Carbon disulfide was distilled off, the residue was poured into water (250 mL) and extracted in chloroform (2 x 100 mL). The solution was dried over anhydrous sodium sulfate and the solvent was evaporated off to obtain the crude product which was purified by column chromatography using petroleum ether- ethyl acetate (90:10 v/v) as the eluent.

Yield = 5 g (44%).
m.p. = 66-67° C (Lit. 67-68°C) [35].

3.3.1.2.2 Synthesis of 4-(phenyl sulfonyl) acetophenone

Into a 100 mL round bottom flask equipped with a magnetic stirring bar, were taken 4-acetyl diphenyl sulphide (4.56 g, 0.02 mol), potassium carbonate (3.31g, 0.024 mol), methanol (50 mL) and acetonitrile (1.6 mL). 30 % Hydrogen peroxide (27.2 g, 0.24 mol) was added drop-wise to the reaction mixture. The reaction mixture was stirred at room temperature and the progress of reaction was monitored by TLC. After completion of the reaction (24 h), solvent was evaporated off and the reaction mixture was extracted with ethyl acetate. The solution was washed with dilute hydrochloric acid and water, dried over anhydrous sodium sulfate, filtered and ethyl acetate was removed on a rotary evaporator. The residue obtained was purified by column chromatography using petroleum ether- ethyl acetate (90:10 v/v) as the eluent.

Yield = 3.64 g (70 %)

m.p. = 135°C (Lit.m.p. 137-138 C)[36]

3.3.1.2.3 Synthesis of 1,1-bis-[4-hydroxyphenyl-(4-phenylsulfonyl phenyl)]ethane

Into a 250 mL two necked round bottom flask equipped with a magnetic stirring bar, a HCl gas inlet, and a reflux condenser, 4-(phenyl sulfonyl) acetophenone (25.0 g, 0.096 mol), phenol (100 g , 1.06 mol) and 3-mercaptopropionic acid (1 mL) were added. Anhydrous hydrogen chloride gas was bubbled through the reaction mixture for 8 h at 60°C. On completion of reaction, excess phenol was removed by distillation under reduced pressure. The reaction mixture was dissolved in ethyl acetate (500 mL) and washed repeatedly with aqueous sodium bicarbonate, brine and water and dried over anhydrous sodium sulfate. Ethyl acetate was evaporated off, to obtain a brown solid, which was purified by Soxhlet extraction using toluene.

Yield = 16.53 g (40 %)

m.p. = 260 °C

HPLC purity = 99.8%

3.3.1.3 Synthesis of 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl] ethane

3.3.1.3.1 Synthesis of 4-acetyl biphenyl

Into a three necked 2 litre round bottom flask equipped with a stirrer, two dropping funnels and a reflux condenser, aluminium chloride (94.67 g, 0.71mol) and carbon disulfide (200 mL) were added. The reaction mixture was cooled to 10°C. Acetyl chloride (55.8 g, 0.71 mol) (50.48 mL in 50 ml carbon disulfide) and biphenyl (100 g, 0.65 mol in 100 mL carbon disulfide) were added drop wise with stirring over a period of 1h. The addition was continued for 1h. On completion of addition, the dropping funnels were removed and the reaction mixture was refluxed for 3 h. The solvent was distilled off and the viscous residue was added slowly to 500 mL of ice water. The pale yellow precipitate obtained was filtered, taken in methanol and treated with activated charcoal and recrystallized from ethanol to obtain a white solid product.

Yield = 75 g (76.4 %)

m.p. = 116 ^{o}C (Lit. m.p. = 116-118 ^{o}C)[37]

3.3.1.3.2 Synthesis of 1,1-bis-[(4-hydroxyphenyl)-1-biphenyl] ethane

Into a two necked 500 mL round bottom flask equipped with a magnetic stirrer and a HCl gas inlet, 4-acetyl biphenyl (50 g, 0.26 mol), phenol (143.8 g, 1.53 mol) and 3-mercaptopropionic acid (2.6ml, 0.03 mol) were taken. Reaction mixture was heated at 60°C with stirring. Anhydrous HCl gas was bubbled through the reaction mixture for a period of four days till the reaction mixture solidified. The solid was dissolved in ethyl acetate and the solution was washed with portions of sodium bicarbonate solution, brine and water. The solution was dried over anhydrous sodium sulfate, filtered and ethyl acetate was removed to obtain a pale yellow solid which was recrystallized from chlorobenzene followed by column chromatography using petroleum ether- ethyl acetate (90:10 v/v) as the eluent.

Yield = 42.25 g (44.7 %)

m.p. = 184 ^{o}C (Lit. m.p. 184-185 ^{o}C) [38a,b]

HPLC (Purity) = 99.8 %

3.3.1.4 Synthesis of 1,1- bis-[4-(4-aminophenoxy) phenyl-1-(2-naphthyl)] ethane

3.3.1.4.1 Synthesis of 1,1-bis-[4-(4-nitrophenoxy) phenyl-1-(2-naphthyl)] ethane

Into a 250 mL round bottom flask equipped with a magnetic stirrer, a reflux condenser and a nitrogen inlet, 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane (10 g, 0.029 mol), *p*-chloronitrobenzene (10.19 g, 0.064 mol) and potassium carbonate (8.94 g, 0.064 mol) were taken and dissolved in 100 ml dimethyl formamide. The reaction mixture was refluxed for 12h. The reaction mixture was cooled to room temperature and poured into 600 mL of methanol. The solid obtained was filtered and thoroughly washed with water. The crude product was recrystallized from DMF/ methanol mixture to give pale yellow crystals.

Yield = 14 g (82 %)

m.p. = 117 °C

3.3.1.4.2. Synthesis of 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)]ethane

Into a 250 mL round bottom flask equipped with a magnetic stirrer, a reflux condenser and a nitrogen inlet, DNNABP (10 g, 0.017 mol), 10 wt % Pd/C (0.3 g) and ethanol (100 mL) were added. Hydrazine hydrate (20 mL) was added drop wise to the reaction mixture over a period of 1h at reflux temperature under inert atmosphere. After completion of addition, the reaction mixture was refluxed for an additional 6 h. The reaction mixture was filtered while hot to remove Pd/C, concentrated and poured into water to obtain a white solid, which was recrystallized from ethanol/ THF mixture.

Yield = 7.9 g (89 %)

m.p. = 142°C

3.3.1.5 Synthesis of 1,1-bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane

3.3.1.5.1 Synthesis of 1,1-bis-[4-(4-nitrophenoxy) phenyl-1-biphenyl] ethane

Into a 250 mL round bottom flask equipped with a magnetic stirrer , a reflux condenser and a nitrogen inlet, 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl] ethane (10 g, 0.027 mol), *p*-chloronitrobenzene (7.87g, 0.057 mol), and potassium carbonate (7.87 g, 0.057 mol) were taken and dissolved in 100 ml dimethyl formamide. The reaction mixture was refluxed for 12 h. The reaction mixture was cooled to room temperature and poured into 600 mL of methanol. The solid separated out was filtered and thoroughly washed with water. The crude product was recrystallized from chloroform/ methanol mixture to give pale yellow crystals.

Yield = 12.3 g (75%)

m.p. =162 °C

3.3.1.5.2 Synthesis of 1,1-bis-[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane

Into a 250 mL round bottom flask equipped with a magnetic stirrer , a reflux condenser and a nitrogen inlet, DNBBHPE (10 g,0.016 mol), 10 wt % Pd/C(0.3 g) and ethanol (100 mL) were placed. To the reaction mixture hydrazine hydrate (20 ml) was added drop wise over a period of 1h at reflux temperature under nitrogen atmosphere. On completion of addition, the reaction mixture was refluxed for an additional 6 h. The reaction mixture was filtered while hot to remove Pd/C, concentrated and poured into water to obtain white solid, which was purified by repeated dissolution in ethanol and precipitation in water.

Yield = 6.75 (75%)

m.p. = 99°C

3.3.2 Synthesis of bisphenols and diamines containing cardo groups

3.3.2.1 Synthesis of 1,1-bis(4-hydroxyphenyl)-4-perhydrocumyl cyclohexane

3.3.2.1.1 Synthesis of 4-(1-cyclohexyl-1-methyl ethyl) cyclohexanol (HPCP)

p-Cumylphenol (40 g , 0.19 mol) dissolved in isopropanol (150 ml) was hydrogenated using 5 % Ru/C (1.2 g) as catalyst in a Parr reactor at 175^{o}C and at hydrogen pressure of 1400 psi. At the end of the reduction the catalyst was filtered off and the filtrate was passed through a short column of silica gel (100-200 mesh) to obtain a colorless solution. Isopropanol was distilled off and the residue was refluxed with 10% NaOH solution (100 ml) to remove *p*-cumylphenol present, if any. The reaction mixture was extracted with dichloromethane (400 mL) and the solution was washed with water (3 × 100 mL), dried over anhydrous sodium sulfate and filtered. Dichloromethane was evaporated off to obtain a viscous liquid, which solidified on prolonged standing.

Yield = 36.17 g (85 %)

m.p. = 63°C

3.3.2.1.2 Synthesis of 4-(1-cyclohexyl-1-methyl ethyl) cyclohexanone (HPCP-K)

Into a 1 L round bottom flask equipped with a mechanical stirrer was added a mixture of PCC (97 g, 0.45 mol) and silica gel (97 g, 100-200 mesh). Dichloromethane (600 mL) was added to the mixture and 4-(1-cyclohexyl-1-methyl ethyl) cyclohexanol (HPCP) (50 g, 0.22 mol) was added in small portions at room temperature with stirring. The reaction mixture was stirred for 4 h and then filtered through a short silica gel column. The solvent was evaporated off to obtain a solid which was dissolved in ethyl acetate (200 mL), washed with aqueous sodium bicarbonate (2× 200 mL) and water (2× 200 mL), dried over anhydrous sodium sulfate, filtered and ethyl acetate was evaporated off. The residue obtained was recrystallized from methanol.

Yield = 43.95 g (90%)

m.p. = 86°C

3.3.2.1.3 Synthesis of 1,1-bis(4-hydroxyphenyl)-4-perhydrocumyl cyclohexane

Into a 100 ml three-necked round bottom flask equipped with a magnetic stirrer, a HCl inlet and a reflux condenser connected to a scrubber were placed 4-(1-cyclohexyl-1-methyl ethyl) cyclohexanone (11 g, 0.05 mol), phenol (25.38 g, 0.27 mol) and 3-mercaptopropionic acid (0.1 mL). Dry HCl gas was bubbled into the reaction mixture at room temperature. The reaction mixture solidified after 2 h. The solid was dissolved in ethyl acetate (250 mL) and neutralized by washing with aqueous sodium bicarbonate solution (3× 50 mL) followed by washing with water (3× 50 mL), dried over sodium sulfate, filtered and ethyl acetate was evaporated off. The product obtained was recrystallized twice from toluene.

Yield = 14.11 g (72%)

m.p. = 97°C

HPLC (Purity) = 99.8 %

3.3.2.2. Synthesis of 1,1-bis(4-hydroxy-3,5-dimethylphenyl)-4-perhydrocumyl cyclohexane

Into a 250 ml round bottom flask 15 mL HCl /acetic acid mixture (2:1, v/v), 4-(1-cyclohexyl-1-methyl ethyl) cyclohexanone (11 g, 0.05 mol) and 2,6-dimethylphenol (10.98 g, 0.09 mol) were added and stirred for seven days at room temperature. The reaction mixture was dissolved in ethyl acetate (150 mL) and neutralized by washing with aqueous sodium bicarbonate solution (3× 40 mL) followed by washing with water (2× 40 ml), dried over sodium sulfate, filtered and ethyl acetate was evaporated off. The product obtained was recrystallized from hexane/ toluene mixture.

Yield =12.1 g (60 %)

m.p. = 213°C

HPLC (Purity) = 99.8 %

3.3.2.3 Synthesis of 1,1-bis-(4-hydroxy phenyl)-octahydro-2(1H)-naphthalene

3.3.2.3.1 Synthesis of 2-decalone

Into a 2 L round bottom flask equipped with a mechanical stirrer was added a mixture of PCC (105 g, 0.49 M) and silica gel (105g) in 800 mL dichloromethane. The mixture was cooled to 0°C. A solution of decahydro-2-naphthol (50 g, 0.32 mol) in 500 mL of dichloromethane was added and the reaction mixture was stirred for 6 h. The reaction mixture was filtered through a bed of celite / silica gel. The filtrate was washed repeatedly with aqueous sodium bicarbonate solution and brine and dried over sodium sulfate. The solvent was evaporated off to give a pale yellow liquid which was purified by distillation under reduced pressure.

Yield = 40 g (83%)

b.p. = 65 °C / 0.01 mm Hg

3.3.2.3.2 Synthesis of 1,1-bis-(4-hydroxyphenyl)-octahydro-2(1H)-naphthalene

Into a 500 mL round bottom flask 90 ml of HCl /acetic acid mixture (2:1, v/v), 2-decalone (15 g, 0.1 mol), phenol (94 g, 1 mol) and 3-mercaptopropionic acid (1.03g, 0.01mol) were added and stirred for four days at room temperature till the reaction mixture solidified. The solid obtained was dissolved in ethyl acetate, and the solution was washed repeatedly with aqueous sodium bicarbonate, brine and water, dried over sodium sulfate and filtered. The solvent was evaporated off to give a pale yellow solid which was purified by the treatment with activated charcoal in methanol, followed by soxhlet extraction using petroleum ether.

Yield = 20 g (64 %)

m.p. = 230 ^{o}C

HPLC (Purity) = 99.8 %

3.3.2.4 Synthesis of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane

3.3.2.4.1 Synthesis of 1,1-bis-[4-(4-nitrophenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane

Into a 500 mL round bottom flask equipped with a nitrogen inlet, a reflux condenser and a magnetic stirrer, 1,1-bis-(4-hydroxy-3,5-dimethylphenyl)-4-perhydrocumyl cyclohexane (10 g, 0.02 mol), *p*-chloronitrobenzene (7g, 0.04 mol) anhydrous potassium carbonate (6.02 g, 0.04 mol) and DMF (100 ml) were taken and refluxed for 12 h. The reaction mixture was precipitated in methanol to obtain a pale yellow solid. It was dissolved in chloroform, washed with water, dried over sodium sulfate and filtered. The filtrate was concentrated and re-precipitated in methanol. The solid obtained was filtered and recrystallized from DMF to obtain pale yellow crystalline solid.

Yield: 13.53 g, (90 %)

m.p. = 212°C

3.3.2.4.2 Synthesis of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser were placed 1,1-bis[4-(4-nitrophenoxy)3,5 -dimethyl phenyl)-4-perhydrocumyl cyclohexane] (10 g, 0.014 mol.), 10 wt % Pd/C (0.3 g) and ethanol (100 mL). Hydrazine hydrate (20 mL) was added drop wise to the reaction mixture over a period of 1 h at reflux temperature under inert atmosphere. On completion of addition, the reaction mixture was refluxed for an additional 6 h. The reaction mixture was filtered while hot to remove Pd/C, concentrated and poured into water to obtain a white solid, which was filtered and dried under reduced pressure.

Yield = 7.28 g (80%)

m.p. = 165-166°C

3.3.2.5 Synthesis of 1,1-bis-[4-(4-aminophenoxy)phenyl]-octahydro-2(1H)-naphthalene

3.3.2.5.1 Synthesis of 1,1-bis-[4-(4-nitrophenoxy)phenyl]-octahydro-2(1H)-naphthalene

Into a 500 mL round bottom flask equipped with a nitrogen inlet, a reflux condenser and a magnetic stirrer bar, 1,1-bis-(4hydroxy phenyl)-octahydro-2(1H)-naphthalene (6g, 0.018 mol), *p*-chloronitrobenzene (6.4 g, 0.04 mol), anhydrous potassium carbonate (6.02 g, 0.043 mol.) and DMF (100 ml) were taken and refluxed for 12 h. The reaction mixture was precipitated in methanol to obtain a pale yellow solid. It was dissolved in chloroform, washed with water, dried over sodium sulfate and filtered. The filtrate was concentrated and re-precipitated in methanol. The solid obtained was filtered out and recrystallized from DMF to give pale yellow crystalline solid which was further purified by Soxhlet extraction using methanol.

Yield = 7.5 g (72 %)

m.p.= 182°C

3.3.2.5.2 Synthesis of 1,1-bis-[4-(4-aminophenoxy)phenyl]-octahydro-2(1H)-naphthalene

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet and a reflux condenser were placed 1,1-bis[4-(4-nitrophenoxy) phenyl) octahydro-2(1H)-naphthalene (DNDCHBP) (5 g, 0.088 mol), 10 wt % Pd/C (0.15 g) and ethanol (100 mL). To the reaction mixture hydrazine hydrate (10 mL) was added dropwise over a period of 1 h at reflux temperature under nitrogen atmosphere. After completion of addition the reaction mixture was refluxed for an additional 6 h. The reaction mixture was filtered while hot to remove Pd/C, concentrated and poured into water to obtain a white solid. The obtained solid was then filtered and dried under reduced pressure.

Yield = 3.6 g (80 %)

m.p. = 106°C

3.3.3 Synthesis of diacid monomers containing cardo groups

3.3.3.1 Synthesis of 1,1-bis[4-(4-carboxyphenoxy) phenyl)]-4-per-hydrocumyl cyclo hexane

3.3.3.1.1 Synthesis of 1,1-bis[4-(4-cyanophenoxy)phenyl)]-4-perhydrocumyl cyclohexane

Into a 250 mL round bottom flask equipped with a magnetic stirrer , a reflux condenser and a nitrogen inlet, 1,1-bis (4-hydroxyphenyl)-4-perhydrocumyl cyclohexane (5 g, 12.6 m mol) was taken in 35 mL N-methyl-2-pyrrolidone. To the reaction mixture anhydrous potassium carbonate (3.52 g, 0.025 mol) was added. The reaction mixture was heated at 160°C for 3h. The reaction mixture was cooled to 60°C and *p*-fluorobenzonitrile (3.09 g, 0.025mol) was added. The reaction mixture was heated at 160°C for an additional 6 h, cooled to room temperature and poured into 500 mL of water. The precipitated solid was collected by filtration, thoroughly washed with water and dried. The crude product was purified by recrystallization from acetonitrile to give white powder.

Yield = 6.43 g (85%)

m.p.= 150°C

3.3.3.1.2 Synthesis of 1,1-bis[4-(4-carboxyphenoxy)phenyl)]-4-per-hydrocumyl cyclohexane.

Into a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, 1,1-bis[4-(4-cyanophenoxy)phenyl)]-4-perhydrocumyl cyclohexane (5 g, 8.4 mmol), potassium hydroxide (4.41 g, 84 mmol), ethanol (30 mL), and water (30 mL). were taken. The reaction mixture was refluxed for 72 h and filtered while hot to remove any insoluble impurities and cooled to room temperature. The filtrate was acidified with concentrated HCl. The precipitated white powder was isolated by filtration, washed repeatedly with water, and dried under vacuum at 150°C.

Yield = 5.1 g (96 %)

m.p. = 245°C

3.3.3.2 Synthesis of 1,1-bis[4-(4-carboxyphenoxy)3,5-dimethylphenyl]-4-per-hydrocumyl cyclohexane

3.3.3.2.1 Synthesis of 1,1-bis[4-(4-cyanophenoxy)3,5-dimethylphenyl]-4-per-hydrocumyl cyclohexane

Into a 250 mL round bottom flask equipped with a magnetic stirrer, a reflux condenser and a nitrogen inlet, 1,1-bis-(4-hydroxy-3,5 dimethyl phenyl) -4-perhydrocumyl cyclohexane (5 g, 11.1 mmol) was taken in N-methylpyrrolidone (35 mL). To the reaction mixture anhydrous potassium carbonate (3.52 g, 0.025 mol) was added. The suspension was heated at 160°C for 3h. The reaction mixture was cooled to 60°C and *p*-fluorobenzonitrile (3.4 g, 0.028 mol) was added. The reaction mixture was heated at 160°C for additional 6 h, cooled to room temperature and poured into 500 mL of water. The precipitated solid was collected by filtration, thoroughly washed with water and dried. The crude product was purified by recrystallization from acetonitrile to give white powder.

Yield = 5.44 g (75%)

m.p.= 158°C

3.3.3.2.2 Synthesis of 1,1-bis[4-(4-carboxyphenoxy)3,5-dimethyl phenyl)]-4-per-hydrocumyl cyclohexane

Into a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 1,1-bis[4-(4-cyanophenoxy) 3,5 dimethyl phenyl)]-4-perhydrocumyl cyclohexane (5 g , 7.7 mmol), potassium hydroxide (3.5g, 61 mmol), ethanol (30 mL), and water (30 mL). The reaction mixture was refluxed for 72 h. and filtered while hot to remove any insoluble impurities and cooled to room temperature. The filtrate was acidified with concentrated HCl. The precipitated white powder was isolated by filtration, washed repeatedly with water, and dried under vacuum at 150°C.

Yield = 4.4 (85%)

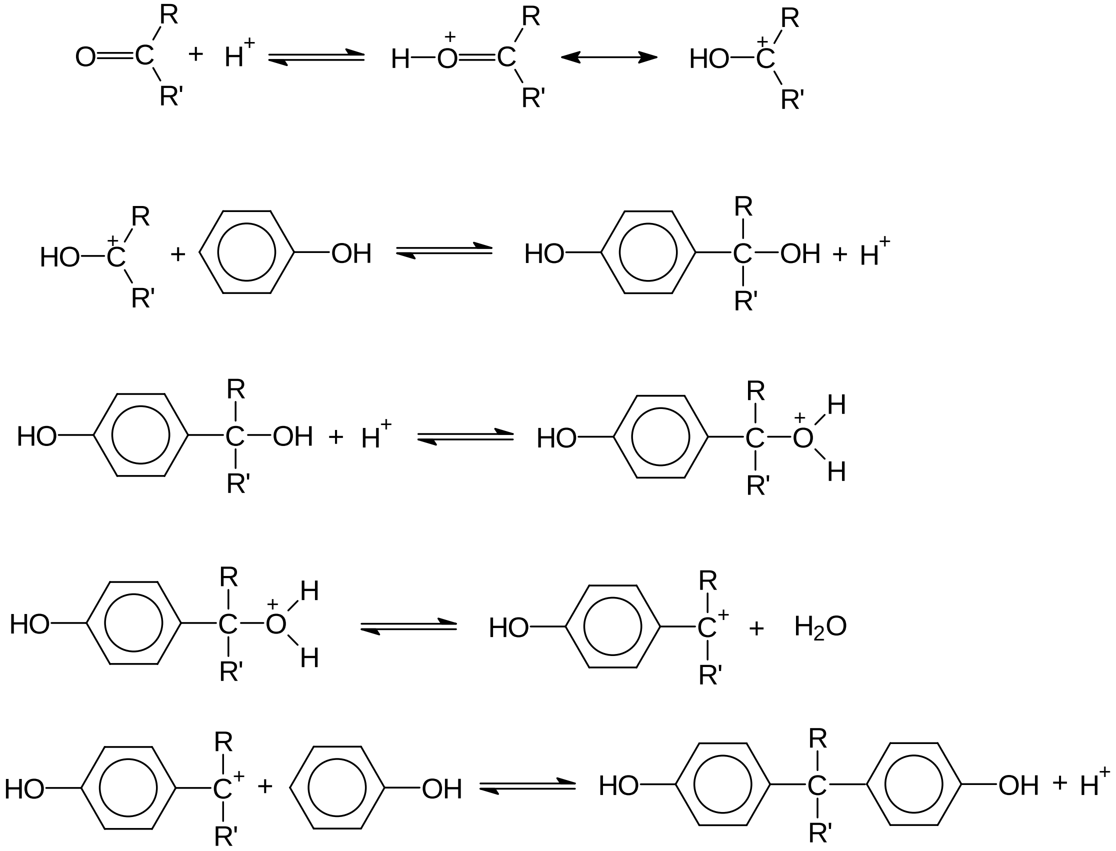
m.p.= 194°C

3.4 Results and Discussion

Aromatic polyamides, polyimides and polyesters are important classes of high performance polymers. The key reasons for insolubility and high melting character of these polymers are the lack of chain flexibility and strong interchain interactions due to high symmetry and highly polar groups and also extensive hydrogen bonding in case of polyamides. As mentioned in Chapter 1, there are several strategies to modify properties of these polymers so as to make them processable. These strategies generally suffer from a trade-off between thermal properties and solubility since the same structural features that enhance one decreases the other. A careful optimization of these properties is required to obtain processable materials without sacrificing inherent thermal stability.

The synthesis of new monomers enriches polycondensation chemistry by opening routes to prepare a wide range of polymers. For instance, once a new bisphenol is obtained, extended bis (ether amine)s and bis (ether acid)s can be synthesized therefrom. Moreover diamines can be converted to diisocyanates by simple organic transformations which themselves are very useful monomers. Diacids can be converted to diacyl hydrazides by known routes and polyamide-imides and polyhadrazides can be obtained therefrom. Therefore, it is of continuing interest to synthesize new monomers such as bisphenols, diamines and diacids.

A large number of bisphenols have been synthesized in the past three decades with a view to overcome the traditional processing problems caused by the limited solubility and poor processability of these polymers. Bisphenols are usually synthesized by the acid–catalyzed condensation of an aldehyde or a ketone with phenol. The reaction proceeds with an electrophilic attack of the proton from acid catalyst on the molecule of ketone or aldehyde. For reactions involving the substitution of a proton in an aromatic ring, both the rate of reaction and the equilibrium distribution of products are influenced by the density of electrons at the centre of reaction. *p, p'*-Isomer is most likely to form since the density of electrons in *para* position of the phenol is higher than that in the *ortho* position. Also, *p, p'*-isomer formation is favored from thermodynamic point of view. The formation of *o, p*-isomer and *o*, *o*'-isomer are observed. Mechanism of formation of bisphenol is as shown in **Scheme 3**.



Scheme 3: Mechanism of bisphenol synthesis.

In the present approach towards obtaining processable polymers, bisphenols were synthesized first. Starting from these bisphenols extended bis (ether amine)s and extended bis (ether acid)s were obtained using simple organic transformations. **Table 3.6** presents the synthesized bisphenols, diamines and diacids

Table 3.6: Synthesized bisphenols, diamines and diacid monomers

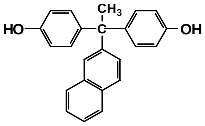
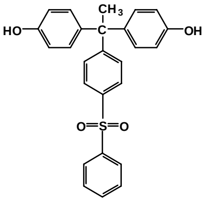
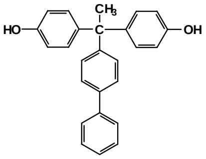
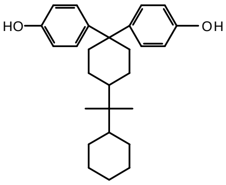
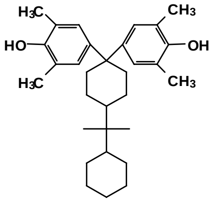
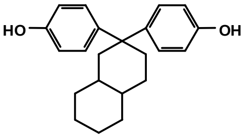
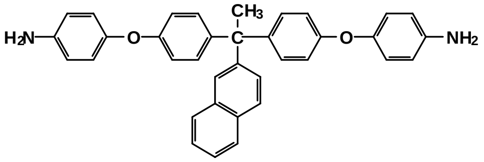
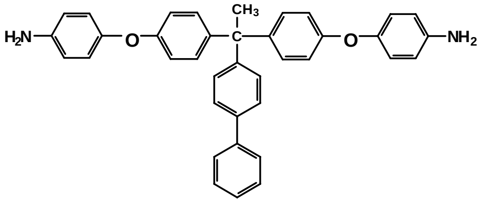
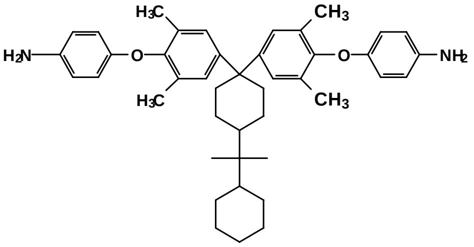
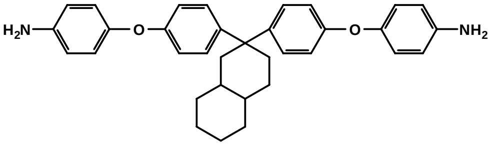
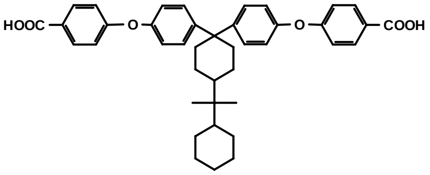
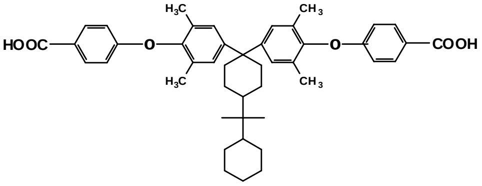
Sr. No.	Bisphenol	Structure
1.	1,1-Bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane **(NABP)**	
2.	1,1-Bis-[4-hydroxyphenyl-1-(4-phenylsulphonyl phenyl)]ethane (**DPSBP**)	
3.	1,1-Bis–[(4-hydroxyphenyl)-1-biphenyl]ethane (**BBHPE**)	
4.	1,1–Bis-(4-hydroxyphenyl)-4-perhydrocumyl cyclohexane (**PCPBP**)	
5.	1,1-Bis-(4-hydroxy-3,5-dimethylphenyl)-4-perhydrocumylcyclohexane (**TMPCPBP**)	
6.	1,1-Bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (**DCHBP**)	

Table 3.6: Synthesized bisphenols, diamines and diacid monomers continued……….

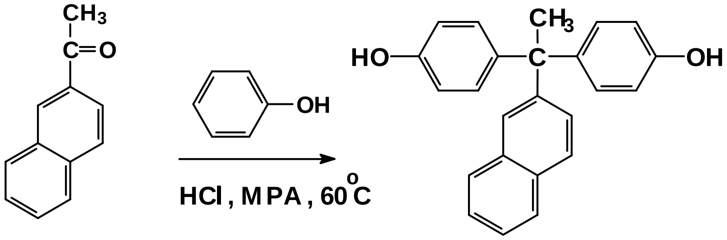
Sr. No.	Diamines/ Diacids	Structure
7.	1,1-Bis-[4-(4-aminophenoxy) phenyl-1-(2-naphthyl)]ethane **(NABPDA)**	
8.	1,1-Bis–[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane **(BBHPDA)**	
9.	1,1-Bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4- perhydro cumylcyclohexane **(TMDA)**	
10.	1,1-Bis-[4-(4-aminophenoxy) phenyl]octahydro-2(1H)-naphthalene **(DCHDA)**	
11.	1,1–Bis-[4-(4-carboxyphenoxy) phenyl]-4-perhydrocumylcyclohexane **(PCPDA)**	
12.	1,1-Bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane **(TMPCPDA)**	

3.4.1 Synthesis and characterization of bisphenols and diamines containing bulky pendant groups

3.4.1.1 Synthesis and characterization of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane (NABP)

Scheme 3.1 depicts synthesis of 1,1-bis-[{4-hydroxyphenyl-1-(2-naphthyl)}]ethane (**NABP**). NABP was prepared by reaction of 2-acetonaphthone with excess phenol in the presence of 3-mercaptopropionic acid and dry HCl gas. NABP was purified by recrystallization from toluene.

Synthesis of NABP has been previously reported.[39,40]



Scheme 3.1: Synthesis of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane

NABP was characterized by FTIR, NMR, ^{13}C NMR and mass spectrometry and the purity was checked by HPLC.

In the FTIR spectrum of NABP (Figure 3.1) a band at 3411 cm^{-1} was observed which corresponds to the phenolic hydroxyl group. Two strong bands and a weak band at 745, 812 and 861cm^{-1}, respectively were observed which are characteristic of out of plane –CH bending vibrations of β- substituted naphthalene.

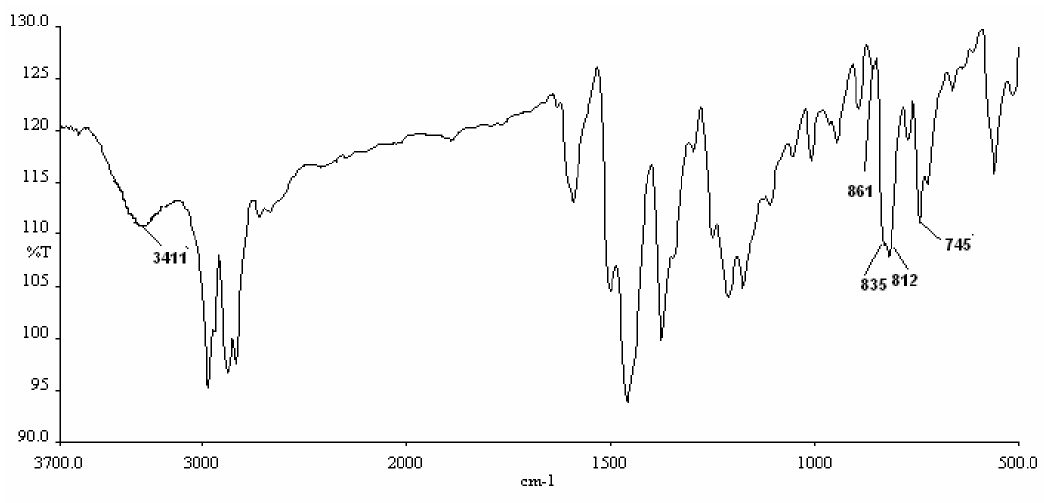


Figure 3.1: FT-IR spectrum of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane

^{1}H-NMR spectrum of NABP is shown in **Figure 3.2**. A singlet observed at 9.28 δ ppm is assigned to proton of hydroxyl group. The seven protons of naphthalene ring exhibited a multiplet in range 7.22 -7.76 δ ppm. Doublets at 6.84 δ ppm and 6.69 δ ppm were observed due to the protons 'c' and 'b' present at *meta* and *ortho* position to the hydroxyl group respectively. A singlet corresponding to methyl group attached to bridge carbon atom appeared at 2.11 δ ppm.

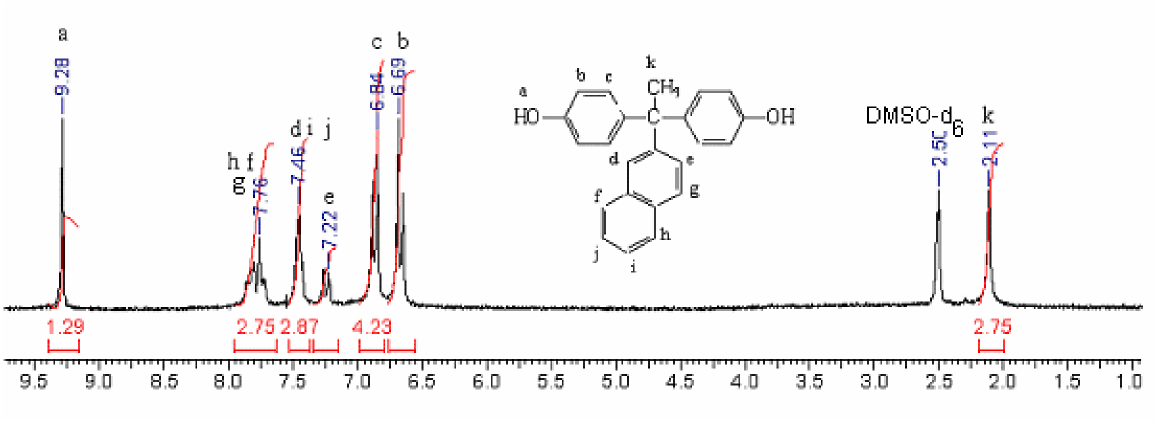


Figure 3.2: ^{1}H-NMR spectrum of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane in DMSO-d$_6$.

^{13}C-NMR spectrum of NABP along with assignments of the carbon atoms is shown in **Figure 3.3.**

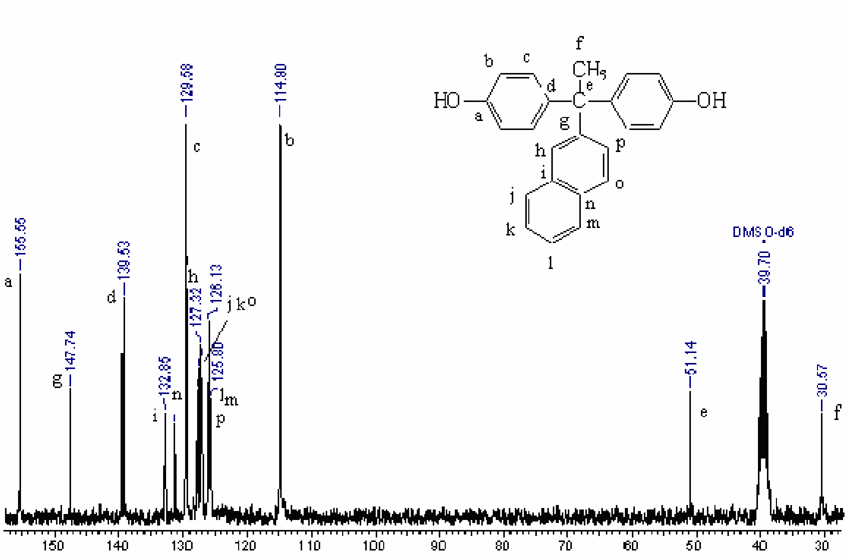


Figure 3.3: ^{13}C-NMR spectrum of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane in DMSO-d_6.

The mass spectrum of NABP **(Figure 3. 4)** showed molecular ion peak at 340 as expected from its molecular weight.

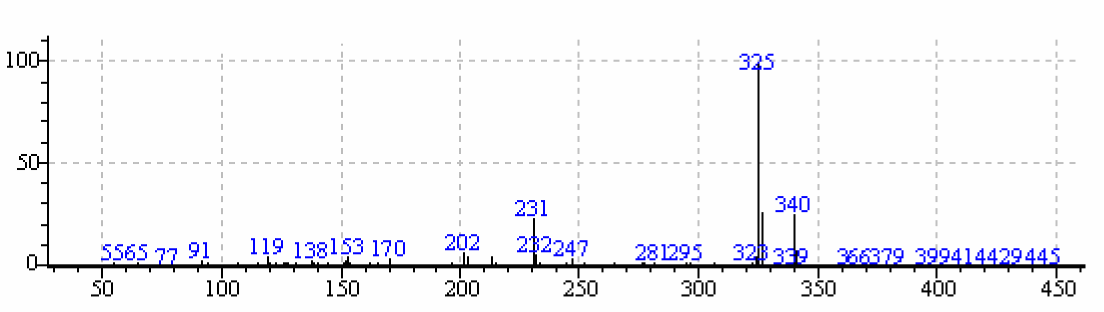


Figure 3.4: Mass spectrum of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane

The purity of NABP determined by HPLC was found to be 99.8 % **(Figure 3.5)**

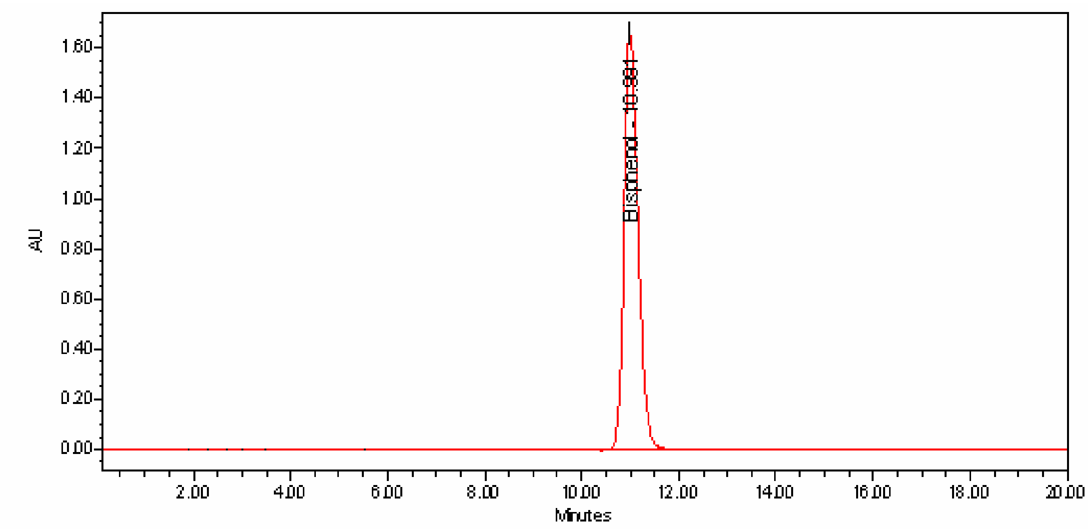
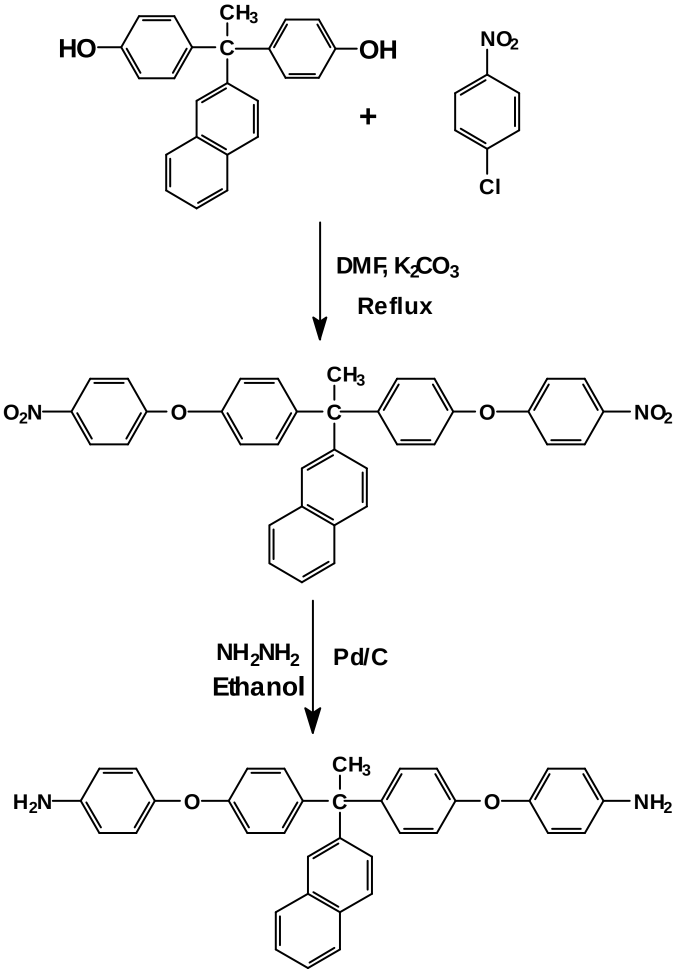


Figure 3.5 : HPLC trace of 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)]ethane

3.4.1.2 Synthesis and characterization of 1,1-bis-[4-(4-aminophenoxy) phenyl-1-(2-naphthyl)] ethane.

Scheme 3.2 shows the route for synthesis of NABPDA

The dinitro intermediate 1,1 bis-[4-(4-nitrophenoxy)phenyl]-1-(2-naphthyl) ethane (DNNABP) was synthesized by nucleophilic substitution reaction of *p*-chloronitro benzene with NABP in the presence of anhydrous potassium carbonate in N,N dimethyl formamide. DNNABP was reduced to 1,1-bis-[4-(4-aminophenoxy) phenyl]-1-(2-naphthyl) ethane (NABPDA) by hydrazine hydrate in presence of palladium on carbon (10 wt %) in ethanol.



Scheme 3.2: Synthesis of 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2- naphthyl)] ethane

FTIR spectra of NABPDA (spectrum A) and DNNABP (spectrum B) are presented in **Figure 3.6**. DNNABP showed bands at 1342 and 1520 cm^{-1} corresponding to symmetric and asymmetric stretching of nitro group, respectively. NABPDA showed bands at 3444, 3371 cm^{-1} corresponding to primary-NH stretching.

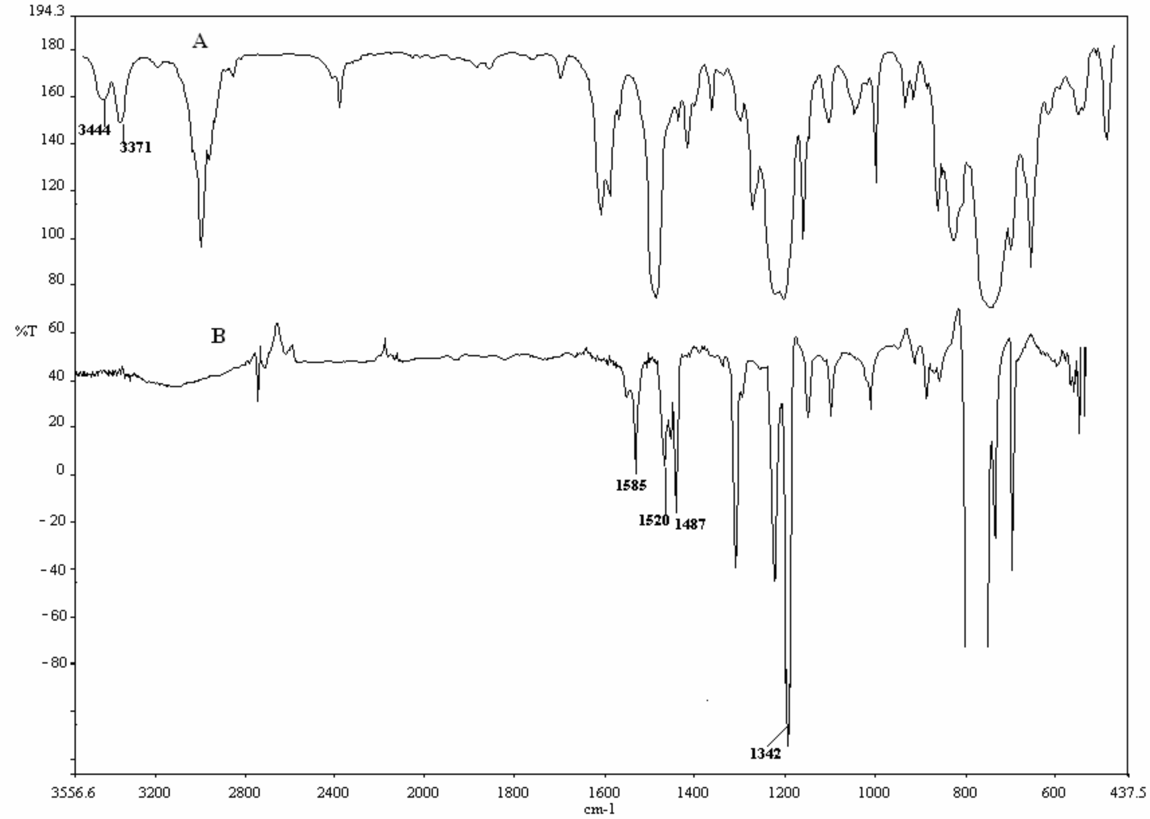


Figure 3.6: FT-IR spectra of 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)] ethane (A) and 1,1 bis-[4-(4-nitrophenoxy) phenyl-1-(2-naphthyl)] ethane(B)

^{1}H NMR spectra of DNNABP and NABPDA along with the assignments are presented in **Figure 3.7** and **Figure 3.8** respectively. The peaks corresponding to aromatic protons e ortho to the nitro group which appeared at 8.20 δ ppm in DNNABP were shifted to 6.68 δ ppm in NABPDA (protons e ortho to amino group in NABPDA) when nitro group was transformed to amino group . The upfield shift of protons in case of NABPDA is due to the shielding effect of amino group, this confirms the complete reduction of DNNABP to NABPDA.

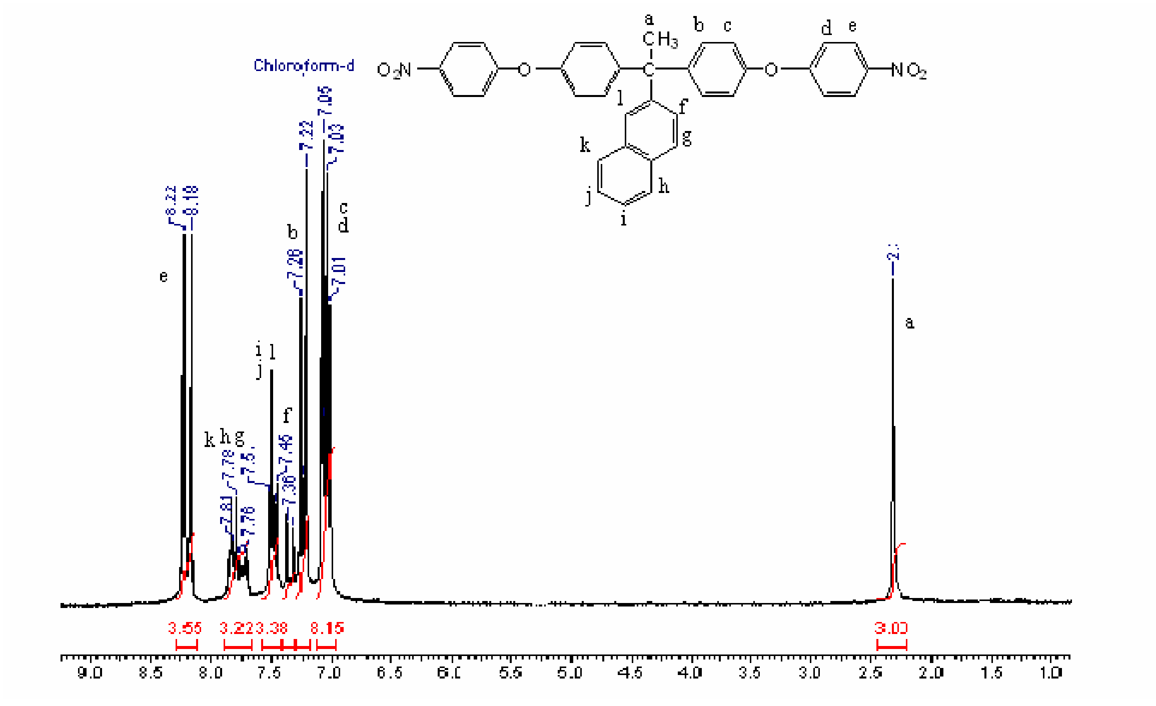


Figure 3.7: ^{1}H-NMR spectrum of 1,1 bis-[4-(4-nitrophenoxy)phenyl-1-(2-naphthyl)] ethane in $CDCl_3$

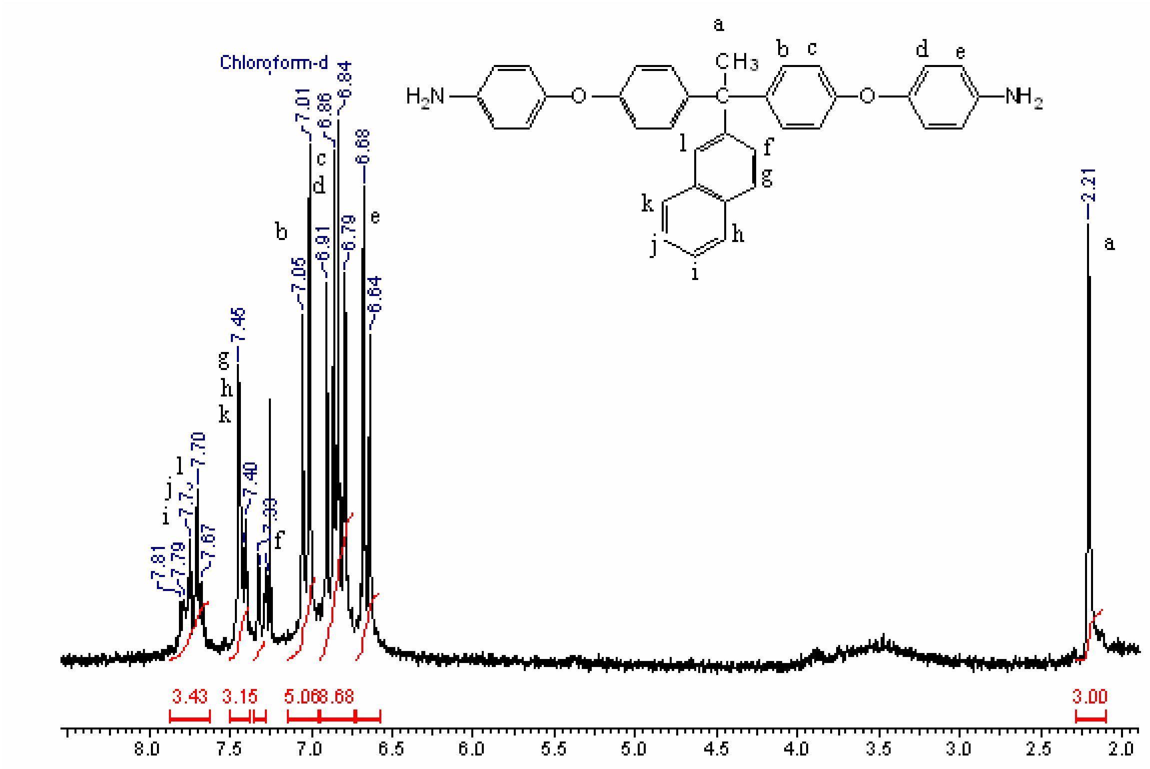


Figure 3.8: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-aminophenoxy)phenyl]-1-(2-naphthyl) ethane in $CDCl_3$

^{13}C NMR spectra of DNNABP and NABPDA are reproduced in **Figure 3.9** and **Figure 3.10** respectively. Carbons j and g of DNNABP are observed at 162.88 δ ppm and 152.96 δ ppm whereas carbons j and g of NABPDA are observed at 146.31 δ ppm and 147.53 δ ppm respectively. The upfield shift of the aromatic carbons *ortho* and *para* to the amino groups in NABPDA were observed because of the resonance effect (+ R) caused by the electron donating amino groups.

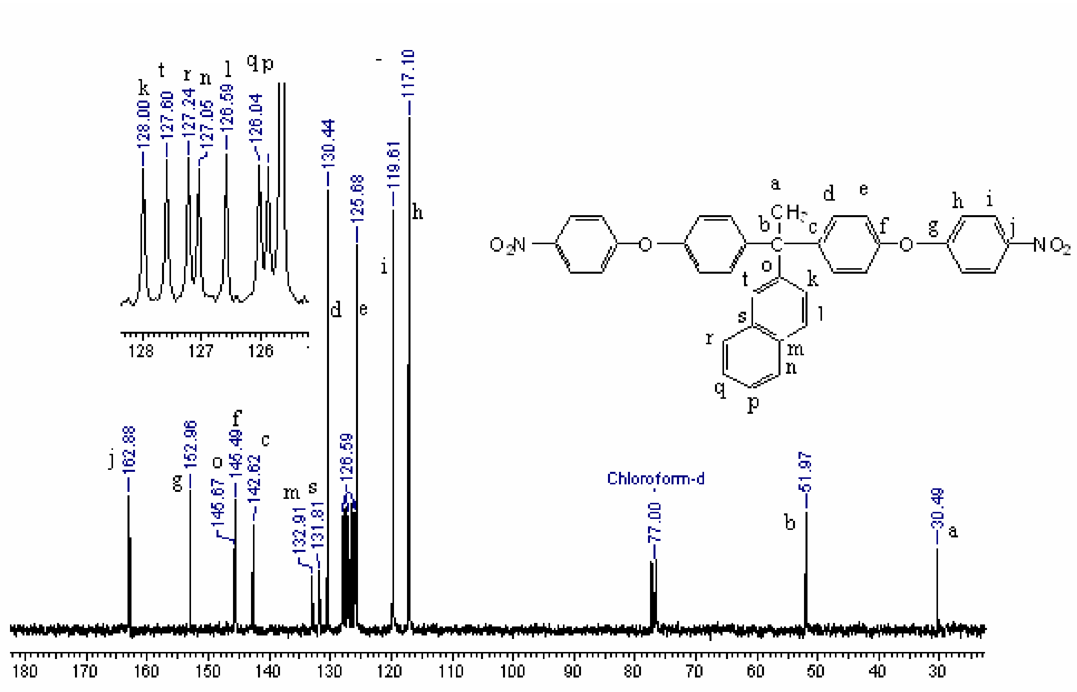


Figure 3.9: ^{13}C-NMR spectrum of 1,1 bis-[4-(4-nitrophenoxy)phenyl-1-(2-naphthyl)] ethane in $CDCl_3$

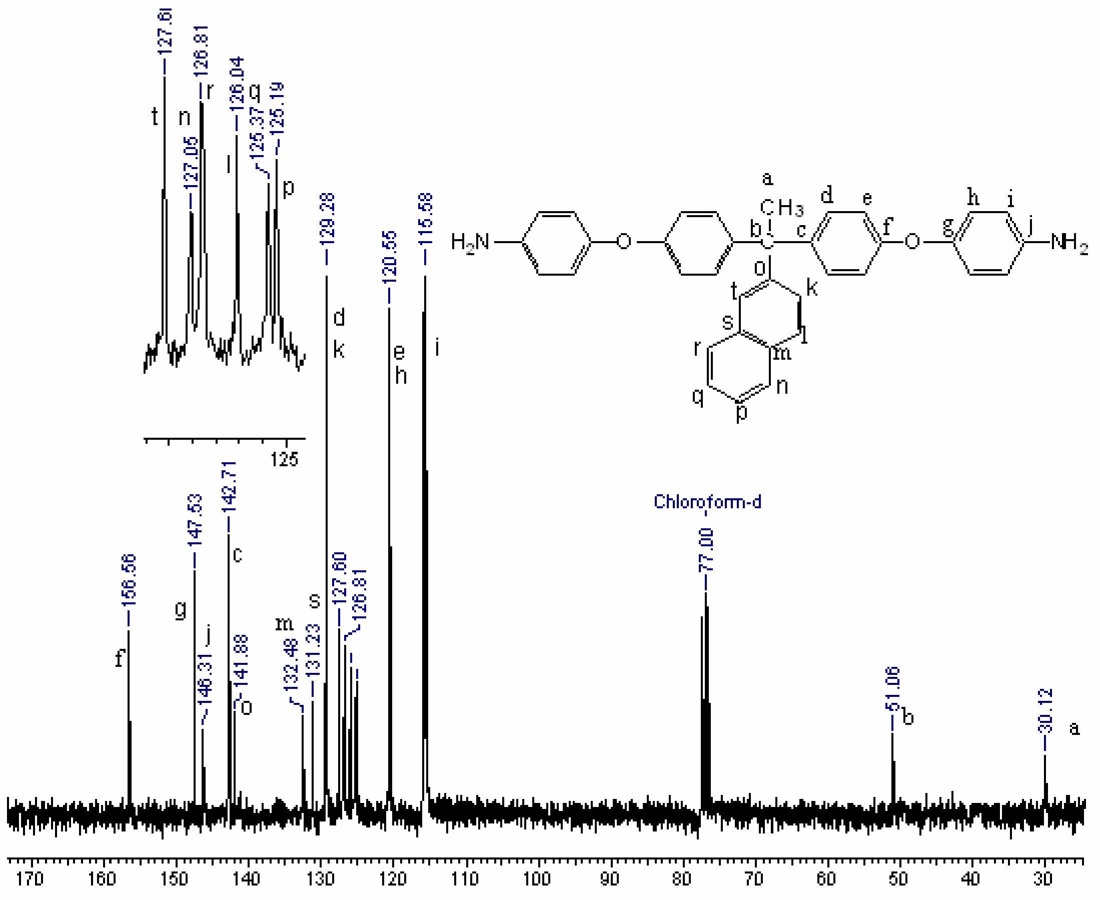
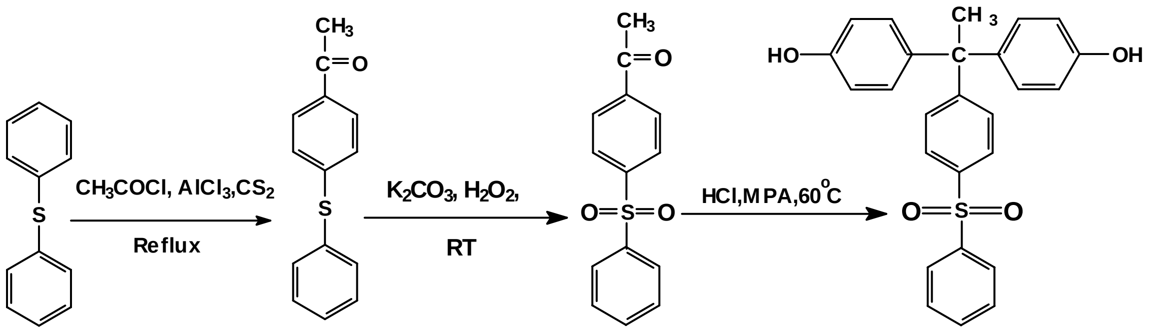


Figure 3.10: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)] ethane in $CDCl_3$

3.4.1.3 Synthesis and characterization of 1,1-bis-[(4-hydroxyphenyl)-1-(4 phenyl sulfonyl phenyl)] ethane (DPSBP)

Scheme 3.3 depicts route for synthesis of DPSBP. The two intermediates 4-(phenyl thio) acetophenone and 4-(phenylsulfonyl) acetophenone have been reported previously in the literature[35,36]. Diphenylsulfide was monoacylated with acetyl chloride in the presence of aluminum chloride to obtain 4-(phenylthio) acetophenone, which was oxidized using hydrogen peroxide / potassium carbonate mixture to form 4-(phenylsulfonyl) acetophenone. 4-(phenylsulfonyl) acetophenone was condensed with phenol in the presence of HCl /3-MPA as catalyst system to obtain DPSBP. DPSBP was characterized by ^{1}H-NMR **(Figure 3.11)** and mass spectra **(Figure 3.12)**



Scheme 3.3: Synthesis of 1,1-bis-[4-hydroxyphenyl-1-(4 phenyl sulfonyl phenyl)] ethane

^{1}H NMR spectrum of DPSBP showed two doublets at 6.68 δ ppm and 6.80 δ ppm for protons ‘c’ and ‘b’ *ortho* and *meta* respectively to hydroxyl group. Protons ‘f’ appeared down field at 7.91 δppm due to electron withdrawing nature of sulfonyl group. Protons ‘e’ appeared as doublet at 7.70 δ ppm and protons‘d’ appeared at 7.20 δ ppm.

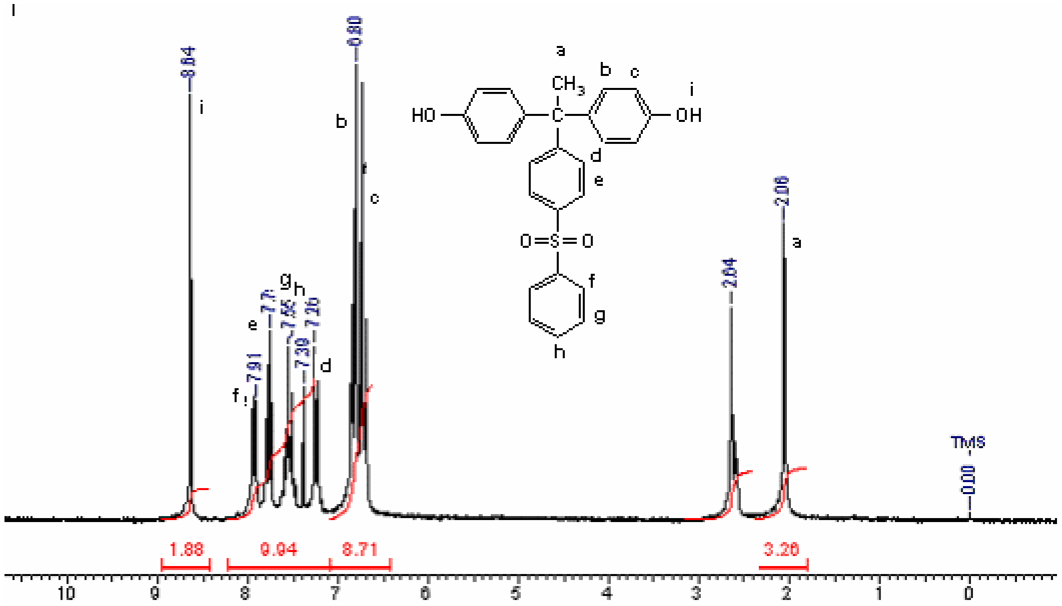


Figure 3.11: ^{1}H-NMR spectrum of 1,1-bis-[4-hydroxyphenyl-1-(4 phenyl sulfonyl phenyl)] ethane in DMSO-d_6

Mass spectrum of DPSBP **(Figure 3.12)** showed molecular ion peak at 415 m/z, indicating the expected molecular weight.

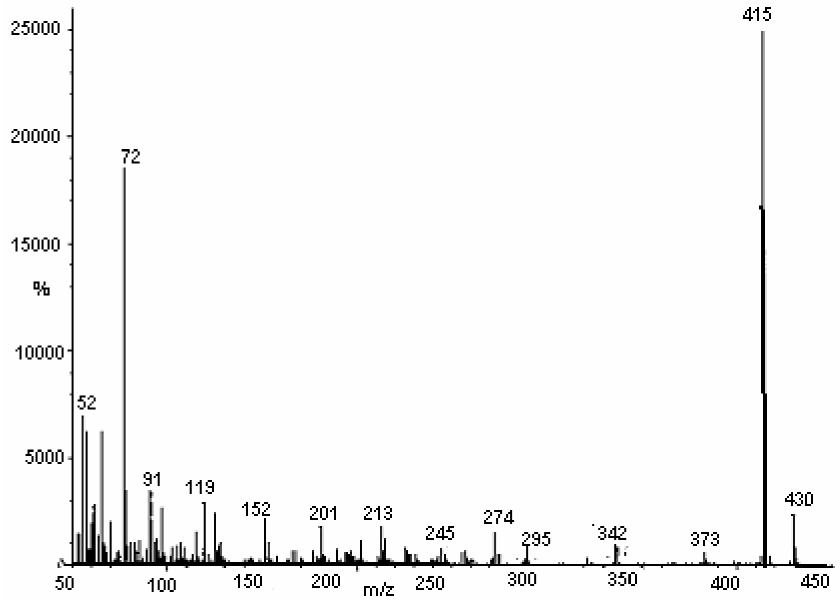


Figure 3.12: Mass spectrum of 1,1-bis-[4-hydroxyphenyl-1-(4 phenyl sulfonyl phenyl)] ethane

The purity of DPSBP was found to be 99.8 % by HPLC (**Figure 3.13**).

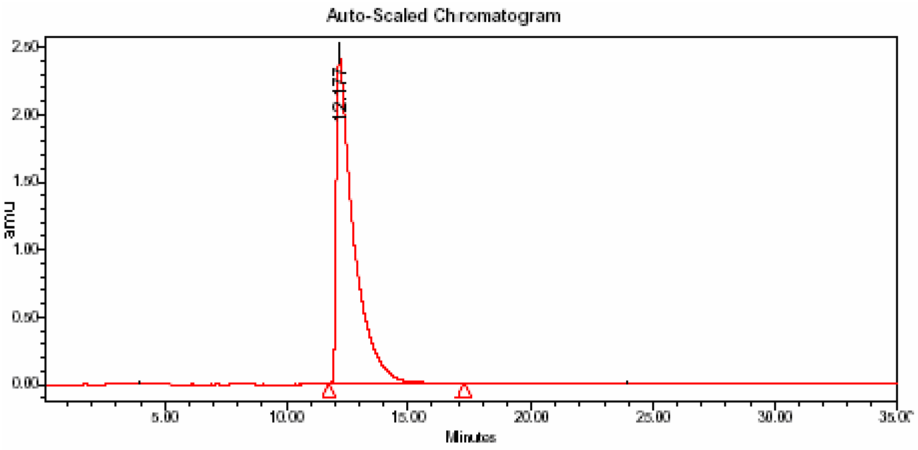
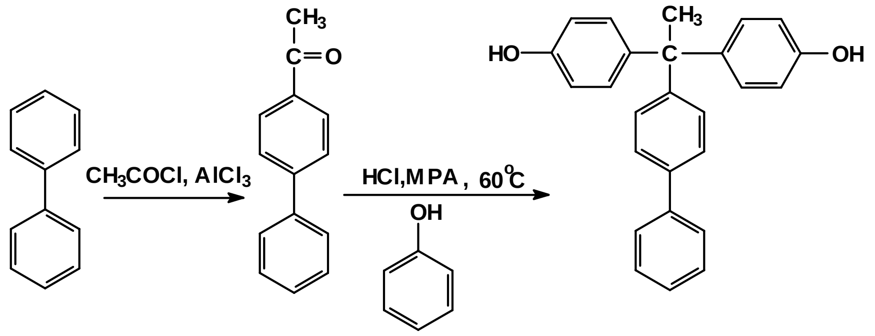


Figure 3.13: HPLC trace of 1,1-bis-[4-hydroxyphenyl-1-(4 phenyl sulfonyl phenyl)] ethane

3.4.1.4 Synthesis and characterization of 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl] ethane (BBHPE)

Scheme 3.4 depicts route for synthesis of bisphenol containing biphenyl pendant group.



Scheme 3.4: Synthesis of 1,1-bis–[4-hydroxyphenyl-(1-biphenyl)] ethane

4-Acetyl biphenyl was synthesized by monoacylation of biphenyl using acetyl chloride as the acylating agent and $AlCl_3$ as the catalyst. 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl]ethane was obtained by the reaction of 4-acetyl biphenyl with excess phenol in the presence of dry HCl gas and 3-mercaptopropionic acid catalyst system at 50 ^{o}C. The role of the 3-mercaptopropionic acid in bisphenol synthesis has been investigated in detail by various researchers.[41,42]. A deep red solid product was obtained after 48 h. The product was isolated by dissolving in ethyl acetate followed by washing with aqueous sodium bicarbonate, brine and water. Excess phenol was removed by distillation and crude product was purified by column chromatography followed by recrystallization from chlorobenzene. Synthesis of 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl]ethane has been previously reported [38a,b].

FT-IR spectra of 4-acetyl biphenyl and BBHPE are given in Figure 3.14. Spectrum A shows a band for phenolic -OH at 3407 cm^{-1} in BBHPE while spectrum B shows the carbonyl stretch at 1680 $cm^{-1}$for the carbonyl group in 4-acetyl biphenyl.

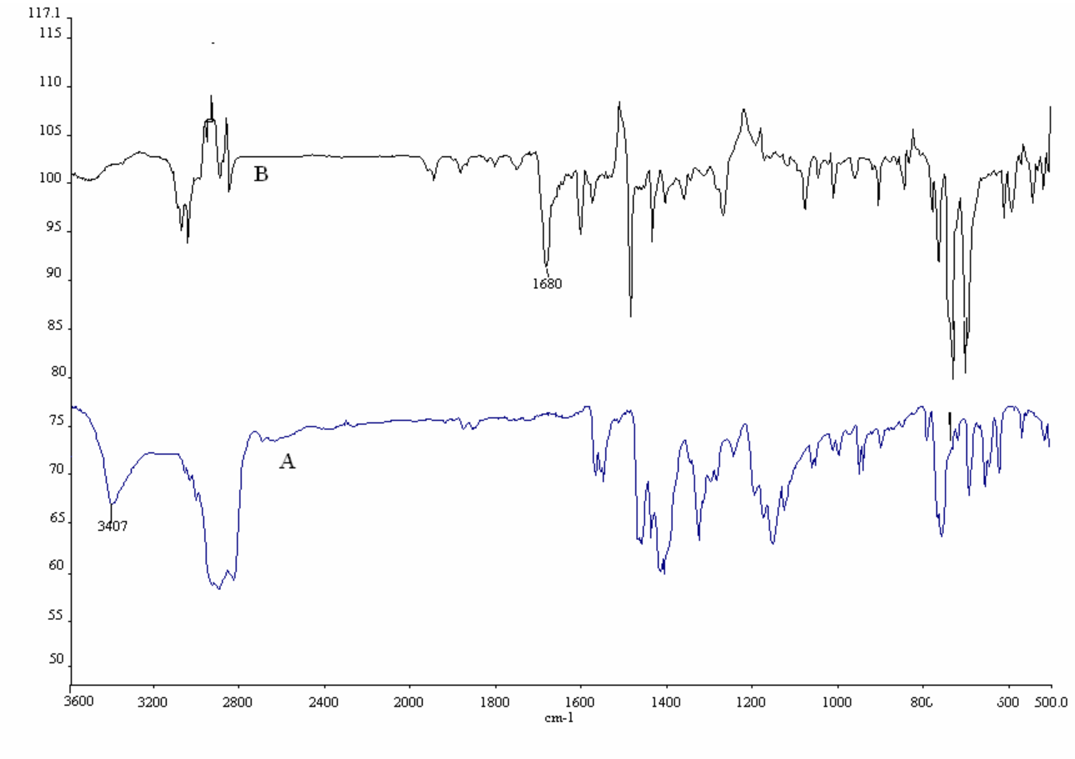


Figure 3.14: FT-IR spectra of 1,1-bis–[4-hydroxyphenyl-(1-biphenyl)] ethane (BBHPE) (A) and 4-acetyl biphenyl (B)

^{1}H-NMR spectrum of 4-acetylbiphenyl is shown in **Figure 3.15.** A doublet at 8.04 δ ppm is observed due to the protons *ortho* to acetyl group. The multiplet in the region 7.40-7.70 δ ppm is observed due to the protons of biphenyl group. A singlet corresponding to methyl group appeared at 2.03 δ ppm

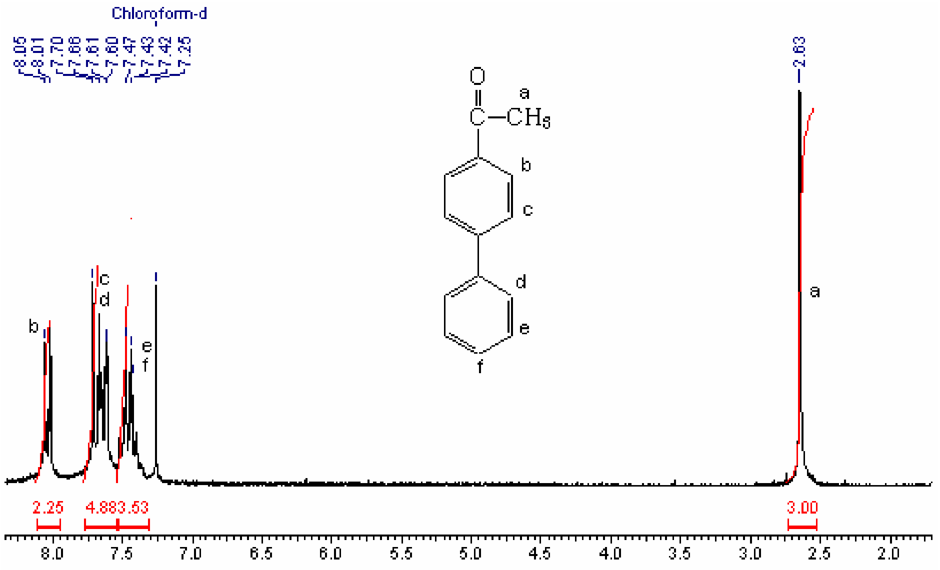


Figure 3.15: ^{1}H NMR spectrum of 4-acetylbiphenyl in CDCl$_3$.

^{1}H-NMR spectrum of 1,1-bis–[4-hydroxyphenyl-(1-biphenyl)]ethane is shown in **Figure 3.16.** A singlet observed at 8.78 δ ppm is assigned to proton of hydroxyl group. The nine protons of biphenyl group exhibited a multiplet in the range 7.06 -7.55 δ ppm. Doublets at 6.70 and 6.96 δ ppm are due to the protons c and b which are *ortho* and *meta* to the hydroxyl group, respectively. A singlet corresponding to the methyl group attached to bridge carbon atom appeared at 2.11 δ ppm.

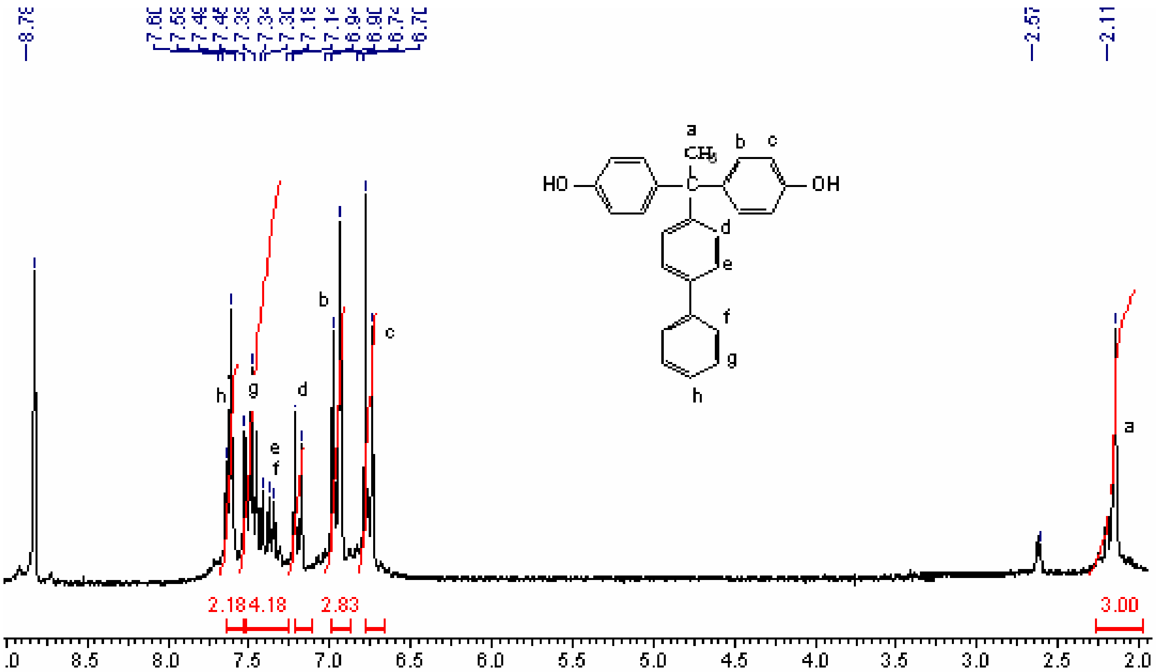


Figure 3.16: ^{1}H-NMR spectrum of 1,1-bis–[4-hydroxyphenyl-(1-biphenyl)]ethane in DMSO-d_6.

^{13}C-NMR spectrum of 1,1-bis (4-hydroxy phenyl) 1- biphenyl ethane along with assignment of the carbon atoms is shown in **Figure 3.17.**

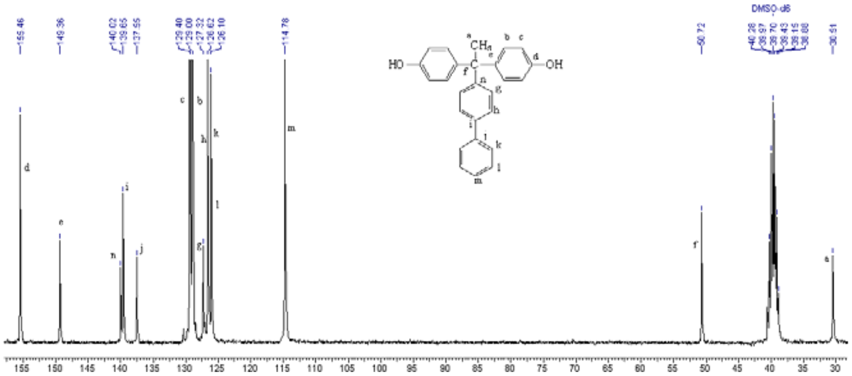


Figure 3.17: ^{13}C-NMR spectrum of 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl] ethane in DMSO-d_6

Mass spectrum of BBHPE **(Figure 3.18)** showed molecular ion peak at 366 m/z, consistent with the molecular weight of BBHPE.

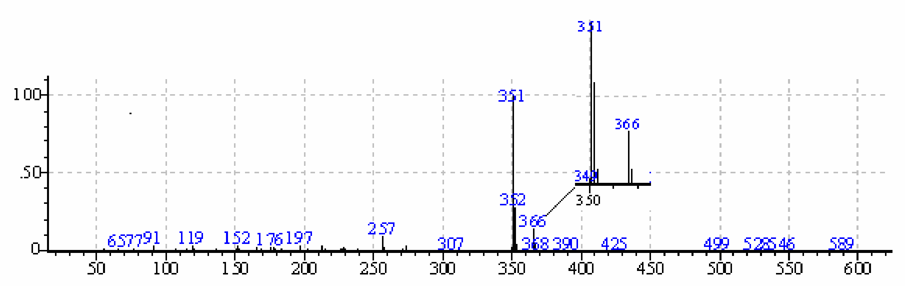


Figure 3.18: Mass spectrum of 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl]ethane

The purity of BBHPE was determined by HPLC and was found to be 99.8 %. **(Figure 3.19)**

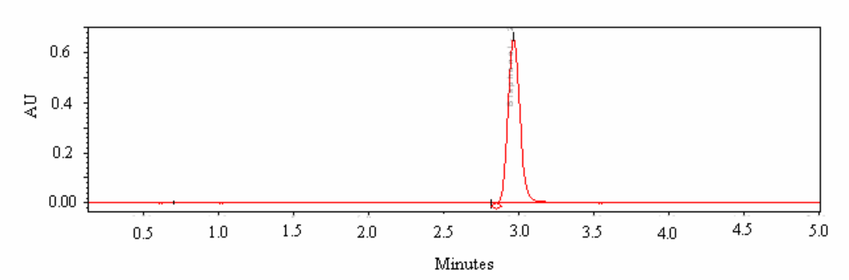
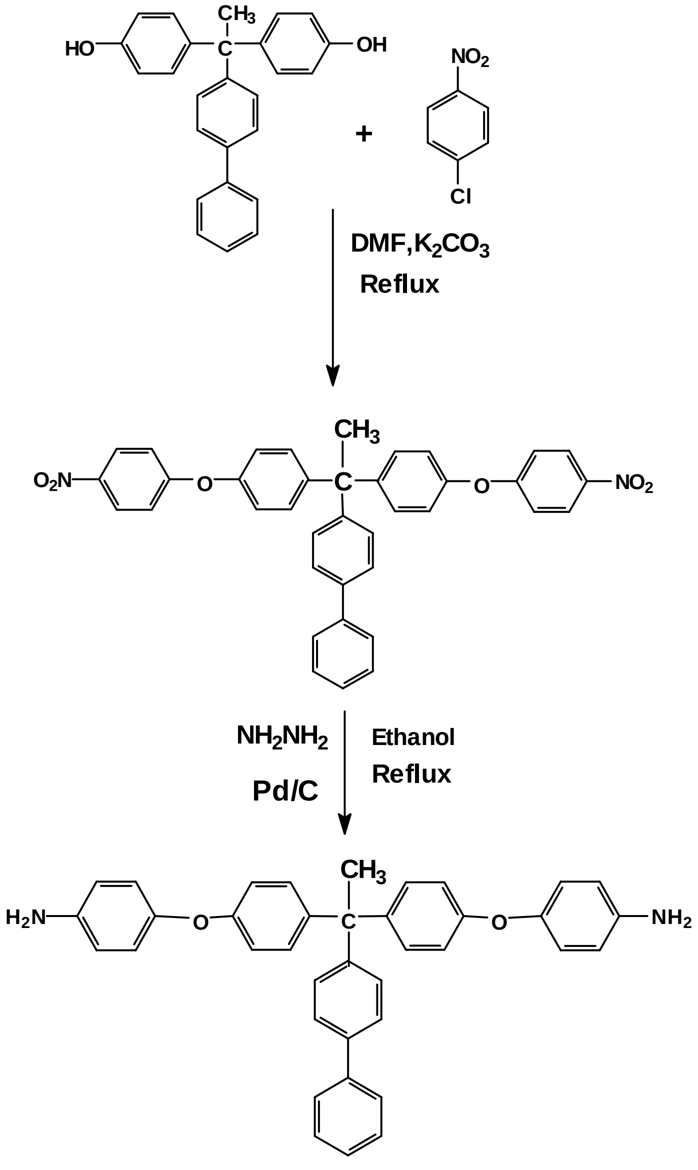


Figure 3.19: HPLC trace of 1,1-bis–[(4-hydroxyphenyl)-1-biphenyl] ethane

3.4.1.5 Synthesis and characterization of 1,1 bis-[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane.

Scheme 3.5 depicts route for synthesis of BBHPDA.



Scheme 3.5 Synthesis of 1,1 bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane

FT-IR spectra of DNBBHPE and BBHPDA are presented in **Figure 3.20**. Spectrum

The dinitro intermediate 1,1-bis-[4-(4-nitrophenoxy) phenyl-1-biphenyl] ethane was synthesized by nucleophilic substitution reaction of p-chloronitrobenzene with BBHPE in the presence of anhydrous potassium carbonate in N,N-dimethyl formamide. The reduction of DNBBHPE was carried out by hydrazine hydrate in the presence of palladium on carbon (10 wt %) in ethanol to obtain 1,1 bis-[4-(4-aminophenoxy) phenyl-1- biphenyl] ethane (BBHPDA)

B for DNBBHPE showed characteristic nitro symmetric and asymmetric stretching at 1340 and 1520 cm^{-1} respectively and BBHPDA (spectrum A) showed bands at 3374 and 3457 cm^{-1} corresponding to primary-NH stretching

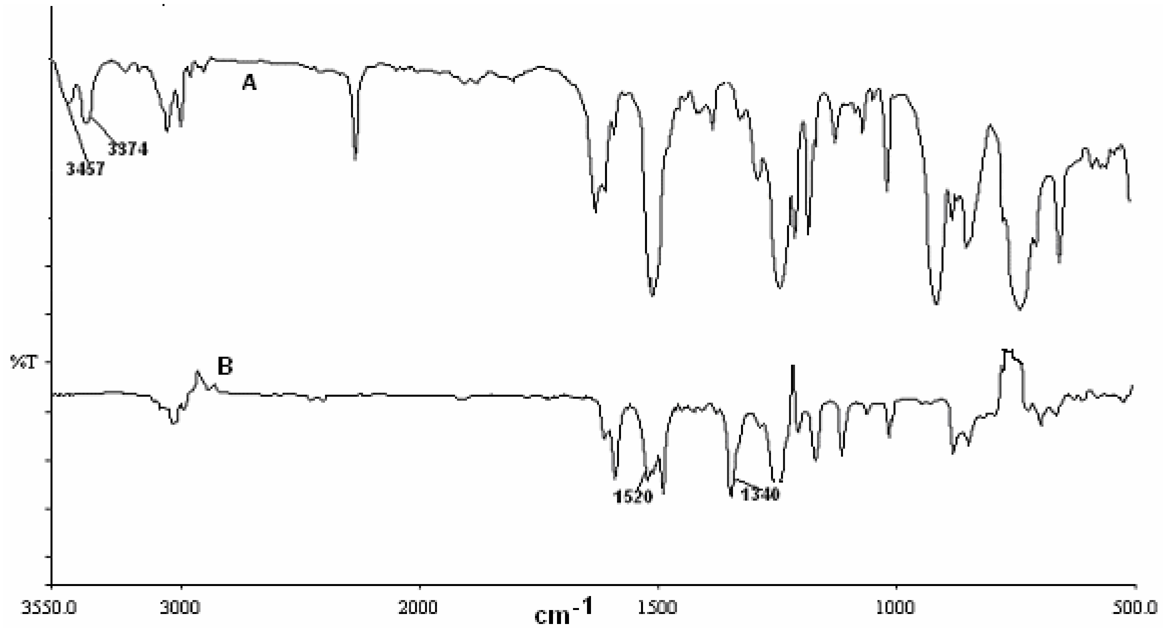


Figure 3.20: FT-IR spectra of 1,1 bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane (A) and 1,1 bis-[4-(4-nitrophenoxy)phenyl-1-biphenyl] ethane (B)

^{1}H-NMR spectra of DNBBHPE and BBHPDA are presented in **Figure 3.21** and **Figure 3.22,** respectively. The peak corresponding to aromatic protons "e" *ortho* to nitro group in DNBBHPE appeared at 8.23 δ ppm (**figure 3.21**).The peak corresponding to aromatic protons ortho to amino group appeared at 6.68 δ ppm (**figure 3.22**). The upfield shift of protons ortho to amino group in case of BBHPDA is due to the shielding effect of amino group.

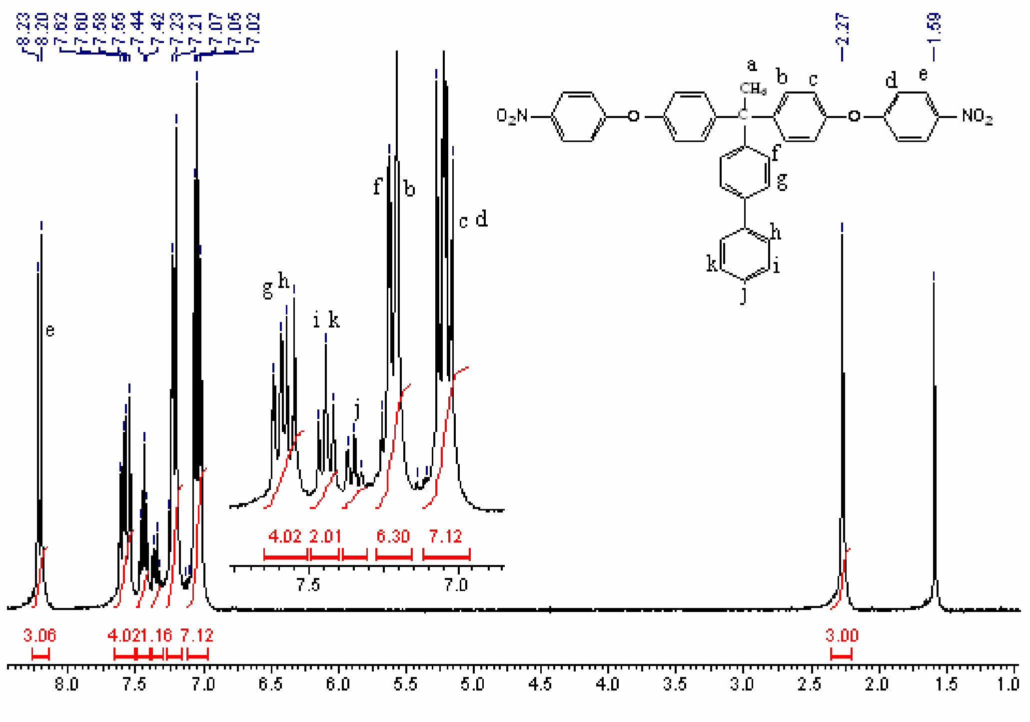


Figure 3.21: ^{1}H-NMR spectrum of 1,1 bis-[4-(4-nitrophenoxy) phenyl-1-biphenyl] ethane in $CDCl_3$

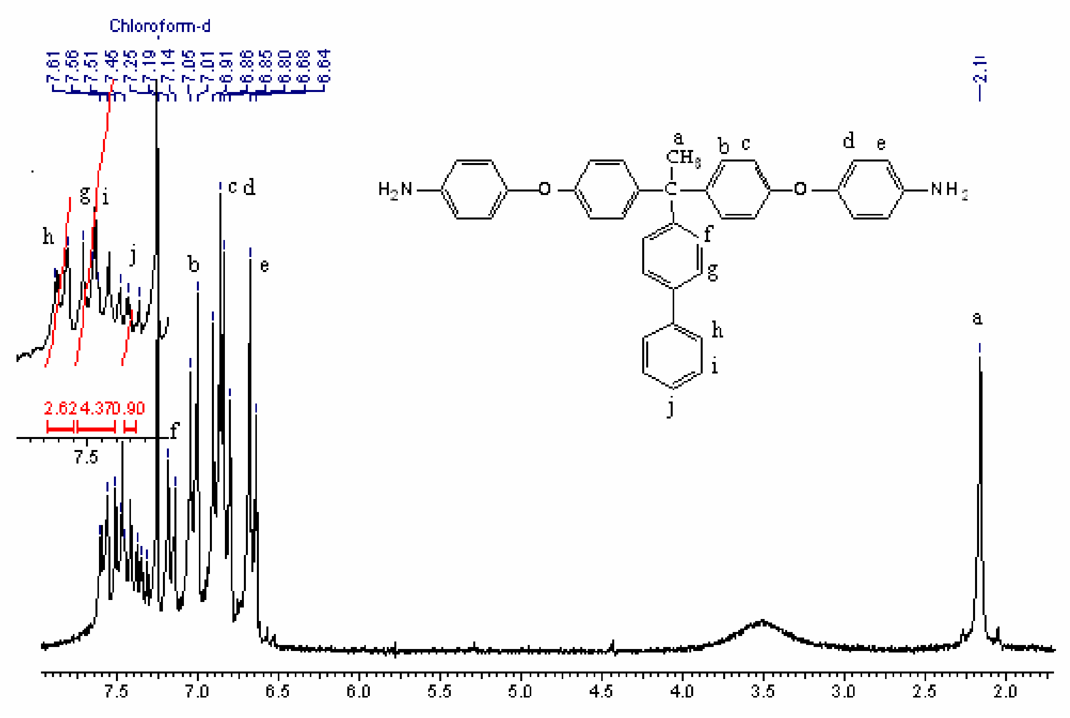


Figure 3.22: ^{1}H-NMR spectrum of 1,1 bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane in $CDCl_3$

^{13}C-NMR spectra of DNBBHPE and BBHPDA are presented in **Figure 3.23** and **Figure 3.24,** respectively**.** Carbons ‘j’ and ‘g’ which were observed at 160.65 δ ppm and 154.45 δ ppm in case of DNBBHPE were shifted upfield and appeared at 148.44 and 148.37 in case of BBHPDA due to the shielding effect caused by the electron donating amino groups.

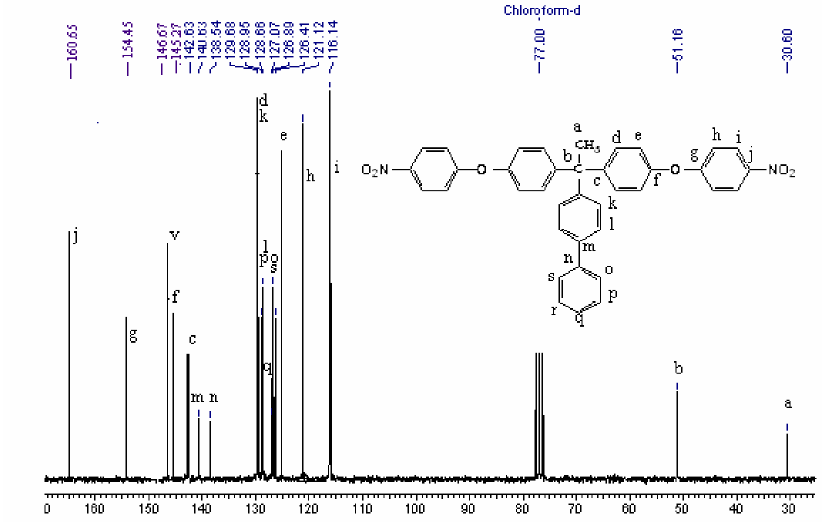


Figure 3.23: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-nitrophenoxy)phenyl-1-biphenyl] ethane in CDCl$_3$

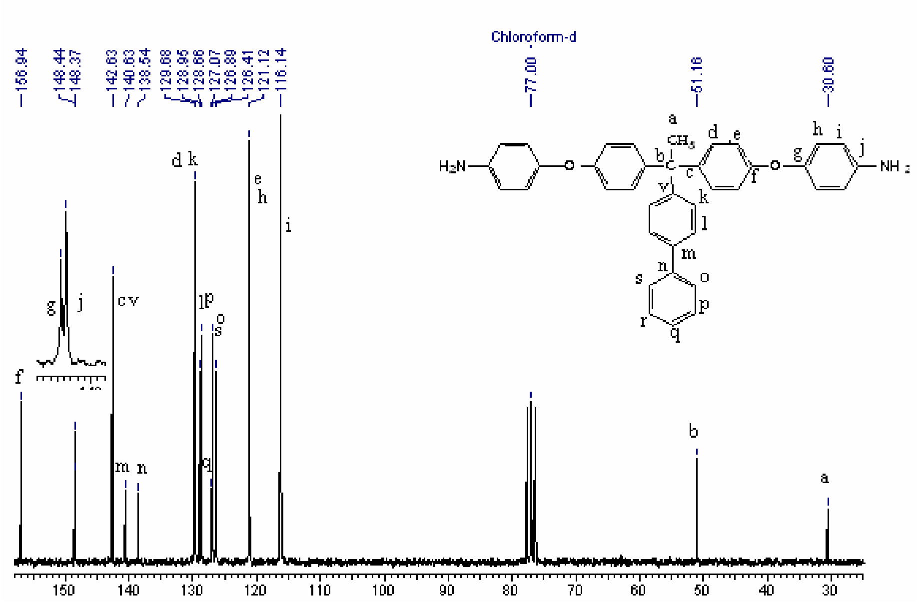


Figure 3.24: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane in $CDCl_3$

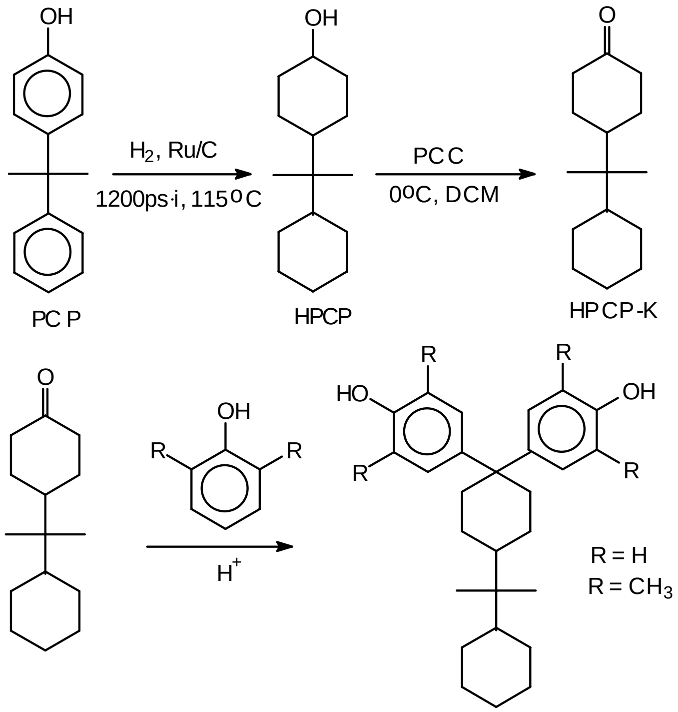
3.4.2 Synthesis and characterization of bisphenols and diamines containing cardo groups

The following three bisphenols (1-3) and two diamine monomers (4,5) containing cardo groups were designed and synthesized starting from *p*-cumylphenol and decahydro 2-naphthol.

1) 1,1-Bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP),
2) 1,1-Bis-(4-hydroxy-3,5-dimethyl phenyl)-4-perhydrocumylcyclohexane (TMPCPBP),
3) 1,1-Bis-[4-(4-aminophenoxy)3,5-dimethyl phenyl]-4-perhydrocumylcyclohexane (TMDA),
4) 1,1-Bis-(4-hydroxyphenyl) octahydro-2(1H)-naphthalene (DCHBP),
5) 1,1-Bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene(DCHDA)

3.4.2.1 Synthesis and characterization of 1,1–bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP)

Scheme 3.6 presents route for synthesis of bisphenols based on *p*-cumylphenol.



Scheme 3.6: Synthesis of bisphenols starting from *p*- cumylphenol

In the first step *p*-cumylphenol was hydrogenated using Ru/C as a catalyst in Parr reactor using isopropanol as solvent. The reaction was stopped when hydrogen absorption had ceased. The catalyst was filtered off and filtrate with black tinge was passed through short column of silica gel (100-200 mesh) to obtain colorless solution. Solvent was distilled off under reduced pressure and the residue was treated with 10% NaOH at reflux temperature to ensure the complete removal of any unreacted *p*-cumylphenol. The reaction mixture was extracted in dichloromethane, washed with water, dried with sodium sulfate and filtered. Dichloromethane was distilled off to obtain viscous liquid, which got partially crystallized on prolonged standing. Serijan et. al.[43] separated the solid and crystallized it from petroleum ether. The solid obtained melted over a temperature range of 80-90°C and was found to be mixture of the isomers of 4-(1-cyclohexyl-1-methylethyl) cyclohexanol, hereafter will be referred to as perhydrocumylcyclohexanol (HPCP). The product was characterized by FT-IR and NMR spectroscopy.

In FT-IR spectrum (**Figure 3.25**) of *p*-cumyl phenol (PCP) (spectrum **A**) characteristic bands for aromatic ring at 1612 cm^{-1} and for –OH stretching at 3275 cm^{-1} were observed. The band at 1612 cm^{-1} disappeared when PCP was hydrogenated to obtain hydrogenated *p*-cumyl phenol (HPCP) and FT-IR spectrum of perhydrocumyl cyclohexanol (HPCP) showed –OH stretching at 3275 cm^{-1}(spectrum **B**). In the second step perhydrocumyl cyclohexanol (HPCP) was oxidized using PCC to obtain perhydrocumylcyclohexanone (HPCP-K). The reaction was monitored by FTIR spectroscopy. FTIR spectrum (**Figure 3.25**, spectrum **C**) showed the presence of C=O stretching at 1706 cm^{-1} and the band around 3275 cm^{-1}observed for –OH stretching in HPCP disappeared.

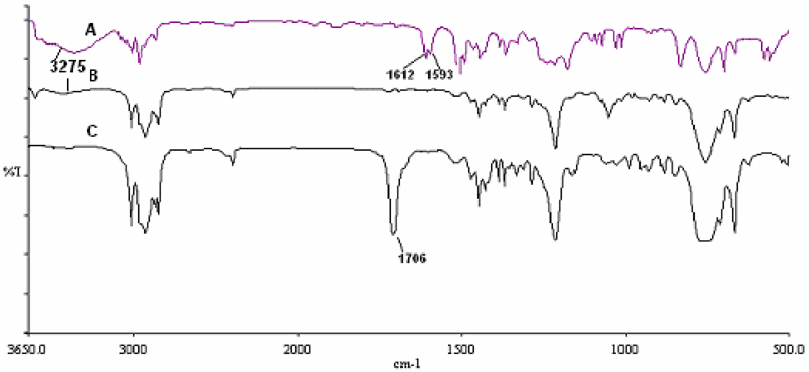


Figure 3.25: FT-IR spectra of PCP (A) , HPCP (B) and HPCP-K(C)

Two isomers of HPCP can be distinguished by ^{1}H-NMR spectroscopy as proton 'a'(axial) and 'e' (equatorial) appeared as multiplets centered at 3.52 and 4.04 δ ppm, respectively (**Figure 3.26**). However, isomer separation and detailed analysis was not carried out as it was beyond the scope of work. ^{1}H NMR spectrum of perhydrocumylcyclohexanone showed the absence of protons on the carbon atom to which –OH group is attached, that were present in ^{1}H NMR spectrum of perhydrocumylcyclohexanol at 3.52 and 4.04 δ ppm**.**

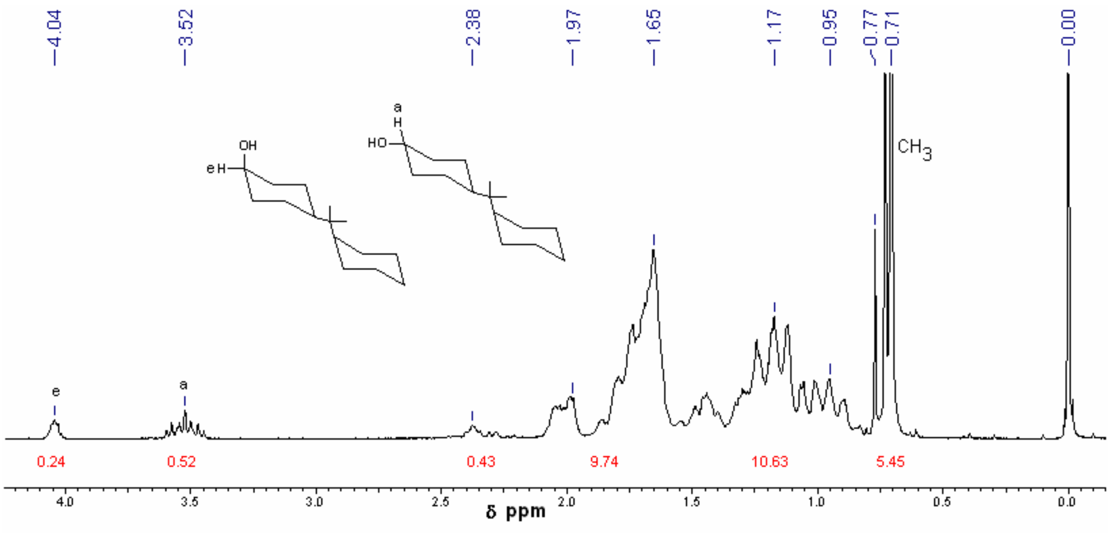


Figure 3.26: ^{1}H-NMR spectrum of perhydrocumylcyclohexanol in CDCl$_3$

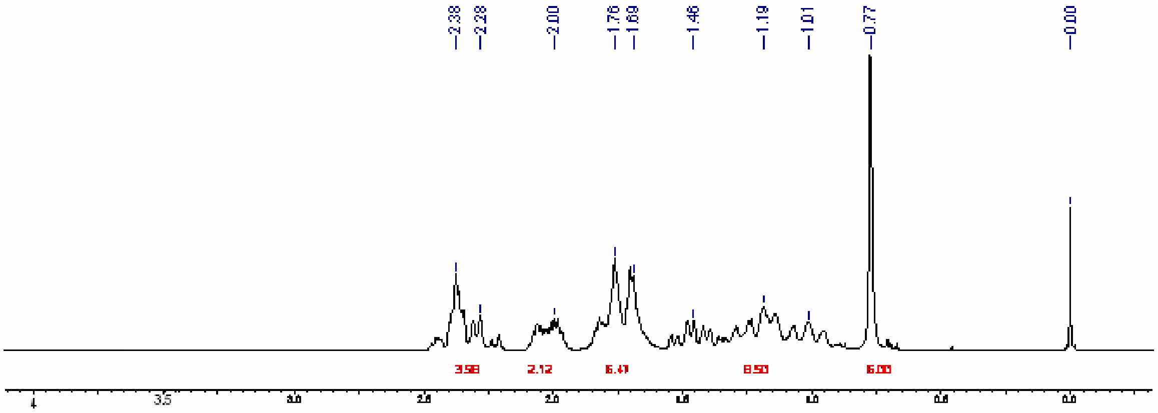


Figure 3.27 : ^{1}H-NMR spectrum of perhydrocumylcyclohexanone in CDCl$_3$

1,1-Bis [(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP) was prepared by hydrogen chloride, 3-mercaptopropionic acid catalyzed condensation of perhydrocumylcyclohexanone with phenol. PCPBP was recrystallized twice from toluene.

PCPBP was characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

FTIR spectrum of PCPBP showed a broad band at 3296 cm^{-1} corresponding to –OH stretching.

^{1}H NMR and ^{13}C NMR spectra along with the assignments are presented in **Figure 3.28** and **3.29** respectively. ^{1}H NMR spectrum showed the presence of diastereotopic phenyl rings, which are magnetically non-equivalent. PCPBP is not symmetrical about a C_2 axis between the two phenolic rings and this results in different environments for two phenyl rings, hence the aromatic rings showed four doublets for protons c, c' and d, d' in ^{1}H NMR spectrum and two sets of four aromatic shifts for carbons 16,16'17,17'18,18'and 19,19' in ^{13}C spectrum. The complete assignment of the spectrum considering axial and equatorial hydrogen atoms of each cyclohexyl ring with the help of 2D NMR spectroscopy has been studied and reported previously.[19]

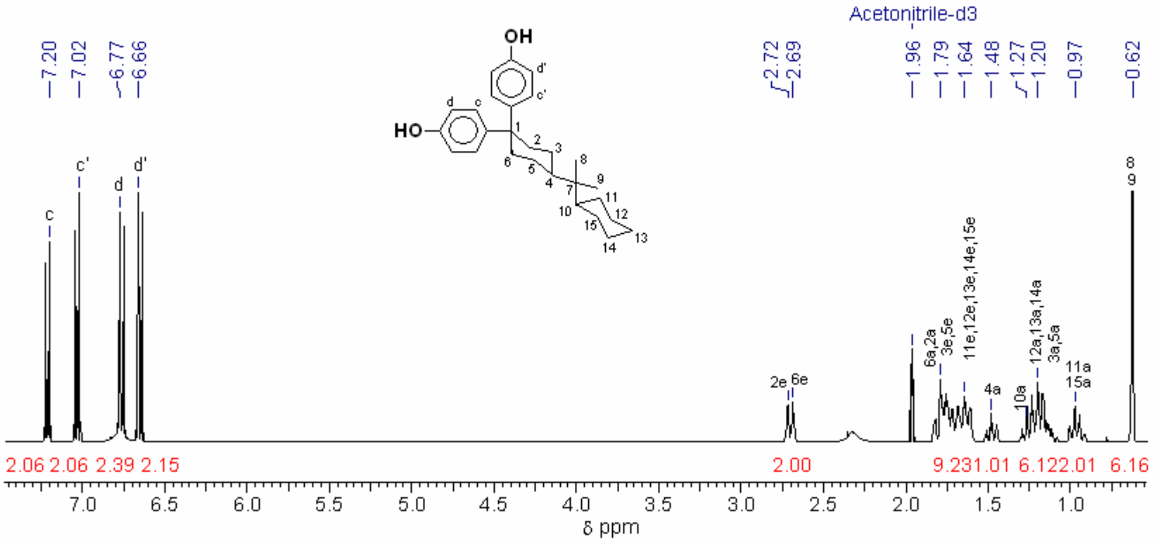


Figure 3.28: ^{1}H-NMR spectrum of 1,1-bis(4-hydroxyphenyl)-4-perhydrocumyl cyclohexane in CD_3CN

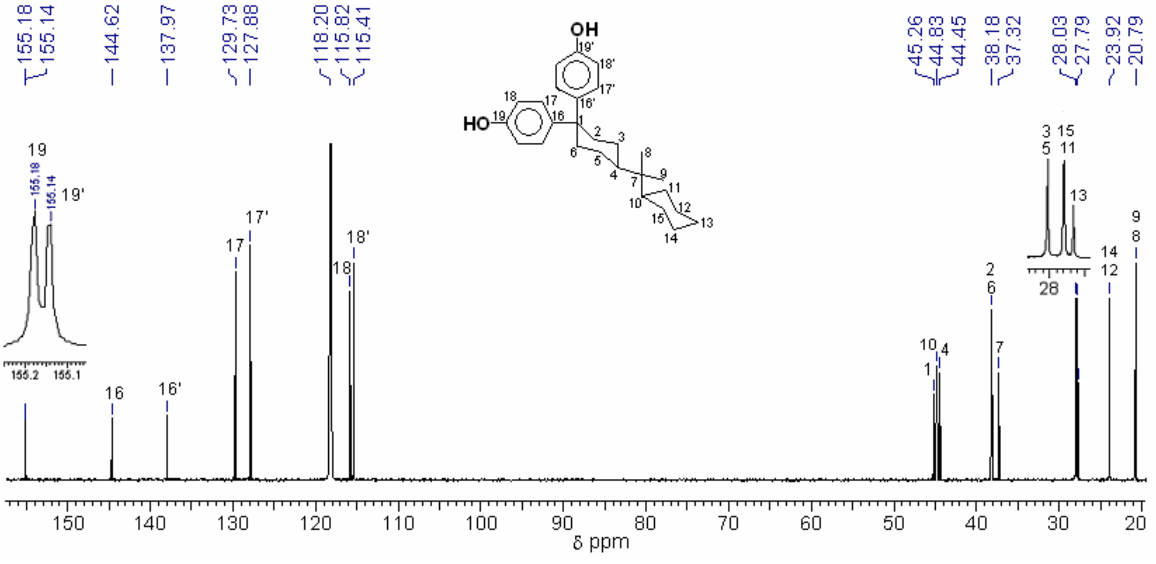


Figure 3.29: ^{13}C-NMR spectrum of 1,1-bis (4-hydroxyphenyl) -4-perhydrocumyl cyclohexane in CD_3CN

The mass spectrum (**Figure 3.30**) of PCPBP showed molecular ion peak at 392 m/z consistent with its molecular weight.

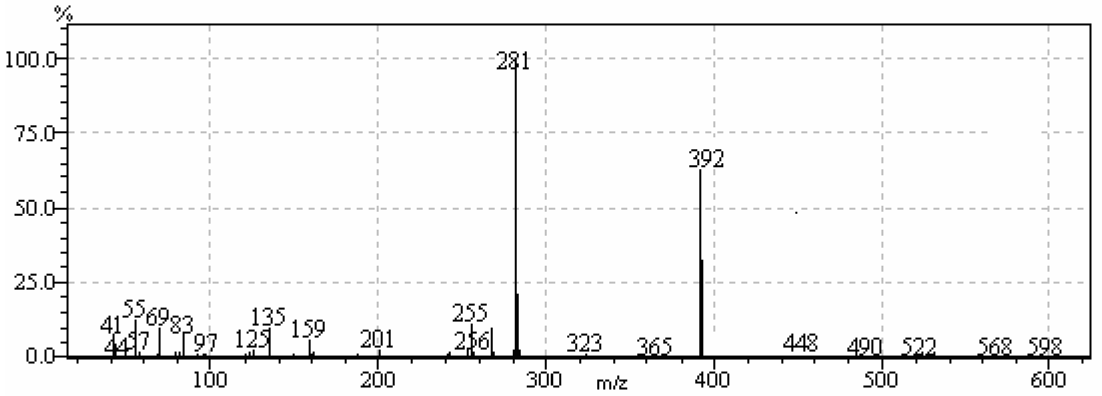


Figure 3.30: Mass spectrum of 1,1-bis(4-hydroxyphenyl) -4-perhydrocumyl cyclohexane

The purity of PCPBP was determined by HPLC, and was found to be 99.8 % (**Figure 3.31**).

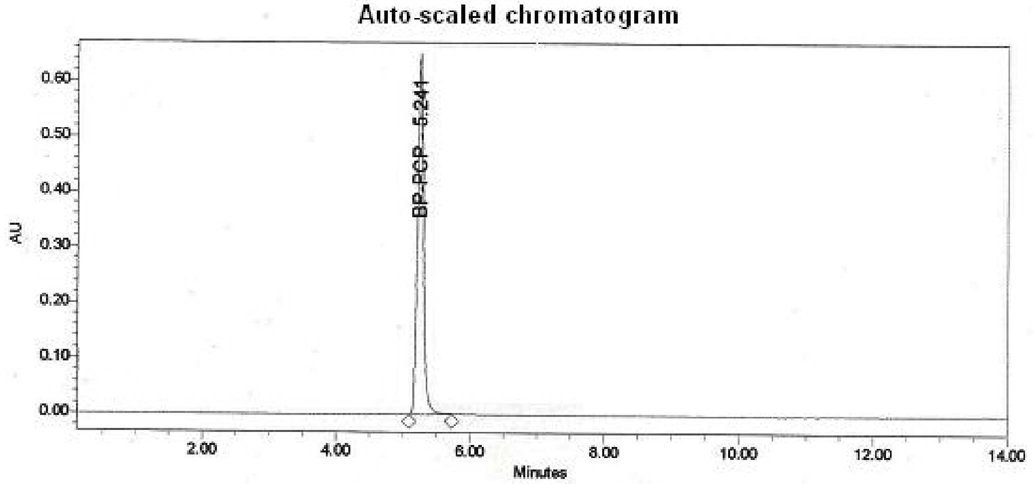


Figure 3.31: HPLC trace of 1,1-bis(4-hydroxyphenyl)-4-perhydrocumyl cyclohexane

3.4.2.2 Synthesis and characterization of 1,1-bis(4-hydroxy-3,5-dimethylphenyl) -4-perhydrocumyl cyclohexane (TMPCPBP)

Scheme 3.6 (R=CH_3) depicts route for synthesis of 1,1-bis (4-hydroxy-3,5-dimethylphenyl) -4-perhydrocumyl cyclohexane (TMPCPBP).

TMPCPBP was synthesized by condensation of perhydrocumylcyclohexanone with 2,6-dimethyl phenol in HCl /acetic acid mixture (2:1, v/v) at room temperature. The solid mass formed at the end of reaction was dissolved in ethyl acetate and the solution was washed with aqueous sodium bicarbonate followed by brine and water, dried over anhydrous sodium sulfate, filtered and ethyl acetate was evaporated off to obtain the crude product which was crystallized from hexane/toluene mixture to yield white crystals of TMPCPBP. TMPCPBP was characterized by FT-IR, ^{1}H and ^{13}C- NMR and mass spectroscopy.

FTIR spectrum of TMPCPBP showed broad band at 3389 cm^{-1} corresponding to –OH stretching . ^{1}H NMR spectrum of TMPCPBP along with assignments is presented in **Figure 3.32.** As observed in ^{1}H NMR spectrum of PCPBP, ^{1}H NMR spectrum of TMPCPBP also showed the presence of diastereotopic phenyl rings, which are magnetically non-equivalent. TMPCPBP molecule is not symmetrical about a C_2 axis between the two phenolic rings and this results in different magnetic environments for two phenyl rings. This was observed in ^{1}H NMR spectrum where the two singlets c and c' are due to the aromatic hydrogen of two different phenyl rings, f ,f' and h, h' due to the methyl groups and hydroxyl groups present on the different phenyl rings. Methyl protons 8 and 9 appeared as singlet at 0.60 δ ppm. The aliphatic protons attached to cyclohexyl rings appeared as multiplets in the range 0.74-2.66 δ ppm.

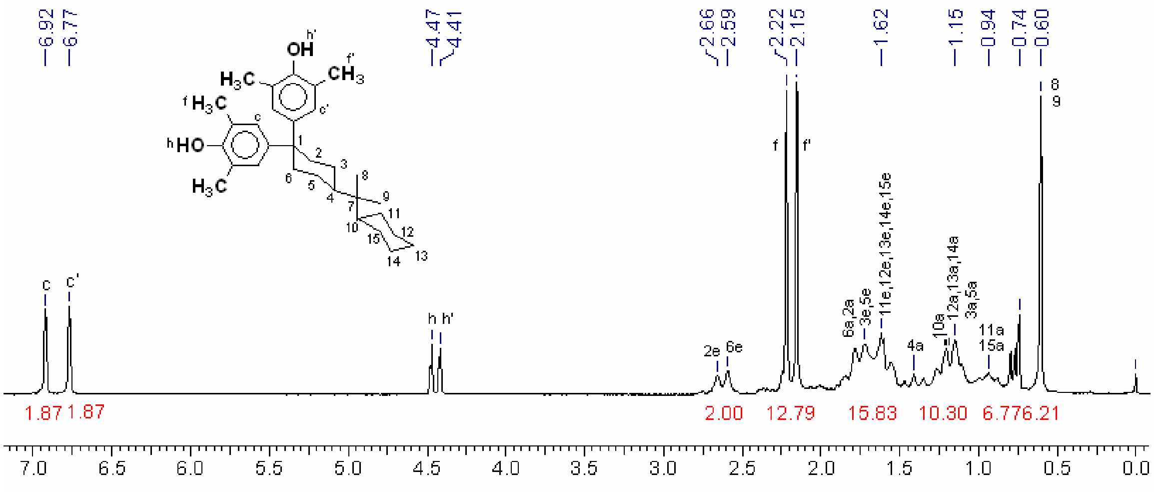


Figure 3.32: ^{1}H-NMR spectrum of 1,1-bis(4-hydroxy-3,5-dimethylphenyl) -4-perhydrocumyl cyclohexane in $CDCl_3$

^{13}C NMR spectrum of TMPCPBP along with assignments are presented in **Figure3.33.**

The peaks for the two nonequivalent aromatic carbons 17, 17’were observed at 128.05 and 126.31 δ ppm. Similarly carbons 16, 16’, 19,19’ and a,a’ also appeared as two different peaks due to difference in the magnetic environment.

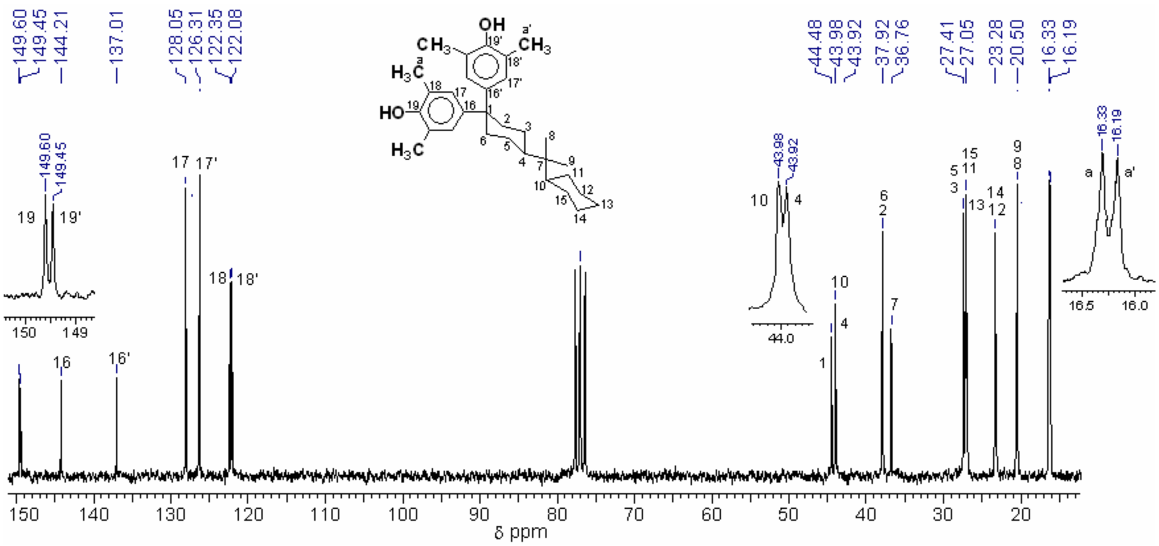


Figure 3.33: ^{13}C-NMR spectrum of 1,1-bis(4-hydroxy-3,5-dimethylphenyl) -4-perhydrocumyl cyclohexane (TMPCPBP) in CDCl$_3$

Mass spectrum of TMPCPBP shows molecular ion peak at 448 m/z which agrees with the expected molecular weight (**Figure 3.34**).

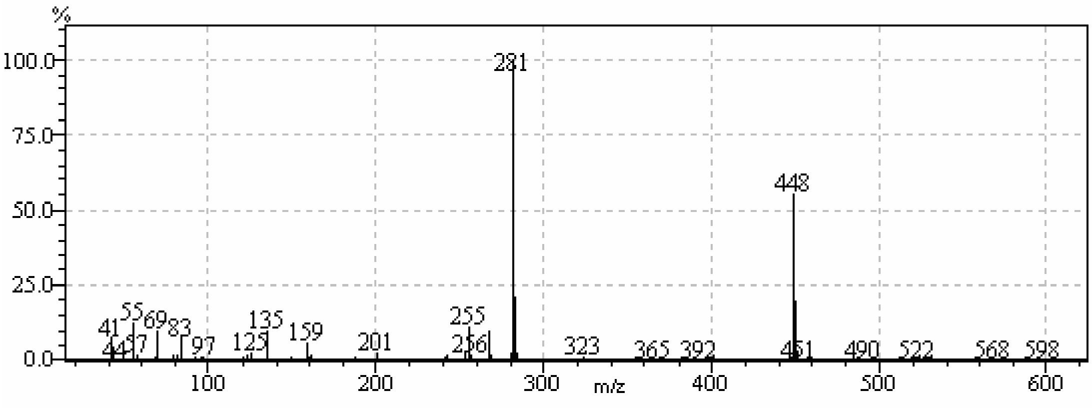


Figure 3.34: Mass spectrum of 1,1-bis(4-hydroxy-3,5-dimethylphenyl) -4-perhydrocumyl cyclohexane

The purity of bisphenol was checked by HPLC and was found to be 99.8 % (**Figure 3.35)**

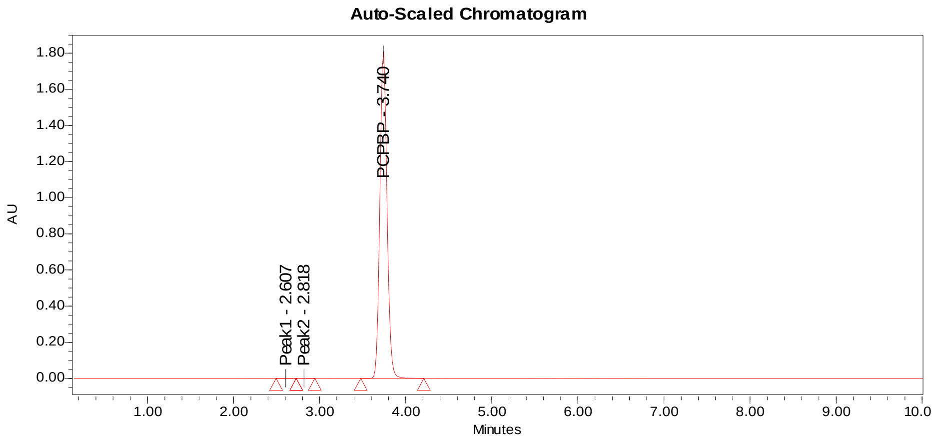
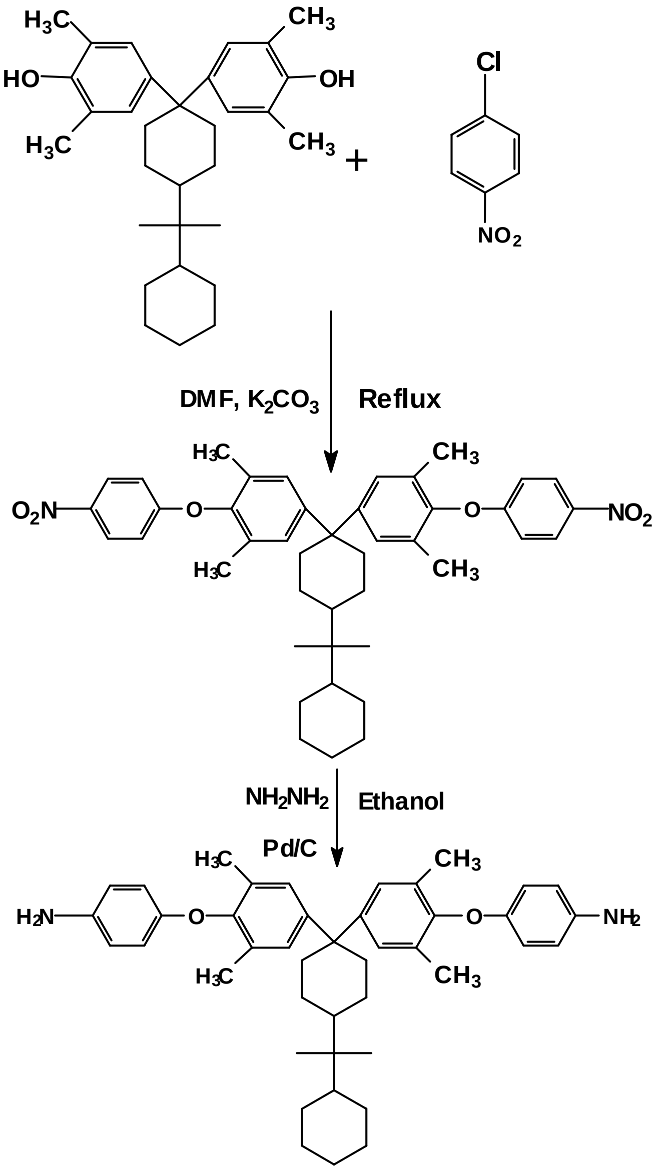


Figure 3.35: HPLC trace of 1,1-bis(4-hydroxy-3,5-dimethylphenyl) -4-perhydrocumyl cyclohexane

3.4.2.3 Synthesis and characterization of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA).

Scheme 3.7 shows route for the synthesis of 1,1-bis-[4-(4-aminophenoxy)3,5-dimethyl phenyl]-4-perhydrocumylcyclohexane (TMDA). The dinitro compound 1,1-bis-[4-(4-nitrophenoxy)-3,5-dimethylphenyl]-4-erhydrocumylcyclohexane (DNTMPCPBP), was synthesized by nucleophilic substitution of *p*- chloronitro benzene with TMPCPBP in DMF in the presence of anhydrous potassium carbonate. This dinitro intermediate was reduced to diamine with hydrazine hydrate using Pd/C as catalyst in ethanol.



Scheme 3.7: Synthesis of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane

IR spectra of DNTMPCPBP and TMDA are shown in **Figure 3.36.** Spectrum ‘A’ showed bands at 3422, 3368 cm^{-1} for -NH_2 group stretching and spectrum B showed bands characteristic for asymmetric and symmetric nitro group stretching at 1517 and 1339 cm^{-},^{1} respectively.

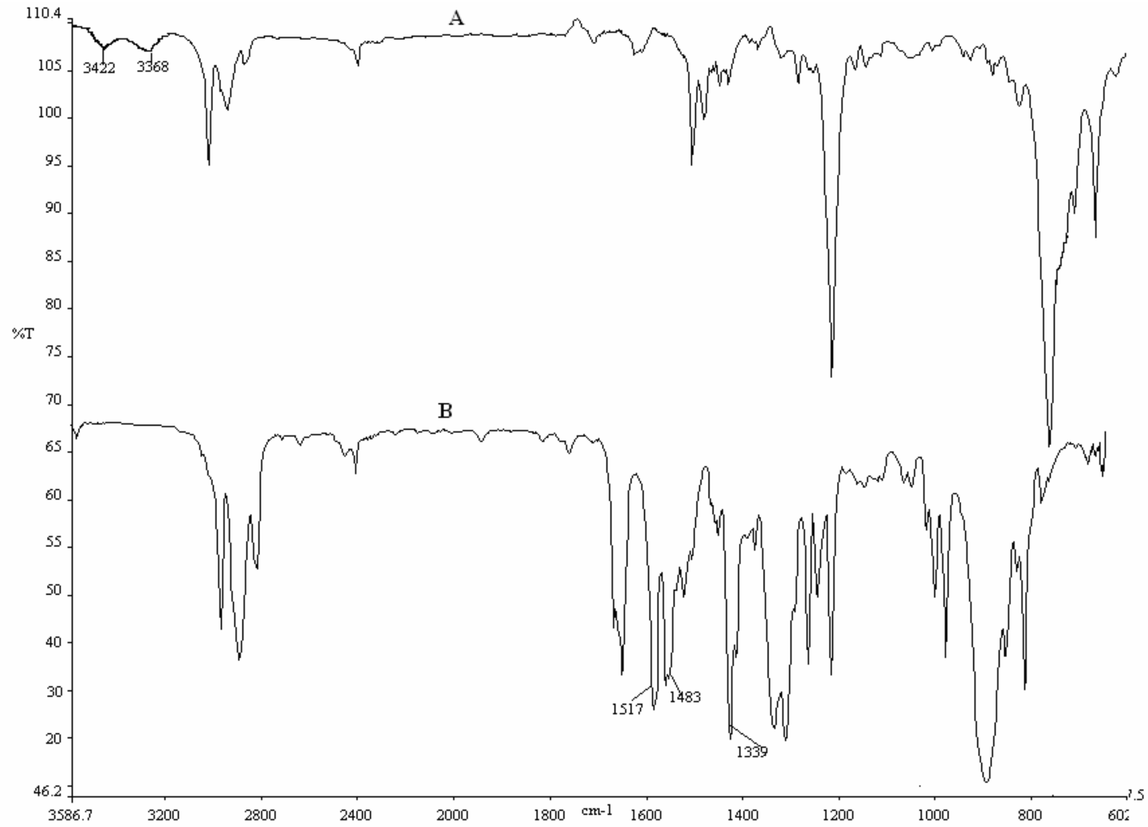


Figure 3.36: FTIR spectra of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (A) and 1,1-bis-[4-(4-nitrophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (B)

^{1}H-NMR spectra of DNTMPCPBP and TMDA are reproduced in **Figure 3.37** and **Figure 3.38** respectively**.** Peaks corresponding to aromatic protons 22, 22’ *ortho* to nitro group in DNTMPCPBP appeared at 8.19 δ ppm and were shifted to 6.53-6.59 δ ppm (*ortho* to amino) in TMDA, when nitro group is transformed to amino group. The upfield shift of protons in case of TMDA is due to the shielding effect of amino group, this confirms the complete reduction of DNTMPCPBP to TMDA.

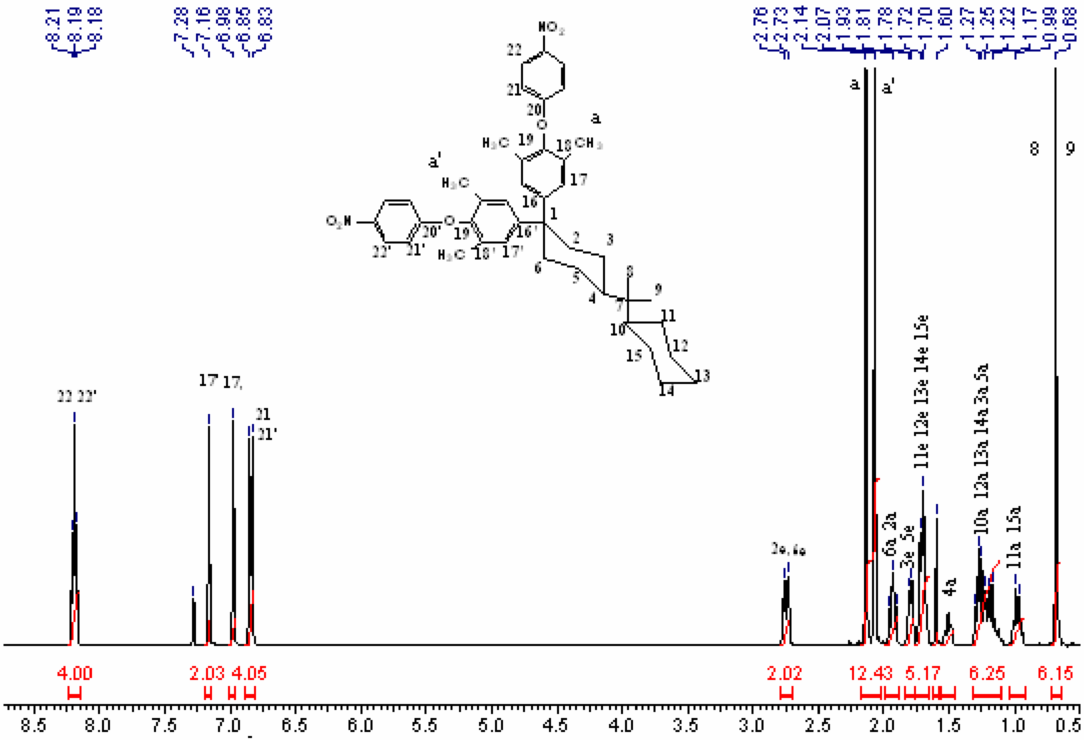


Figure 3.37: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-nitrophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane in $CDCl_3$

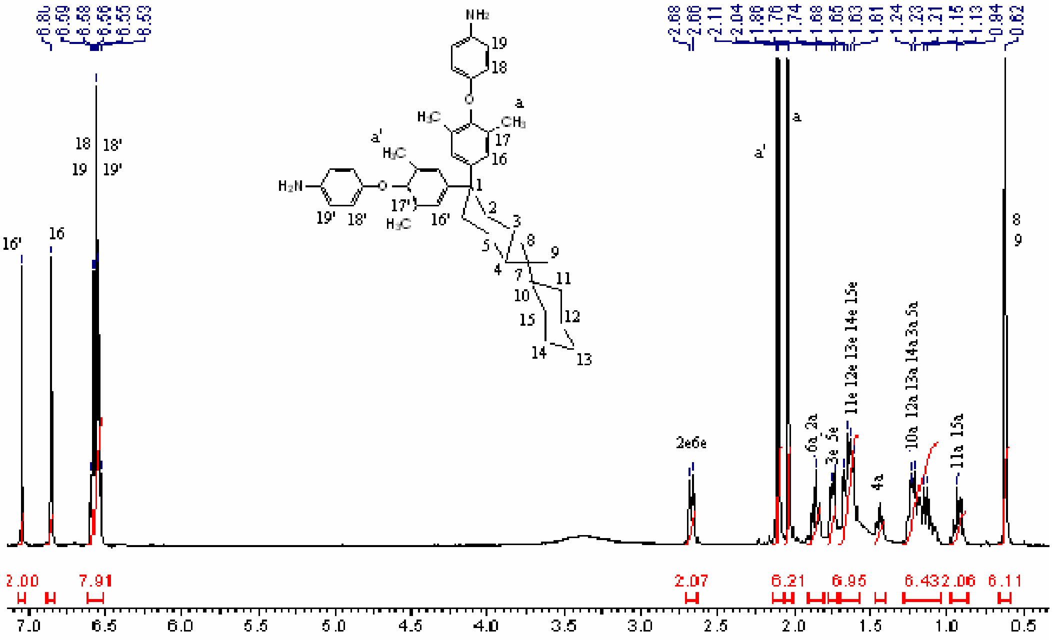


Figure 3.38: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane in $CDCl_3$

^{13}C-NMR spectra of DNTMPCPBP and TMDA along with assignments are given in **Figure 3.39** and **Figure 3.40.** Carbons 23 and 20 of TMDA were observed at 148.08 δ ppm and 149.06 δ ppm respectively whereas in DNTMPCPBP carbons 23 and 20 were observed at 162.94 δ ppm and 149.16 δ ppm. The upfield shift of peaks corresponding to the carbons 23 and 20 is attributed to the shielding effect caused by the electron donating amino group. The spectroscopic data of all other carbons are in good agreement with the proposed structure

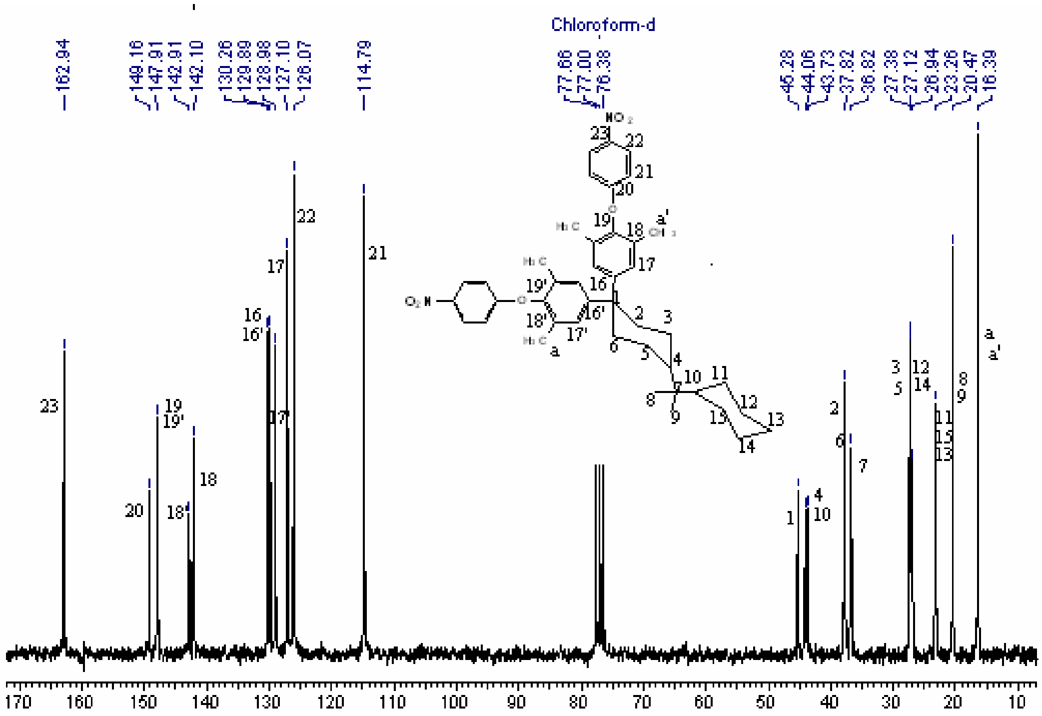


Figure 3.39: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-nitrophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane in $CDCl_3$

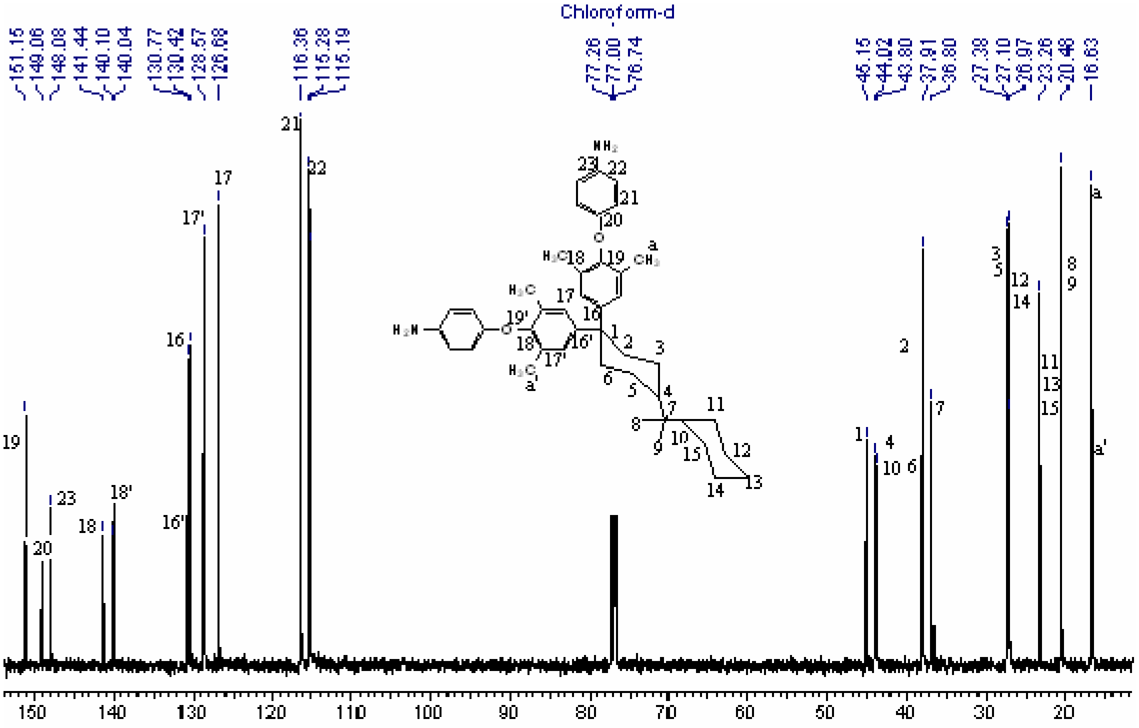
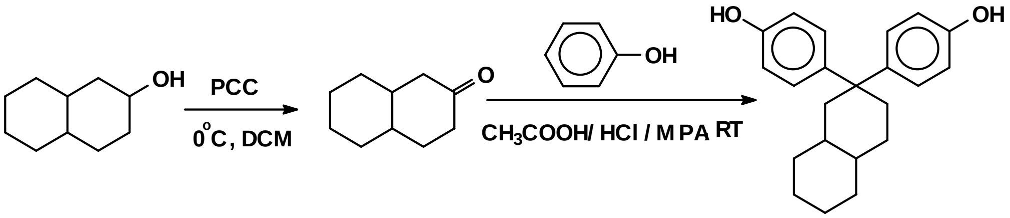


Figure 3.40: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane in CDCl$_3$

3.4.2.4 Synthesis and characterization of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP)

Scheme 3.8 depicts route for synthesis of DCHBP starting from decahydro-2-naphthol.



Scheme 3.8: Synthesis of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene from decahydro- 2-naphthol

Decahydro-2-naphthol was oxidized to 2-decalone using pyridinium chlorochromate [34]. 2-Decalone was condensed with excess of phenol using dry HCl and 3-MPA catalyst system to obtain DCHBP. The compound DCHBP has been reported previously[44,45].

Comparative FTIR spectra of 2-decalone and decahydro-2-naphthol are shown in **Figure 3.41.** The spectrum 'A' for decahydro 2-naphthol showed –OH stretching at 3340 cm^{-1} The band at 1716 cm^{-1} in spectrum B is characteristic of C=O group of ketone and the absence of band at 3340 cm^{-1} in 2-decalone confirms the complete conversion of alcohol to ketone.

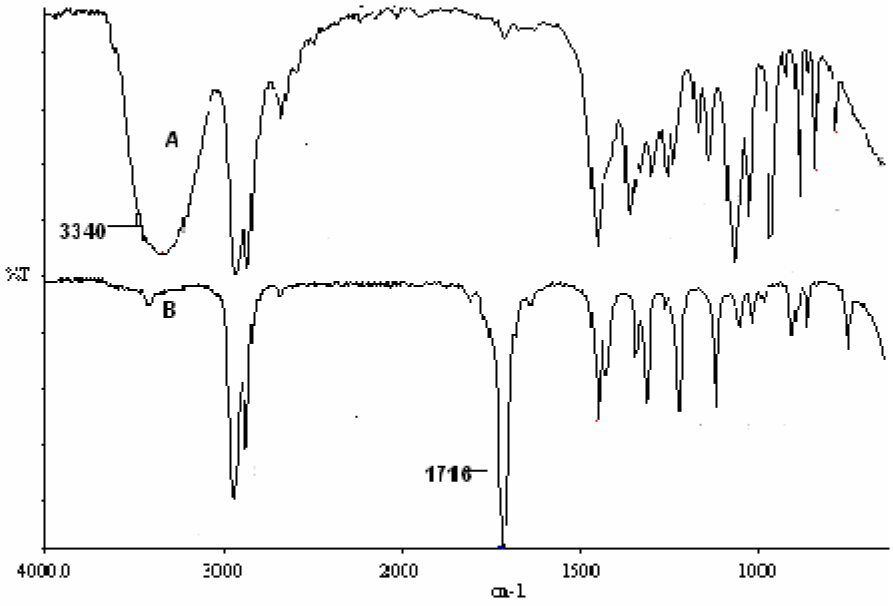


Figure 3. 41: FT-IR spectra of 2-decahydronaphthol (A) and 2-decalone (B)

In FT-IR spectrum of bisphenol DCHBP characteristic band of hydroxyl group was observed at 3540 cm^{-1}.

^{1}H-NMR spectrum of DCHBP is shown in **Figure 3.42.** ^{1}H NMR spectrum showed the presence of diastereotopic phenyl rings, which are magnetically non-equivalent. DCHBP is not symmetrical about a C_2 axis between the two phenolic rings and this result in different environments for two phenyl rings, hence the aromatic rings showed four doublets for protons 11,11' and 12,12' in ^{1}H NMR spectrum.

The peak at 7.13 δ ppm and 6.99 δ ppm were observed due to the protons 11, 11'which are *meta* to hydroxyl group. The peak at 6.69 δ ppm and 6.59 δ ppm were observed due to the protons 12,12' which are *ortho* to hydroxyl group. The sixteen protons of decalene ring appeared as multiplet in the range 1.26-2.36 δ ppm.

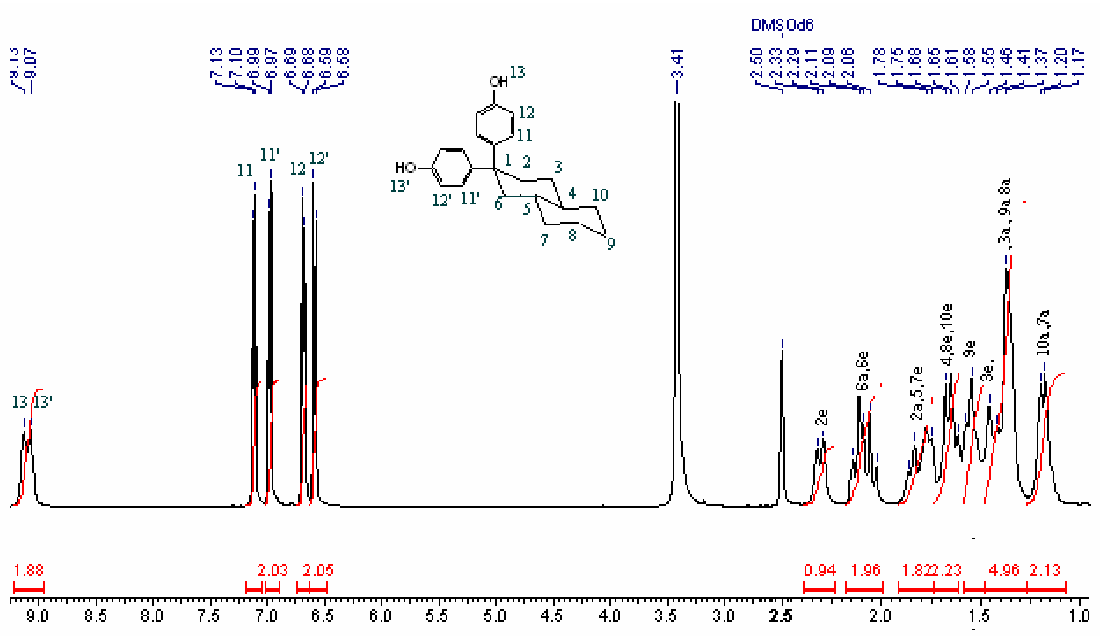


Figure 3.42: ^{1}**H-NMR spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene in DMSO d$_6$**

^{13}C-NMR spectrum of DCHBP along with assignment of the carbon atoms is shown in **Figure 3.43**

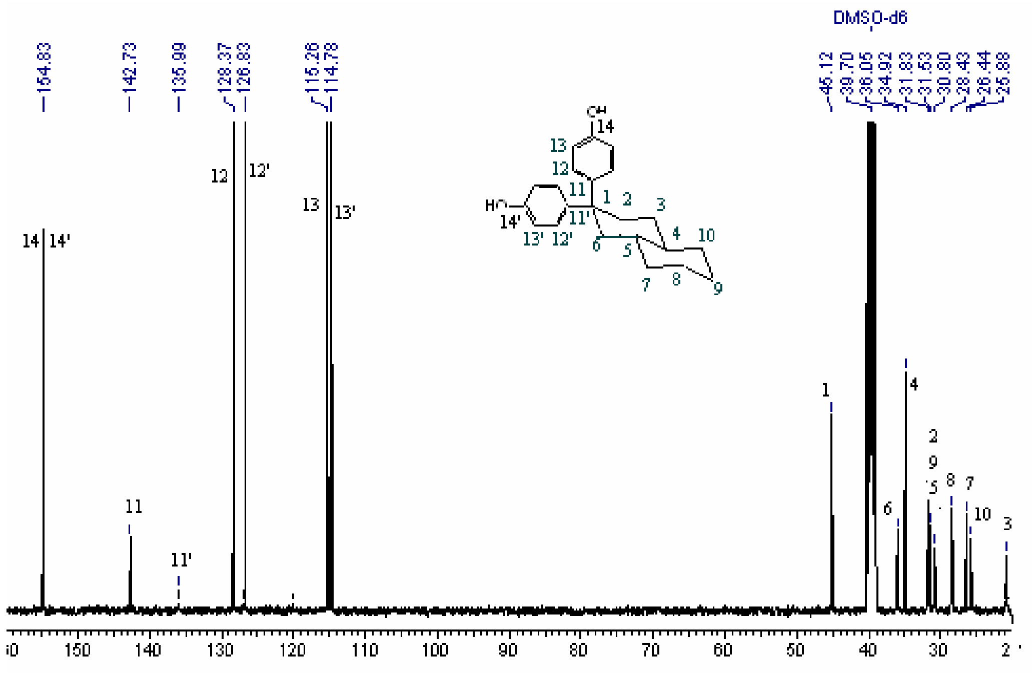


Figure 3.43: ^{13}**C-NMR spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene in DMSO d$_6$**

The position of the of ring protons was assigned with the help of 2D NMR analysis.

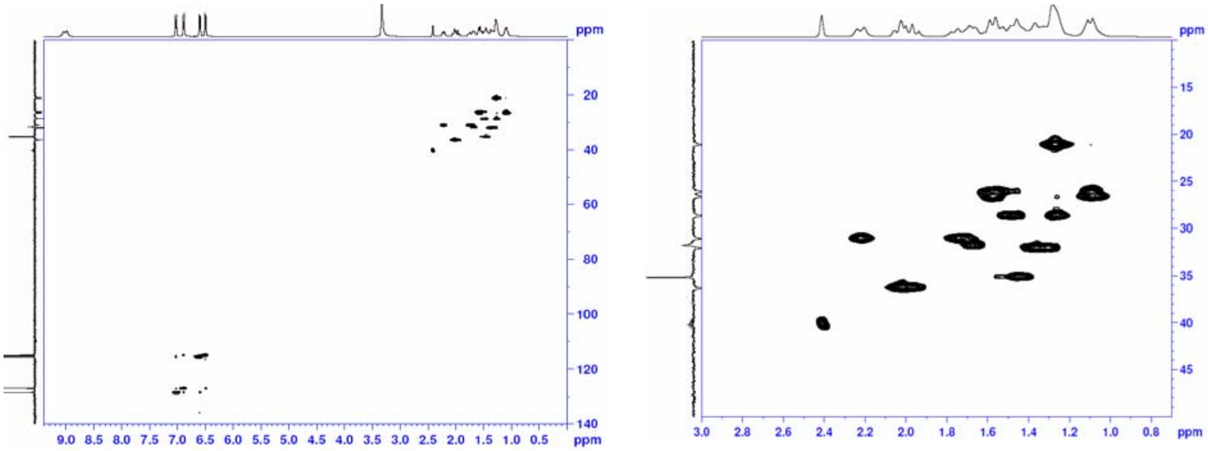


Figure 3.44:^{1}H-^{13}C HSQC spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

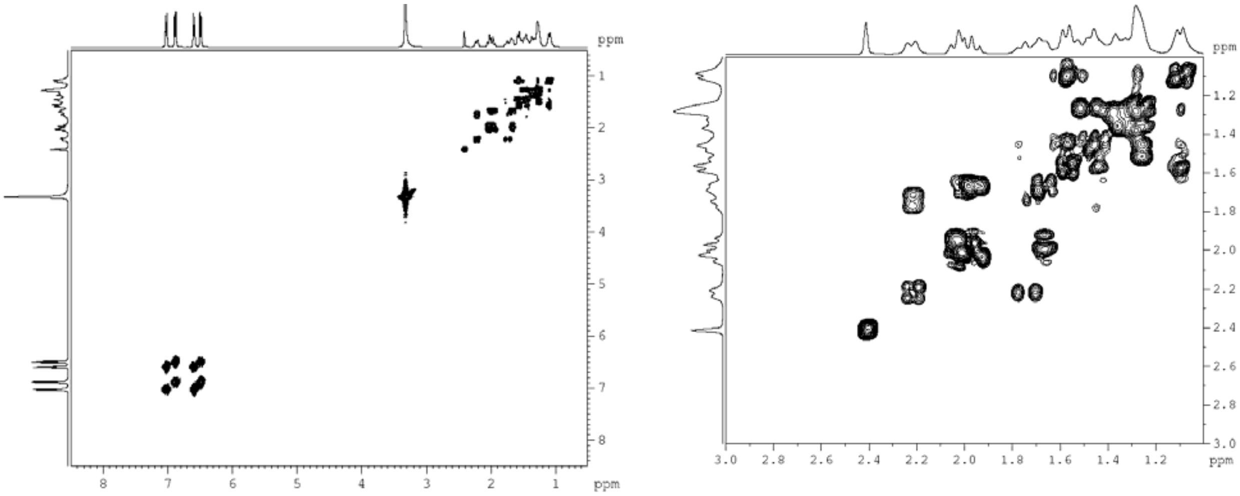


Figure 3.45: HH COSY spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

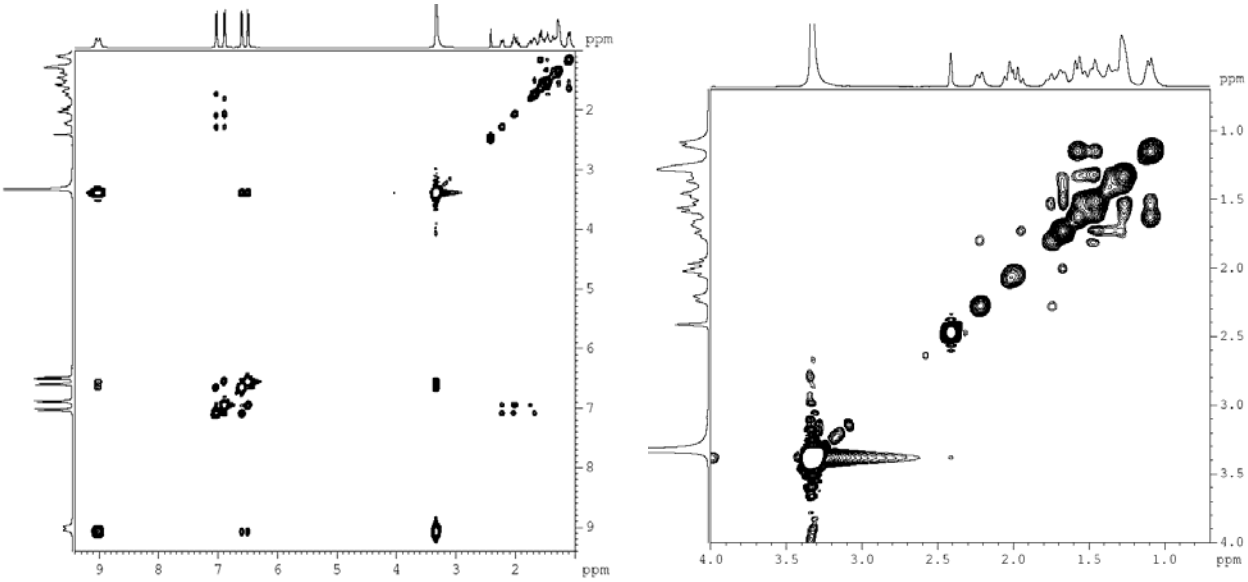


Figure 3.46: NOESY spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

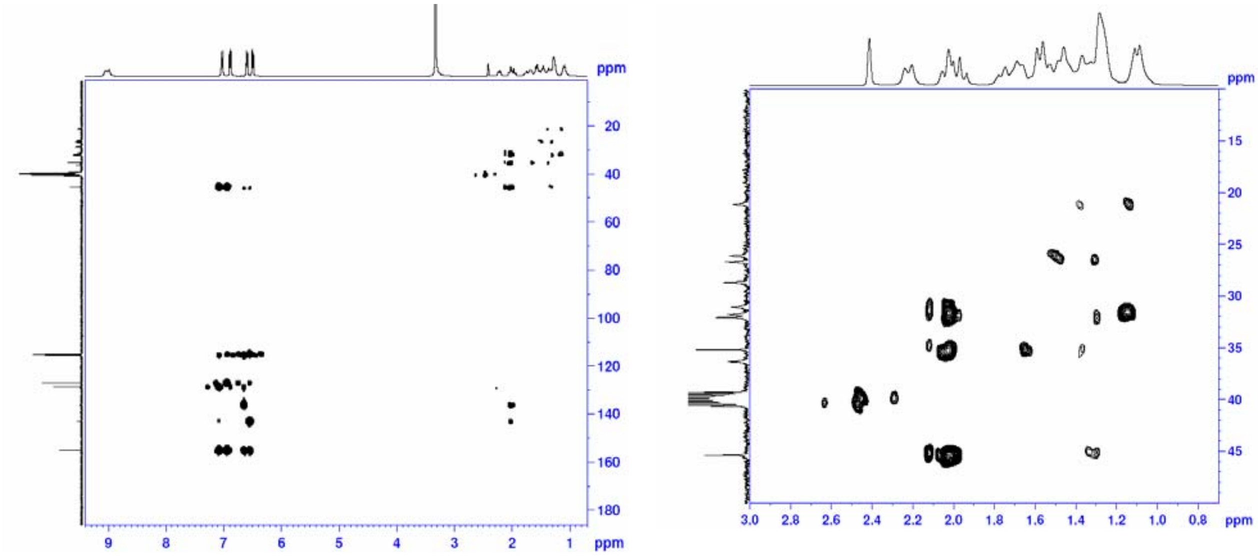


Figure 3.47: HMBC spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

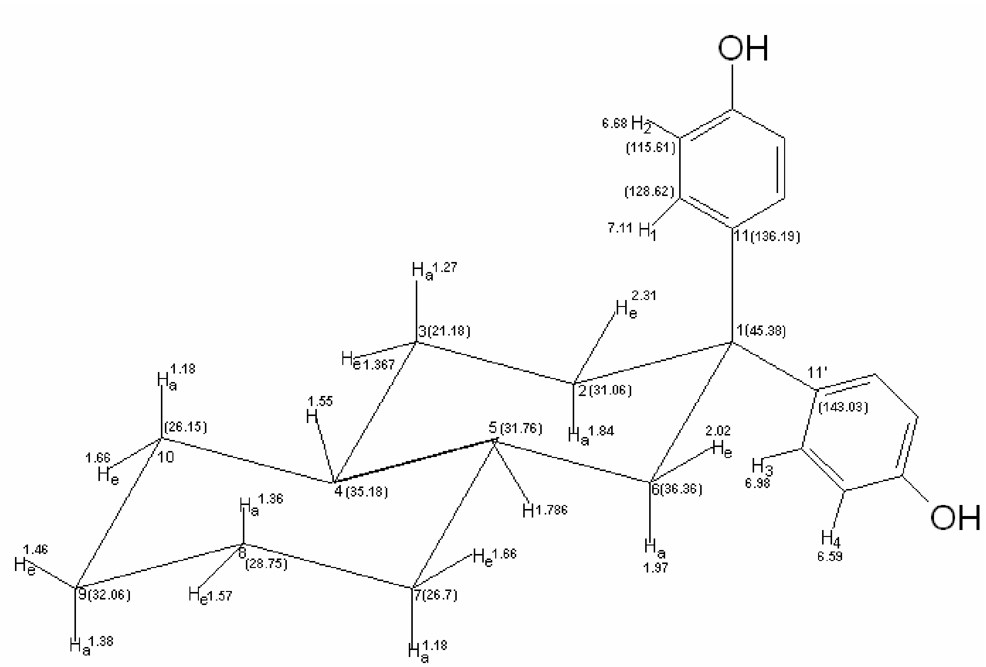


Figure 3.48: Complete structure assignment of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene using 2D NMR

1. From HSQC the following connectivities of the protons to the carbon atoms are obtained as given in **Table: 3.7**

Table 3.7: Protons connected to different carbon atoms present on the fused cyclohexyl rings in DCHBP.

Carbon Atoms δppm	C_2-31.06	C_3-21.18	C_4-35.18	C_5-31.76	C_6-36.36	C_7-26.7	C_8-28.7	C_9-32.06	C_{10}-26.15
Protons δppm	H_{2e}-2.31 H_{2a}-1.84	H_{3e}-1.36 H_{3a}-1.27	H_4 -1.55	H_5-1.78	H_{6e}-2.02 H_{6a}-1.97	H_{7e}-1.66 H_{7a}-1.18	H_{8e}-1.57 H_{8a}-1.36	H_{9e}-1.46 H_{9a}-1.38	H_{10e}-1.66 H_{10a}-1.18

2. ^{13}C NMR spectrum showed that the only aliphatic quaternary carbon is carbon no.1 i.e C_1 (45.38 δ ppm), so C_1 is assigned as the carbon bearing two phenyl rings containing hydroxyl groups.
3. Among all the protons H_{2a}, H_{2e} and H_{6a} and H_{6e} are the deshielded protons, this deshielding is attributed to the substituent effect of phenyl rings containing hydroxyl group, so these two carbons C_2 and C_6 are assigned adjacent to the carbon C_1(45.38 δ ppm) bearing two hydroxyl phenyl group.

4. Among the two phenyl ring bearing carbon atoms C_{11} and C_{11}' , C_{11}(136.19 δ ppm) is more shielded due to gauche effect of two α protons so this ring (possessing C_{11} as connecting carbon atom) is assigned in axial position. Also from HMBC the other two protons of this rings are assigned as H_1 7.11 and H_2 6.68 δ ppm, and hence the other phenyl ring bearing $C_{11'}$ (143.03) is at equatorial position and the other two protons can be assigned as H_3 6.98 and H_4 6.59 δ ppm.

5. HH COSY experiment showed that C_6 methylene protons are coupled with C_5H proton at 1.78 and also showed a weak coupling with C_2H protons (H_{2a} 1.84 and H_{2e} 2.31 δ ppm), so C_5H protons are adjacent to C_6H protons. Moreover C_2H protons appeared close to C_6H protons in three dimensional space.

6. HSQC showed that C_5 carbon is attached to only one proton H_5 (1.78 δ ppm) and C_4 carbon is attached to only one proton (1.55 δ ppm) indicating the carbon atoms, C_4 and C_5 are bridge head carbons.

7. HH COSY experiment showed that C_2H protons H_{2e} and H_{2a} are strongly coupled to each other and these protons also showed coupling with H_{3e} at (1.36 δppm) attached to C_3 i,e C_3 is assigned as immediate neighbor of C_2. Hence all the carbons C_1- C_6 and protons attached to these carbons are assigned.

8. In the second ring, axial protons H_{7a} and H_{10a} are the most shielded protons (1.18 δ ppm) and these protons showed strong coupling (from HH COSY) to the protons appeared at 1.66 δ ppm so these protons are assigned as their equatorial partners. This is also supported by HSQC that carbons C_7 at 26.7 δ ppm and C_{10} at 26.15 δ ppm are attached to the protons H_{7a}1.18 δ ppm , H_{7e}1.67 δ ppm and protons H_{10a}1.18 δ ppm , H_{10e}1.67 δ ppm.

9. Remaining signals are C_9 CH_2 and C_8 CH_2 .The carbon at 28.7 δ ppm is most likely to be C_8 , since the structure is very close to that of trans decalene , C_8 is assigned at 28.7

δ ppm and protons H_{8a} and H_{8e} at 1.36 and 1.57 δ ppm and carbon C_9 at 32.06 δ ppm and H_{9a} and H_{9e} at 1.38 and 1.46 δ ppm.

The mass spectrum of DCHBP **(Figure 3.49)** showed molecular ion peak at 322 m/z consistent with its molecular weight.

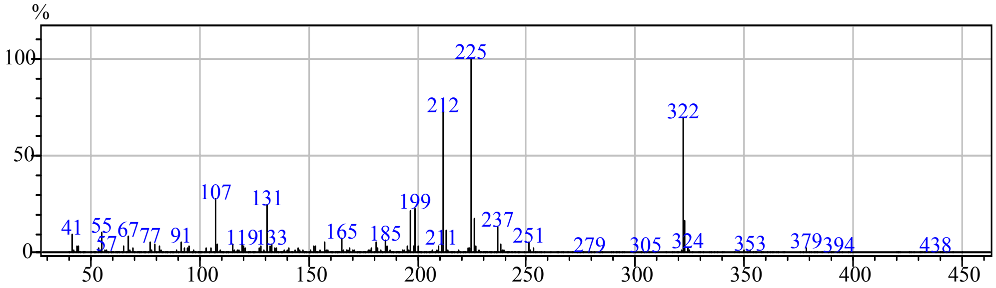


Figure 3.49: Mass spectrum of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

The purity of DCHBP was determined by HPLC and was found to be 99.8 % (**Figure: 3.50**)

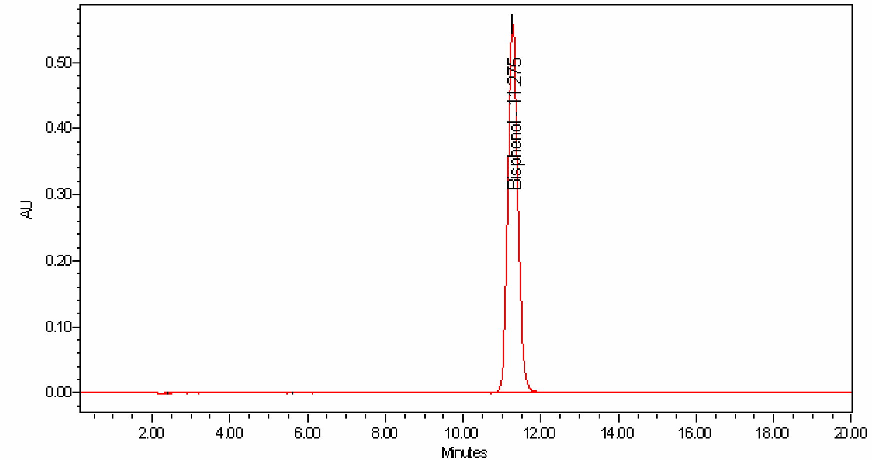


Figure 3.50: HPLC trace of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

The molecular structure of DCHBP was further investigated by single crystal X-ray diffraction analysis. The single crystal for DCHBP was grown during slow crystallization from its solution in methanol. A crystal size of 0.22 x 0.09 x 0.05 mm^3 was used for X-ray structure determination **Table 3.8** presents X-ray crystal data of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP). Selected bond distances and bond angles are given in **Appendix 1**. **Figure 3.51** shows the molecular structure of DCHBP, indicating the presence of two magnetically non equivalent, disteriotopic phenyl rings.

Packing diagram of DCHBP is presented in **Figure: 3.52** DCHBP forms intermolecular hydrogen bonding. Molecules are arranged in head-to- head fashion.

Table 3.8: X-Ray crystal data of 1,1-bis-(4-hydroxyphenyl) octahydro-2(1H)-naphthalene

Identification code	DCHBP
Empirical formula	$C_{44} H_{52} O_4$
Formula weight	644.86
Temperature	298(2) K
Crystal form, colour	Thin needle, Colorless
Crystal size	0.22 x 0.09 x 0.05 mm
Wavelength (Mo $K\alpha$)	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	
a	8.77(2) Å
b	10.31(2) Å
c	11.42(4) Å
alpha	110.12(7) °
beta	108.14(5) °.
gamma	102.04(4) °
Volume	862(4) Å^{3}
Z, Calculated density	1, 1.242 g cm^{-3}
Absorption coefficient	0.078 mm^{-1}
Limiting indices	-9<=h<=9, -11<=k<=10, -12<=l<=12
Reflections collected / unique	5121 / 2396 [R(int) = 0.0789]
Data / parameters	2396 / 242
Max. and min. transmission	0.9961 and 0.9831
Goodness-of-fit on F^{2}	1.353
Final R indices [I>2sigma(I)]	R1 = 0.1476, wR2 = 0.4227

R indices (all data)	R1 = 0.2120, wR2 = 0.4529
Largest diff. peak and hole	0.435 and -0.448 eA^{-3}

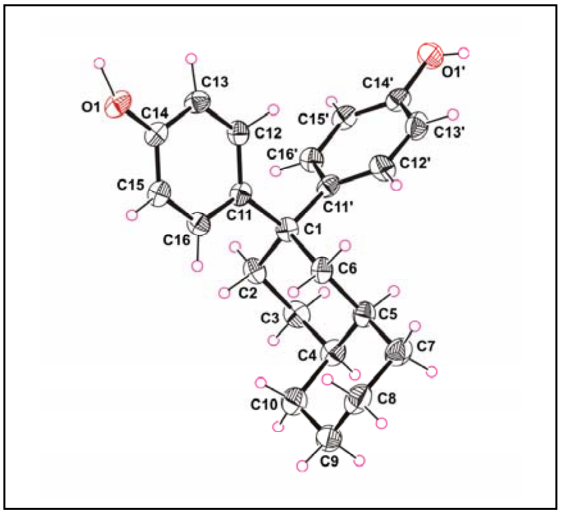


Figure 3.51: ORTEP diagram of 1,1- bis-(4-hydroxyphenyl) octahydro-2(1H)-naphthalene

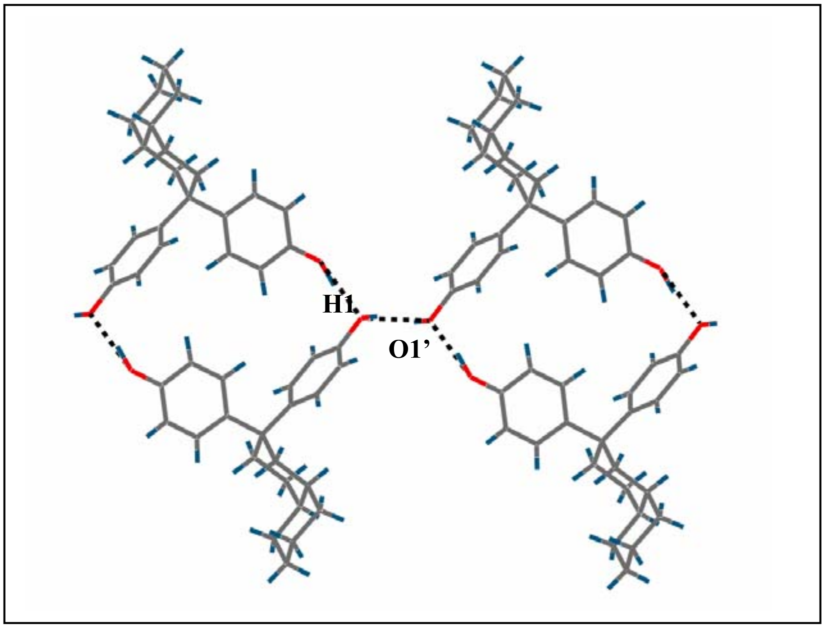


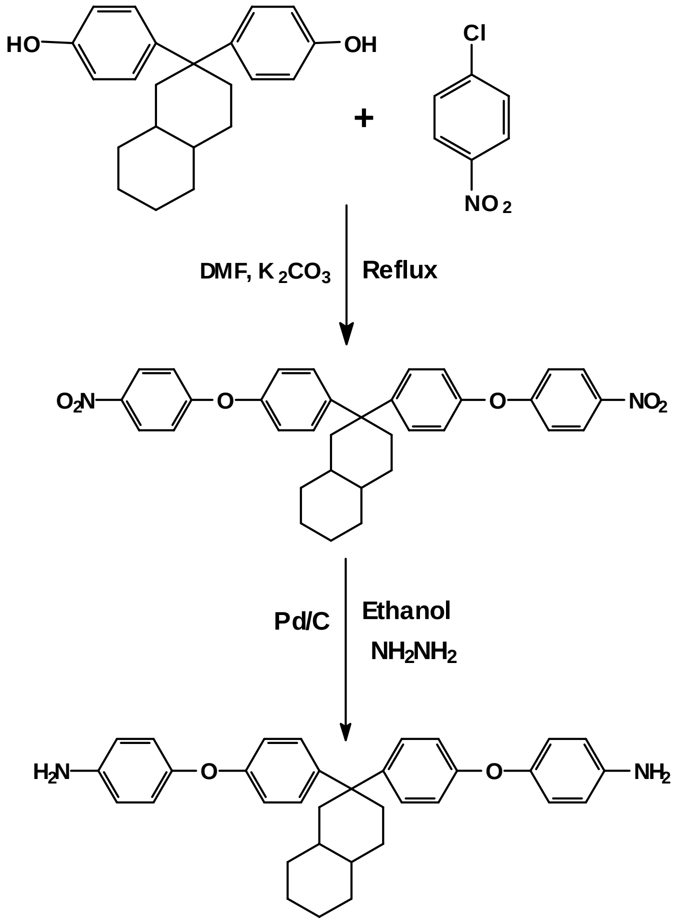
Figure 3.52: Intermolecular H-bonding in 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene

Table 3.9: Analysis of potential hydrogen bonds present in DCHBP

D-H…A	D-H	H…A (Å)	D…A (Å)	D-H…A (°)
O1-H1…O1'	1.02	1.88	2.740 (12)	140

3.4.2.5 Synthesis and characterization of 1,1 bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene

Scheme 3.9 depicts route for synthesis of DCHDA.



Scheme 3.9: Synthesis of 1,1 bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene

The dinitro compound 1,1-bis-[4-(4-nitrophenoxy)phenyl]-octahydro-2(1H)-naphthalene (DNDCHBP), was synthesized by nucleophilic substitution of chlorine in *p*-chloronitrobenzene with DCHBP in DMF in presence of anhydrous potassium carbonate. Dinitro intermediate was reduced with hydrazine hydrate using Pd/C as catalyst in ethanol to obtain the diamine 1,1 bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene (DCHDA).

FT-IR spectra of DNDCHBP and DCHDA are reproduced in **Figure 3.53.** Spectrum B for DNDCHBP shows characteristic nitro group stretching at 1520 and 1342 cm^{-1} while spectrum A shows bands at 3383, 3455 cm^{-1} for –NH stretching.

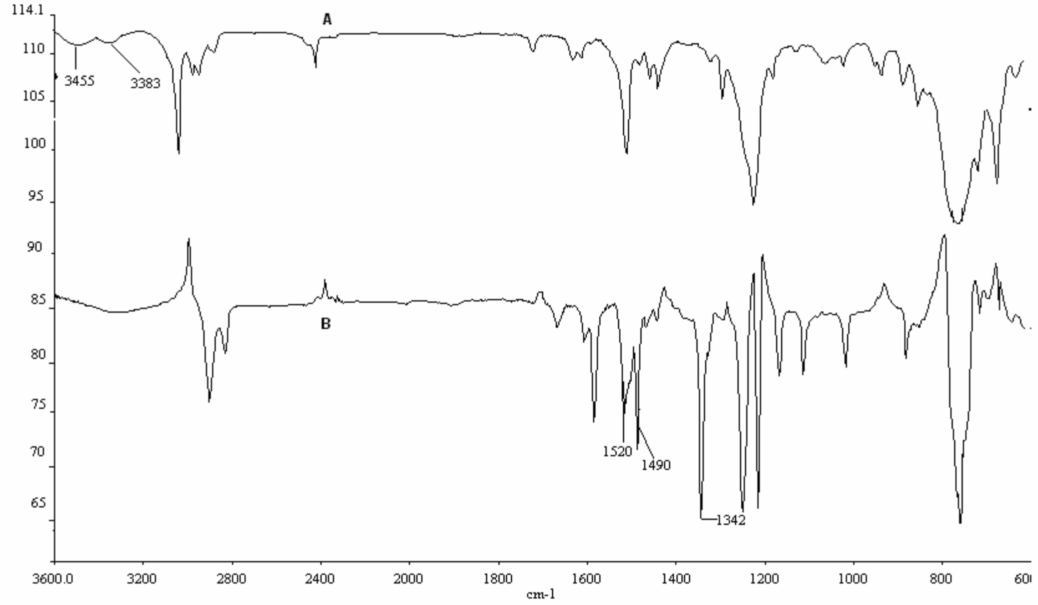


Figure 3.53: FT-IR spectra of 1,1-bis-[4-(4-nitrophenoxy)phenyl]-octahydro-2(1H)-naphthalene and 1,1 bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene

^{1}H-NMR spectrum of DNDCHBP and DCHDA are presented in **Figure 3.54** and **Figure 3.55** respectively. Peaks corresponding to aromatic protons 14,14’ ortho to nitro group in DNDCHBP, which appeared at 8.15-8.22δ ppm are shifted to 6.65- 6.67δ ppm in DCHDA when nitro group is transformed to amino in DCHDA. The upfield shift of protons in case of DCHDA is due to the shielding effect of amino group, this confirms the complete reduction of DNDCHBP to DCHDA.

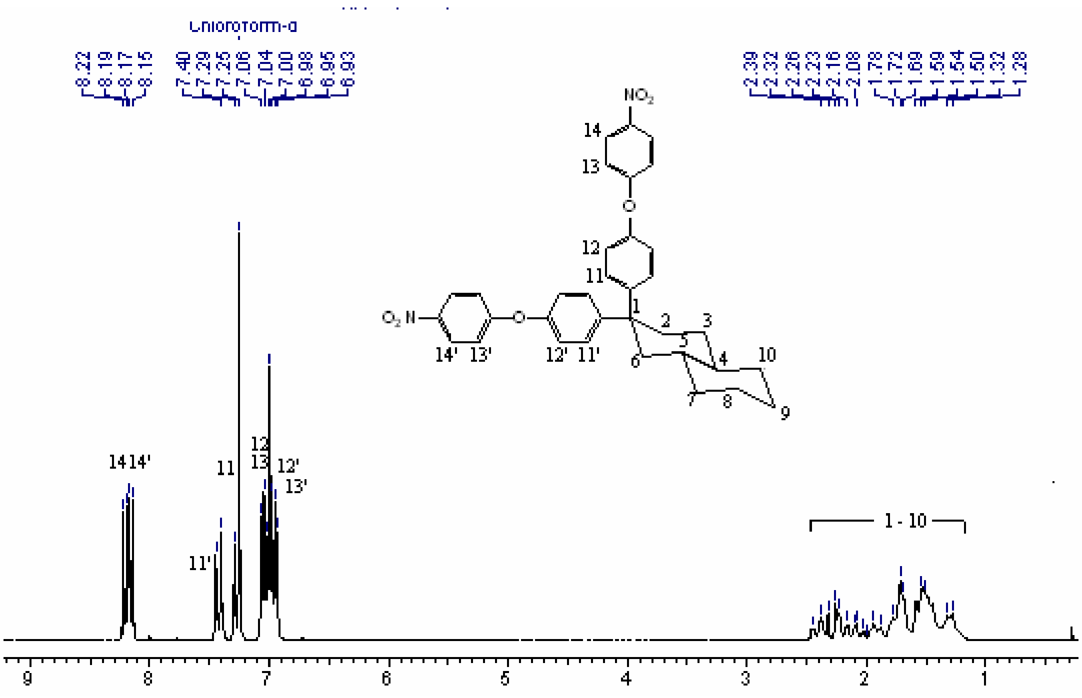


Figure 3.54: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-nitrophenoxy)phenyl]-octahydro-2(1H)-naphthalene in $CDCl_3$

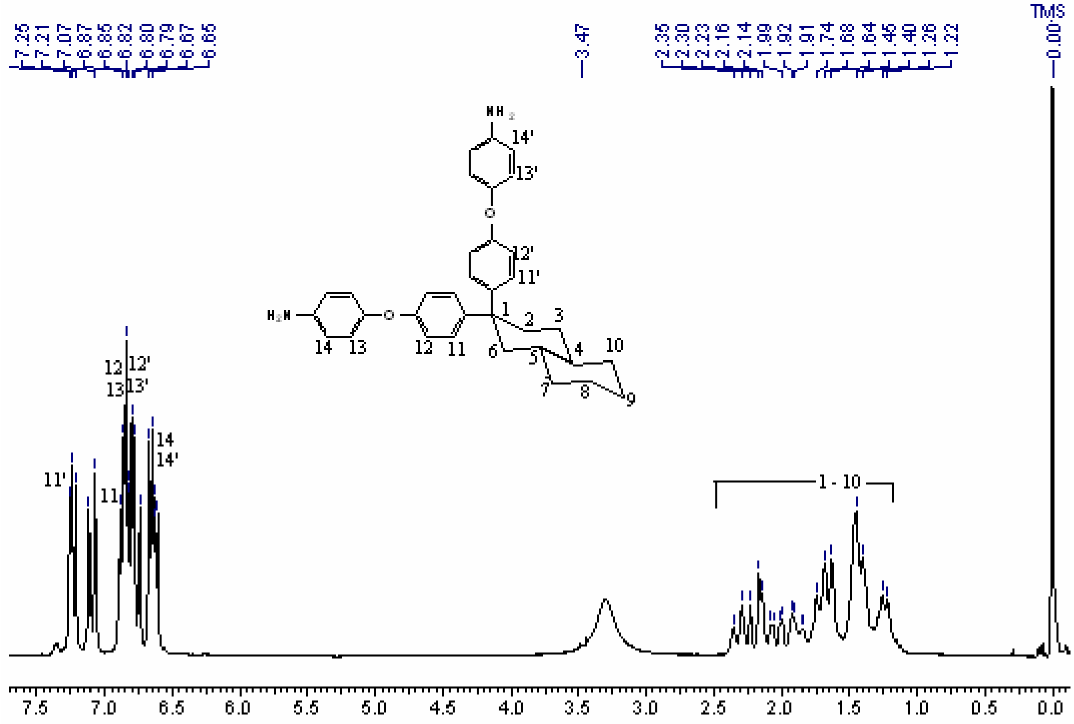


Figure 3.55: ^{1}H-NMR spectrum of 1,1 bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene in $CDCl_3$

^{13}C NMR spectra of DNDCHBP and DCHDA are reproduced in **Figure 3.56** and **Figure 3.57.** Carbons '18' and '15' of DCHDA were observed at 148.33 δ ppm and 148.45 δ ppm respectively where as in DNDCHBP carbons '18' and '15' were observed at 163.31 and 152.93 ppm. The upfield shift of the aromatic carbons *ortho* and *para* to the carbon attached to amino groups were observed when the nitro group was transformed to amino group because of the shielding effect caused by the electron donating amino groups. The spectroscopic data of all the other carbon atoms is in good agreement with the proposed structure.

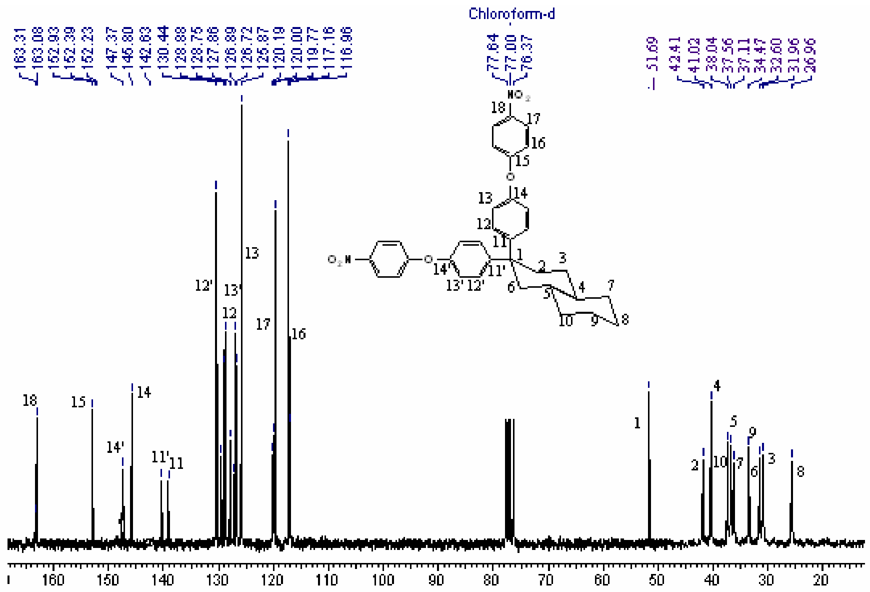


Figure 3.56: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-nitrophenoxy)phenyl]-octahydro-2(1H)-naphthalene in $CDCl_3$

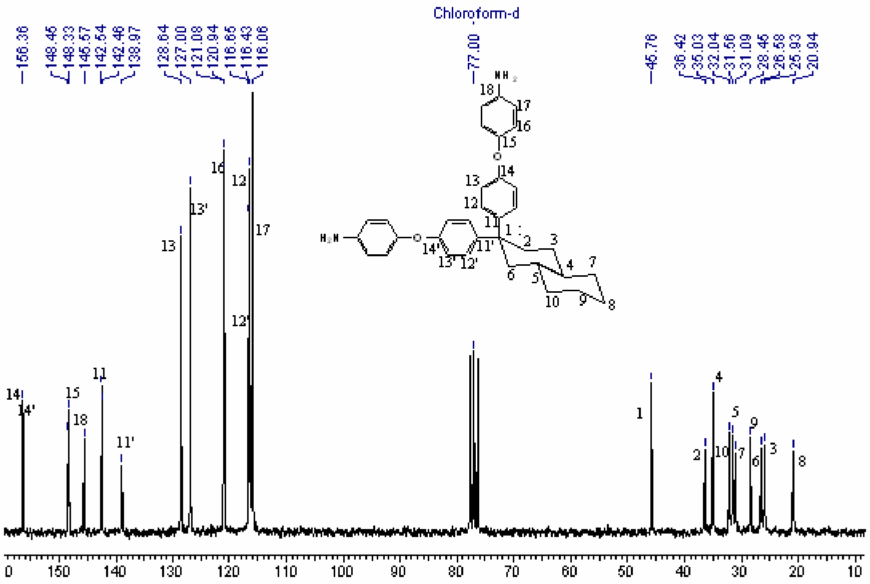


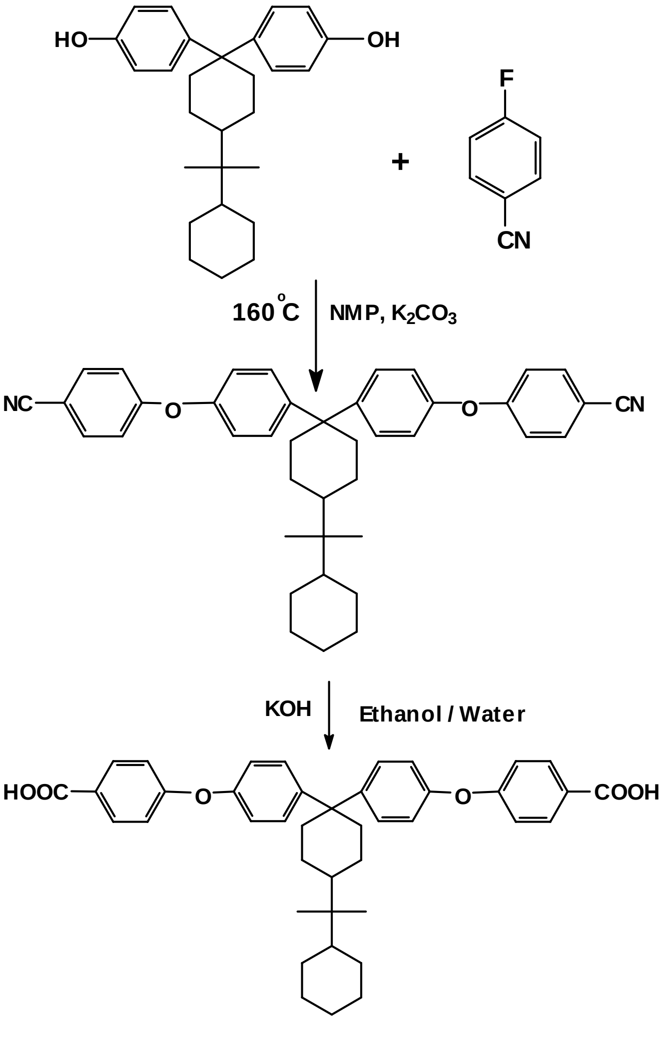
Figure 3.57: ^{13}C NMR spectrum of 1,1 bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene in $CDCl_3$

3.4.3 Synthesis and characterization of diacids containing cardo groups.

Two diacids, namely, 1,1-bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane (PCPDA) and 1,1-bis-[4-(4-carboxy phenoxy)-3,5-dimethyl phenyl]-4-perhydrocumyl cyclohexane (TMPCPDA) were synthesized.

3.4.3.1 Synthesis and characterization of 1,1 bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane (PCPDA)

Scheme 3.10 depicts route for the synthesis of PCPDA



Scheme 3.10 Synthesis of 1,1 bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane

The dicyano intermediate i,e 1,1-bis-[4-(4-cyanophenoxy)phenyl]-4-perhydrocumylcyclohexane (DCNPCPBP) was synthesized by nucleophilic substitution of *p*-

fluoro benzonitrile with PCPBP in NMP in the presence of anhydrous potassium carbonate and was further hydrolyzed by refluxing with KOH in ethanol/ water to give PCPDA.

IR spectra of DCNPCPBP and PCPDA are shown in **Figure 3.58** spectrum A shows characteristic stretching of –CN group at 2226 cm^{-1} while spectrum B shows carbonyl stretching of -COOH group at 1704 $cm^{-1.}$.

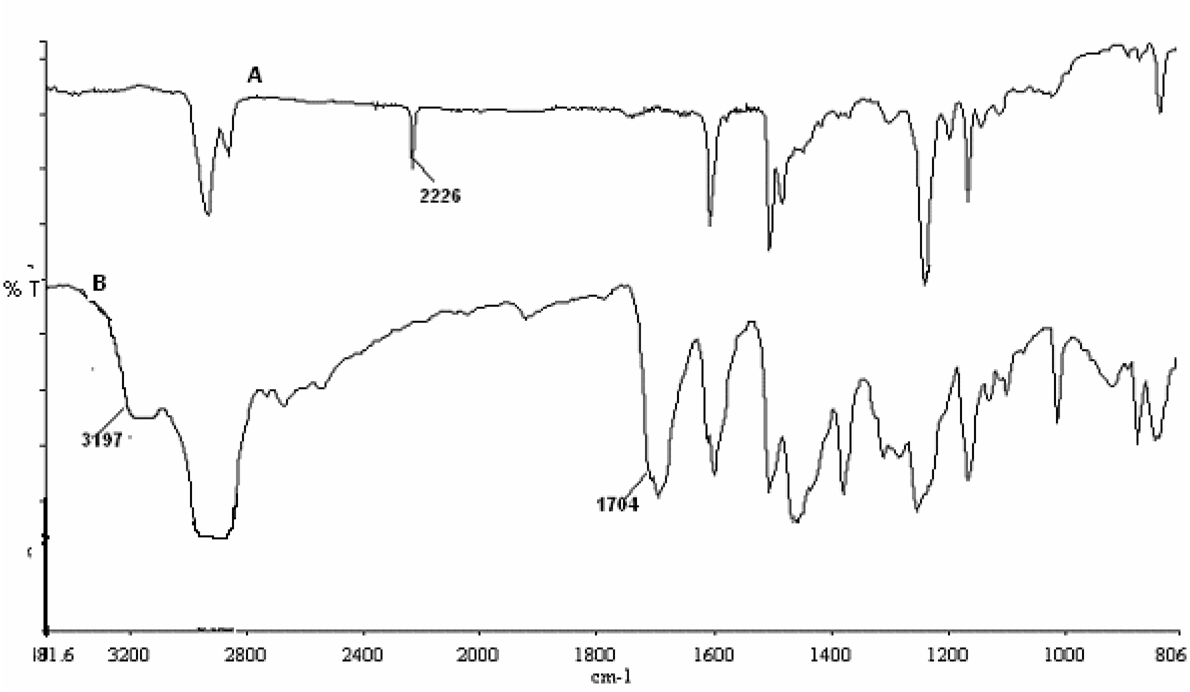


Figure 3.58: FT-IR spectrum of 1,1-bis-[4-(4-cyanophenoxy)phenyl]-4-perhydrocumylcyclohexane (A) and 1,1-bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane(B)

^{1}H-NMR spectra of DCNPCPBP and PCPDA are reproduced in **Figure 3.59** and **Figure 3.60**. The protons 'd' which are ortho to -CN group appeared at 7.59 δ ppm in DCNPCPBP, were shifted down field at 7.93 δ ppm in PCPDA due to the electron withdrawing nature of –COOH group, which confirmed the complete conversion of DCNPCPBP to PCPDA.

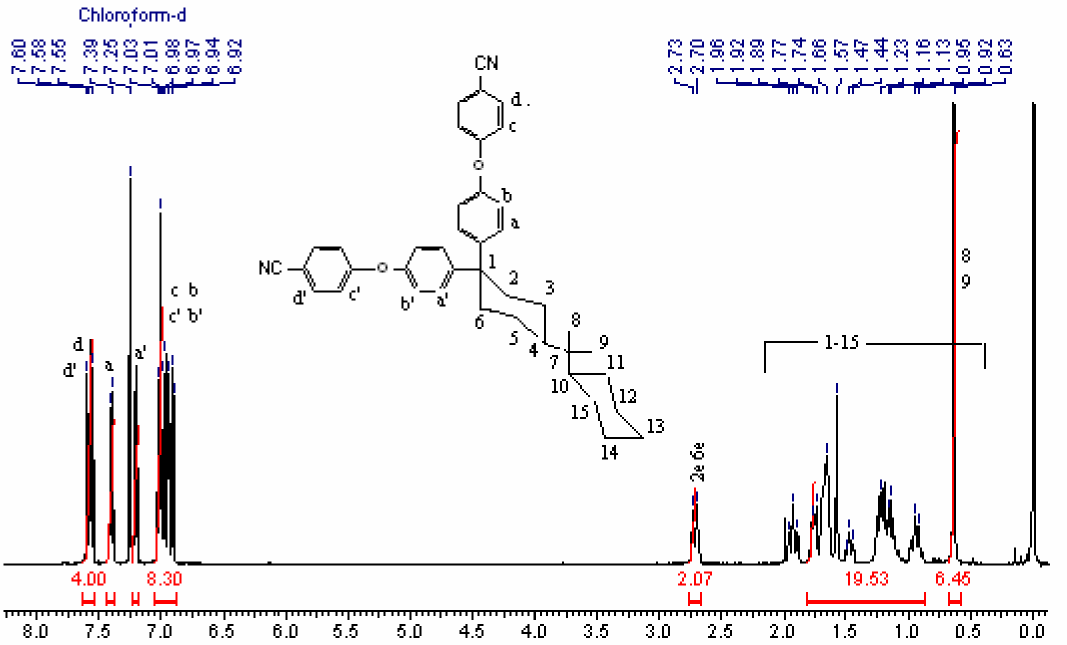


Figure 3.59: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-cyanophenoxy)phenyl]-4-perhydrocumylcyclohexane in $CDCl_3$

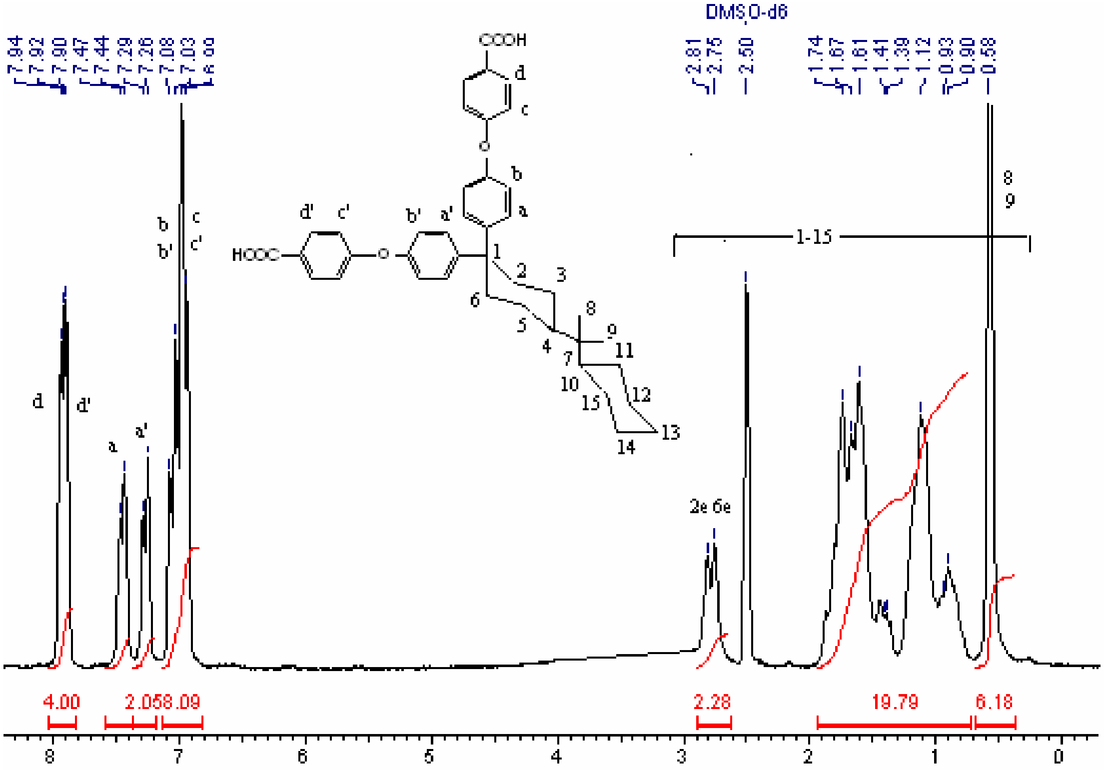


Figure 3.60: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane in DMSO d_6

^{13}C NMR spectrum of DCNPCPBP and PCPDA are given in **Figure 3.61** and **Figure 3.62** respectively**.** Carbon 24 corresponding to –CN group in DCNPCPBP appeared at 117.85 δ ppm and carbon 23 which is attached to cyano group, appeared at 105.71 in DCNPCPBP . These two carbons were shifted down field at 167.13 δ ppm and 125.72 δ ppm respectively in PCPDA , as the cyano group was transformed to acid .Both the carbons 24 and 23 resonated upfield in the case of dicyano compound because of the anisotropic shielding effect of π electrons of C≡N, and a large downfield shift was observed when it was converted to acid. After hydrolysis the resonance peaks of carbon 24 and 23 shifted down field because of the lack of anisotropic field. Spectral data corresponding to other carbon atoms are in good agreement with the proposed structure.

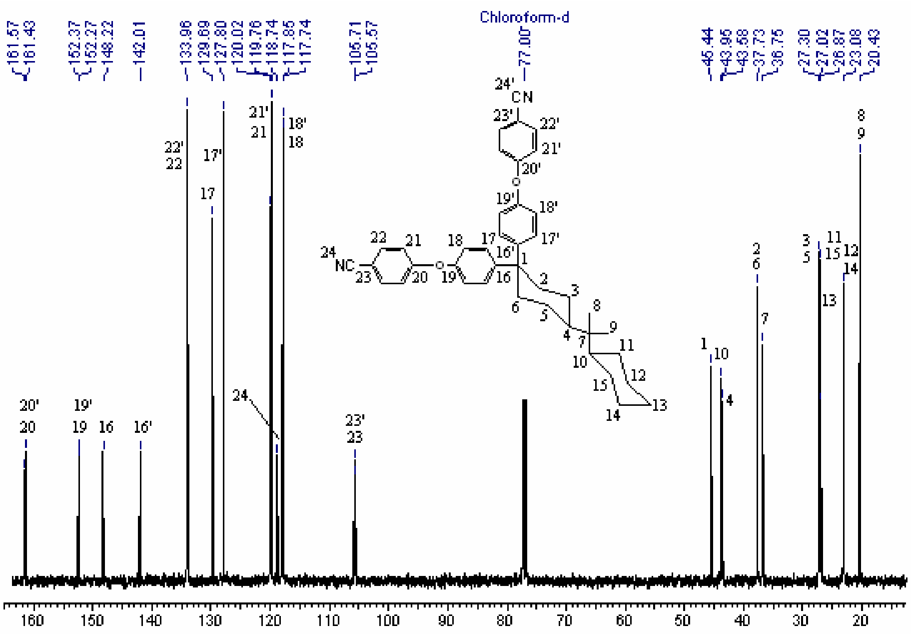


Figure 3.61: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-cyanophenoxy)phenyl]-4-perhydrocumylcyclo-hexane in $CDCl_3$

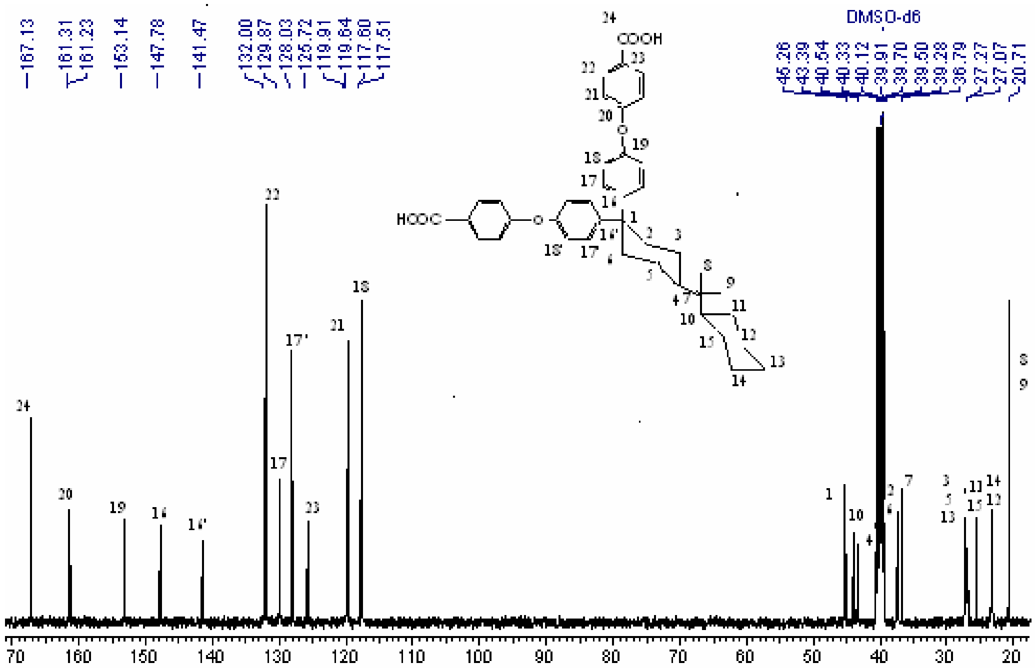


Figure 3.62: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane in DMSO d_6

Since the diacid PCPDA was difficult to recrystallize, the single crystal for dicyano compound DCNPCPBP was grown by slow crystallization from its solution in acetonitrile. A crystal size of 0.22 x 0.09 x 0.05 mm^3 was used for X-ray structure determination. **Table 3.10** presents X-ray crystal data for 1,1-bis-[4-(4-cyanophenoxy)phenyl]-4-perhydrocumylcyclohexane. Selected bond distances and bond angles are given in **Appendix 2. Figure 3.63** shows the molecular structure of DCNPCPBP. The inner phenylene rings are orthogonally attached to C_1 because of the steric hindrance caused by perhydrocumyl cyclohexylidene group

Table 3.10: X-Ray crystal data for 1,1-bis-[4-(4-cyanophenoxy)phenyl]-4-perhydrocumylcyclohexane (DCNPCPBP)

Crystal data.

Identification code		DCNPCPBP
Empirical formula		$C_{41} H_{42} N_2 O_2$
Formula weight		594.77
Temperature		298(2) K
Crystal form, colour		Thin needle,Colorless
Crystal size		0.22 x 0.09 x 0.05 mm
Wavelength (Mo *K*α)		0.71073 A
Crystal system, space group		Monoclinic, $P2_1/n$
Unit cell dimensions		
	a	14.8496(8) Å
	b	9.0601(5) Å
	c	25.0607(14) Å
	alpha	90 °
	beta	96.359(1) °.
	gamma	90 °
Volume		3350.7(3) $Å^3$
Z, Calculated density		4, 1.179 g cm^{-3}
Absorption coefficient		0.072 mm^{-1}
Limiting indices		-17<=h<=17, -10<=k<=10, -29<=l<=27
Reflections collected / unique		24606 / 5898 [R(int) = 0.0397]
Data / parameters		5898 / 408
Max. and min. transmission		0.9986 and 0.9607
Goodness-of-fit on F^2		1.066
Final R indices [I>2sigma(I)]		R1 = 0.0529, wR2 = 0.1099
R indices (all data)		R1 = 0.0783, wR2 = 0.1218
Largest diff. peak and hole		0.148 and -0.135 eA^{-3}

Selected bond length and bond angles are listed in **Appendix -2.**

The ORTEP diagram of DCNPCPBP is shown in **Figure 3.63.** DCNPCPBP forms intermolecular hydrogen bonding as shown in **Figure 3.64**

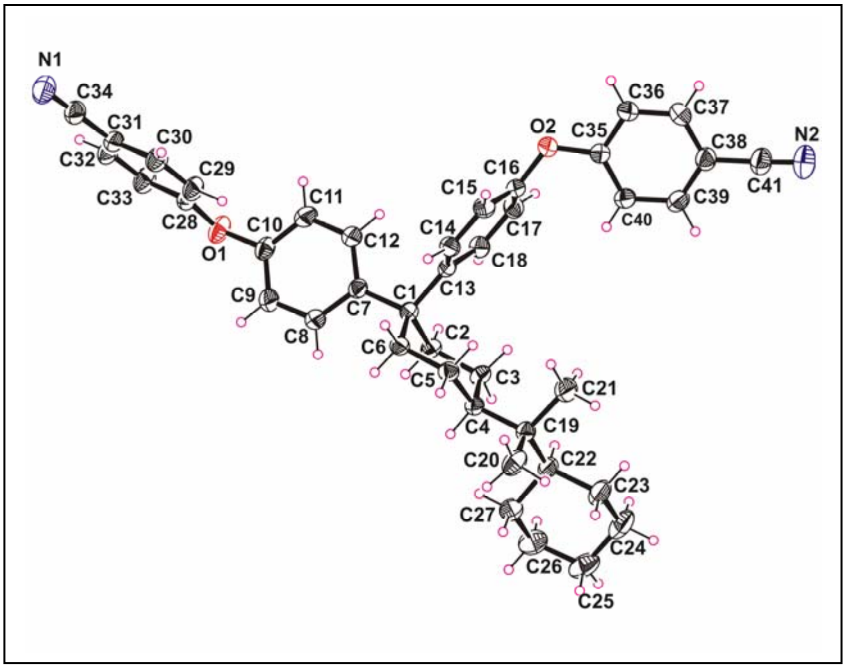


Figure 3.63: ORTEP diagram of 1,1-bis-[4-(4-cyano phenoxy) phenyl]-4-perhydrocumyl cyclohexane

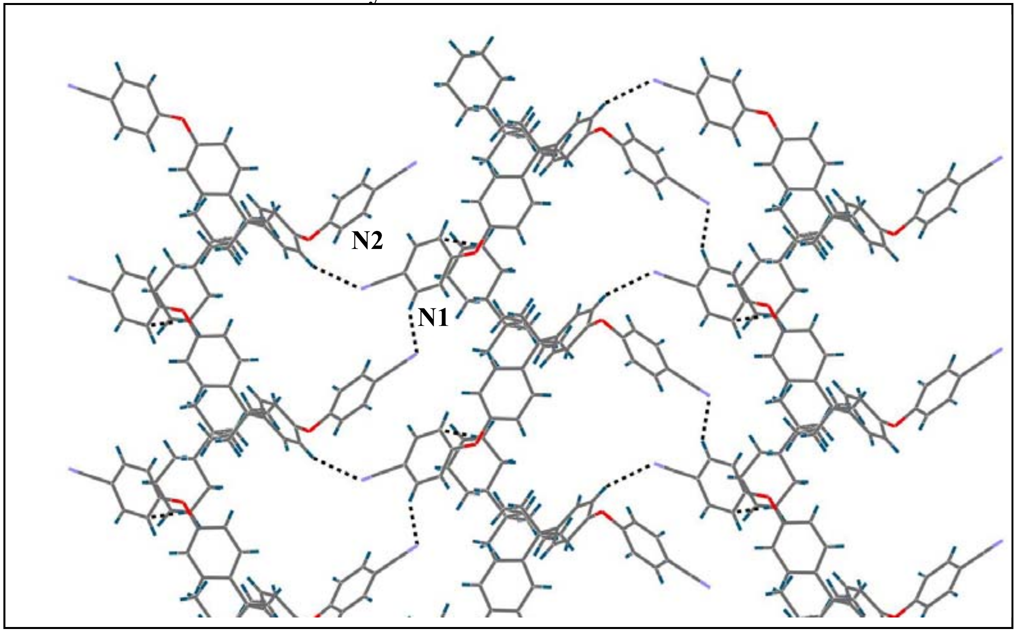


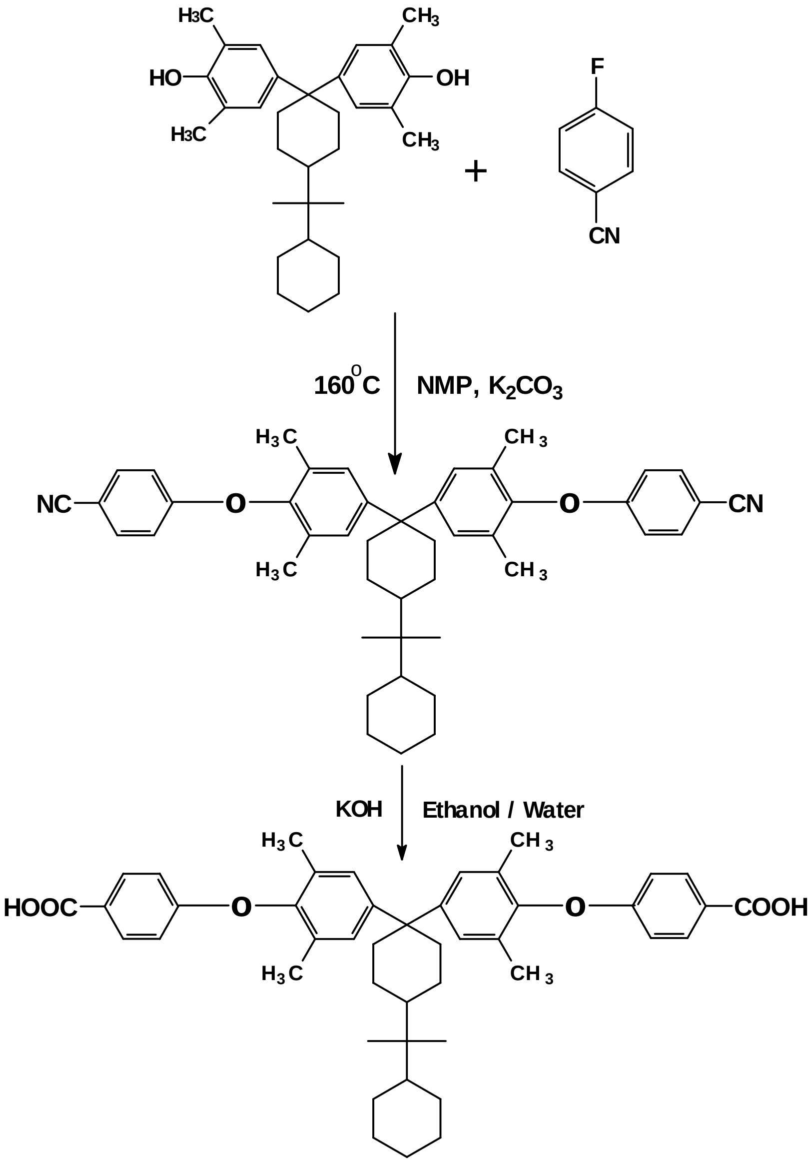
Figure 3.64: H-bonding in 1,1-bis-[4-(4-cyano phenoxy) phenyl]-4-perhydrocumyl cyclohexane

Table 3.11: Analysis of potential H-bonding in 1,1-bis-[4-(4-cyano phenoxy) phenyl]-4-perhydrocumyl cyclohexane

D-H…A	D-H	H…A (Å)	D…A (Å)	D-H…A (°)
C37-H37…N1	1.02	2.650	3.386(3)	136
C9-H9…N2	1.02	2.640	3.497(3)	154

3.4.3.2 Synthesis and characterization of 1,1 bis-[4-(4-carboxy phenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane

Scheme 3.11 presents route for synthesis of TMPCPDA.



Scheme 3.11: Synthesis of 1,1 bis-[4-(4-carboxy phenoxy)-3,5- dimethylphenyl]-4-perhydrocumyl cyclohexane

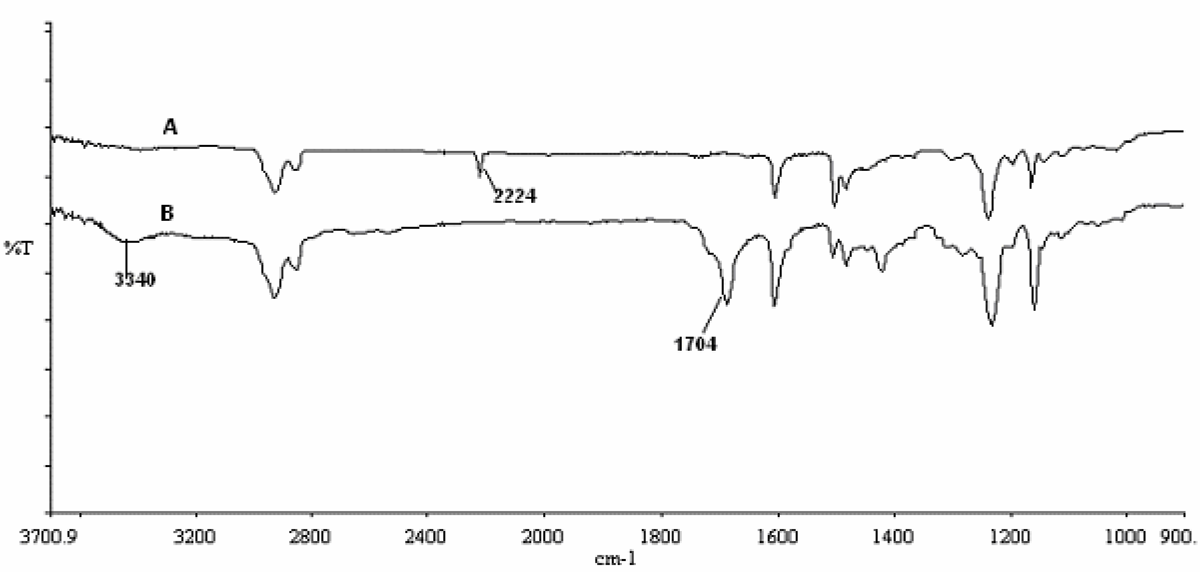


Figure 3.65: FT-IR Spectra of 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (A) and 1,1 bis-[4-(4-carboxy phenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane(B)

The dicyano intermediate 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane was synthesized by nucleophilic substitution of *p*-fluorobenzonitrile with TMPCPBP in NMP in presence of anhydrous potassium carbonate and was further hydrolyzed by refluxing with KOH in ethanol/ water to give TMPCPDA.

FT-IR spectra of DCNTMPCPBP and TMPCPDA are reproduced in **Figure 3.65**. Spectrum 'A' for DCNTMPCPBP, shows stretching of cyano group at 2224 cm^{-1} and spectrum 'B' for TMPCPBP shows characteristic band of carbonyl group of –COOH at 1704 cm^{-1}.

^{1}H NMR spectra of DCNTMPCPBP and TMPCPDA are given in **Figure 3.66** and **Figure. 3.67** respectively.

The protons 18 and 17 in DCNTMPCPBP appeared at 7.57 δ ppm and 6.77 δ ppm and were shifted to 7.88 δ ppm and 6.71 δ ppm (protons 19 and 18 in TMPCPDA) when the cyano group was transformed to acid group. Due to presence of diasteriotopic phenyl rings methyl groups 19 and 19'in DCNTMPCPBP and 17 and 17' in TMPCPDA appeared as two separate singlets at 2.02, 2.09 δ ppm and 2.03, 1.97 δ ppm, respectively. Similarly protons 16 and 16’ also appeared as two distinct peaks at 6.92 δ ppm and 7.10 δ ppm in DCNTMPCPBP and at 7.04 δ ppm and at 7.22 δ ppm in TMPCPDA.

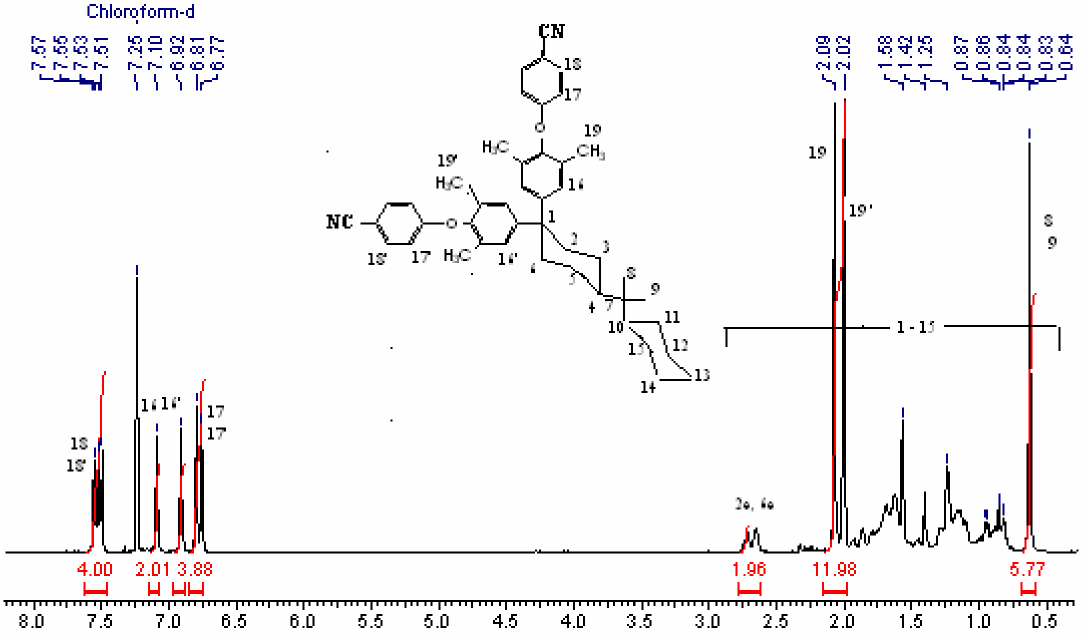
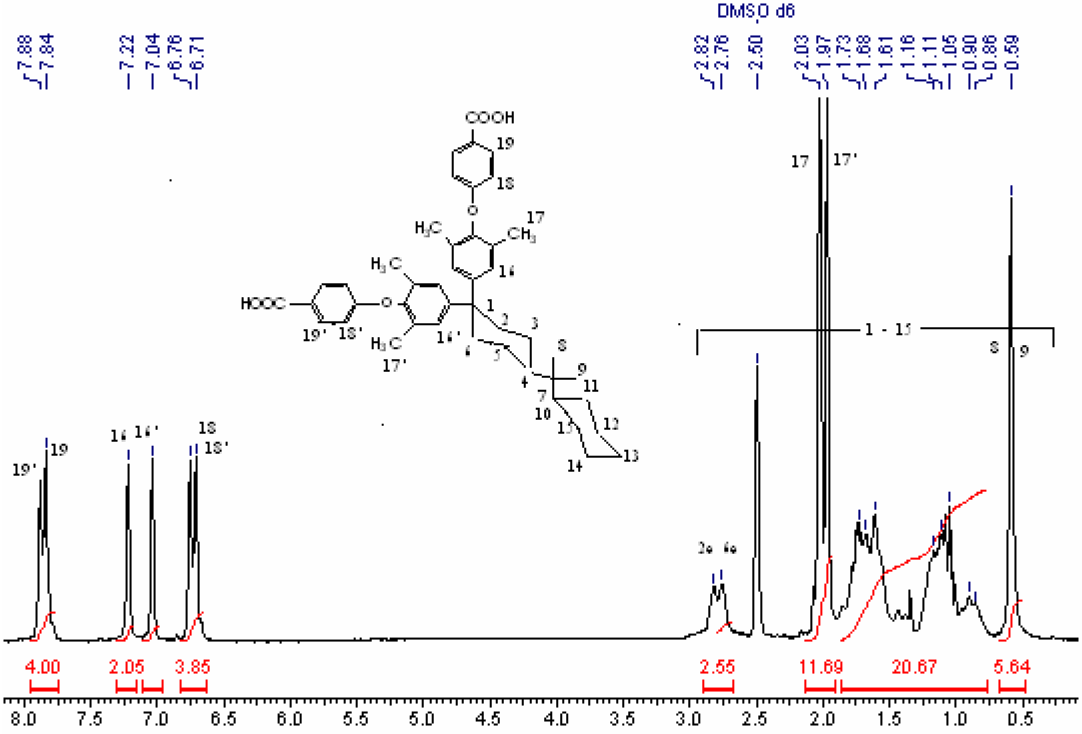


Figure 3.66: ^{1}H-NMR spectrum of 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclo-hexane in $CDCl_3$

Figure 3.67: ^{1}H-NMR spectrum of 1,1 bis-[4-(4-carboxy phenoxy)-3,5- dimethylphenyl]-4-perhydrocumyl cyclohexane in DMSO d_6



The ^{13}C NMR spectra of DCNTMPCPBP and TMPCPDA are shown in **Figure 3.68** and **Figure 3.69** respectively**.**

Carbon 24 corresponding to –CN group in DCNPCPBP appeared at 118.96 δ ppm and carbon 23 which is attached to cyano group, appeared at 104.74δ ppm in DCNTMPCPBP. These two carbons were shifted down field at 167.13 δ ppm and 124.66 δ ppm respectively in TMPCPDA , as the cyano group was transformed to acid .Both the carbons 24 and 23 resonated upfield in the case of dicyano compound because of the anisotropic shielding effect of π electrons of -C≡N group and a large downfield shift was observed when it was converted to-COOH group. After hydrolysis the resonance peaks of carbon 24 and 23 shifted down field because of the lack of anisotropic field. Spectral data corresponding to other carbon atoms are in good agreement with the proposed structure.

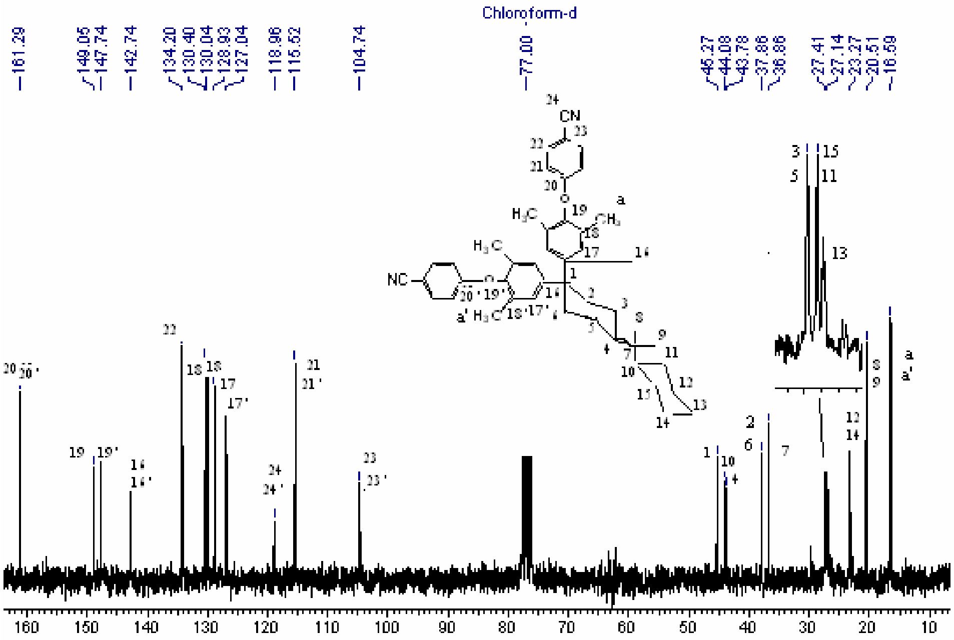


Figure 3.68: ^{13}C-NMR spectrum of 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane in $CDCl_3$

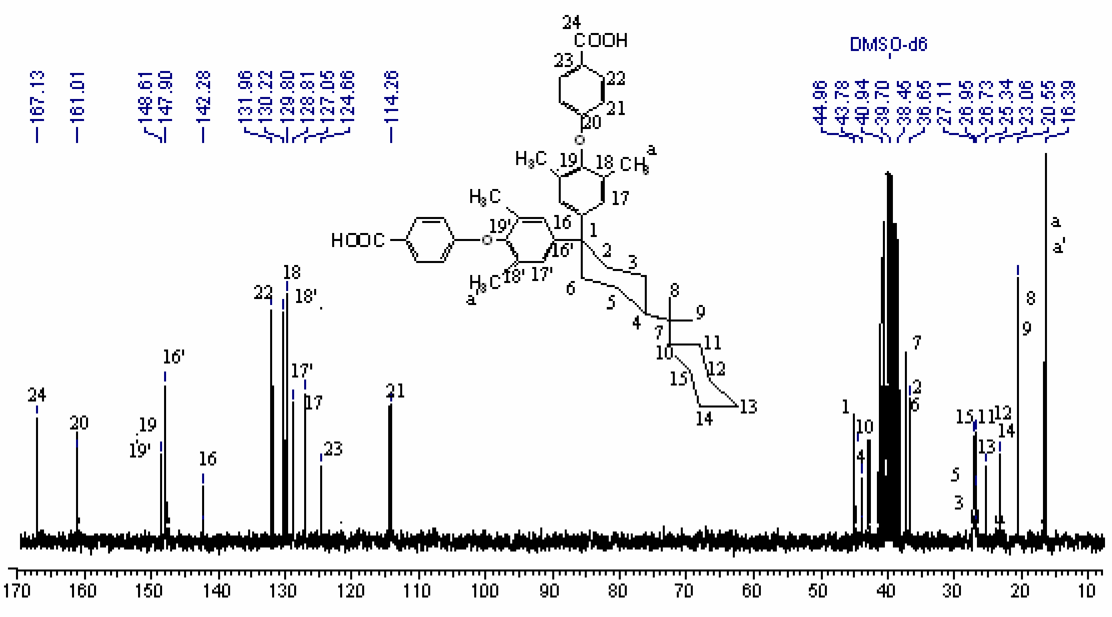


Figure 3.69: ^{13}C-NMR spectrum of 1,1 bis-[4-(4-carboxy phenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane in DMSO d_6

Since the diacid TMPCPDA was difficult to recrystallize, the single crystal for dicyano compound DCNTMPCPBP was grown by slow crystallization from its solution in acetonitrile. A crystal size of 0.32 x 0.18 x 0.10 mm^3 was used for X-ray structure determination. **Table 3.12** presents X-Ray crystal data for 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (DCNTMPCPBP)

Selected bond distances and bond angles are given in **Appendix 3. Figure 3.70** shows the molecular structure of DCNPCPBP, the four phenylene rings along with four methyl groups are arranged in a twisted manner because of the steric hindrance caused by four methyl group and perhydrocumyl cyclohexylidene group.

Table 3.12: X-Ray crystal data for 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (DCNTMPCPBP)

Crystal data.

Identification code	DCNTMPCPBP
Empirical formula	C45 H52 N2 O2
Formula weight	678.88
Temperature	298(2) K
Crystal form, colour	Thin plate, Colorless
Crystal size	0.32 x 0.18 x 0.10 mm
Wavelength (Mo $K\alpha$)	0.71073 A
Crystal system, space group	Monoclinic, P2$_1$/n
Unit cell dimensions	
a	9.2481(10) Å
b	35.400(4) Å
c	13.0203(14) Å
alpha	90 °
beta	109.918(2) °
gamma	90 °
Volume	4007.6(7) Å^3
Z, Calculated density	4, 1.125 g cm^{-3}
Absorption coefficient	0.070 mm^{-1}
Limiting indices	-10<=h<=10, -39<=k<=42, -15<=l<=13
Reflections collected / unique	20210 / 7034 [R(int) = 0.0787]
Data / parameters	7034 / 484
Max. and min. transmission	0.9929 and 0.9781
Goodness-of-fit on F^2	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1448
R indices (all data)	R1 = 0.1872, wR2 = 0.2010
Largest diff. peak and hole	0.156 and -0.159 eA^{-3}

Selected bond length and bond angles are listed in **Appendix -3.** The ORTEP diagram of DCNTMPCPBP is shown in **Figure 3.70.** DCNTMPCPBP does not show hydrogen bonding.

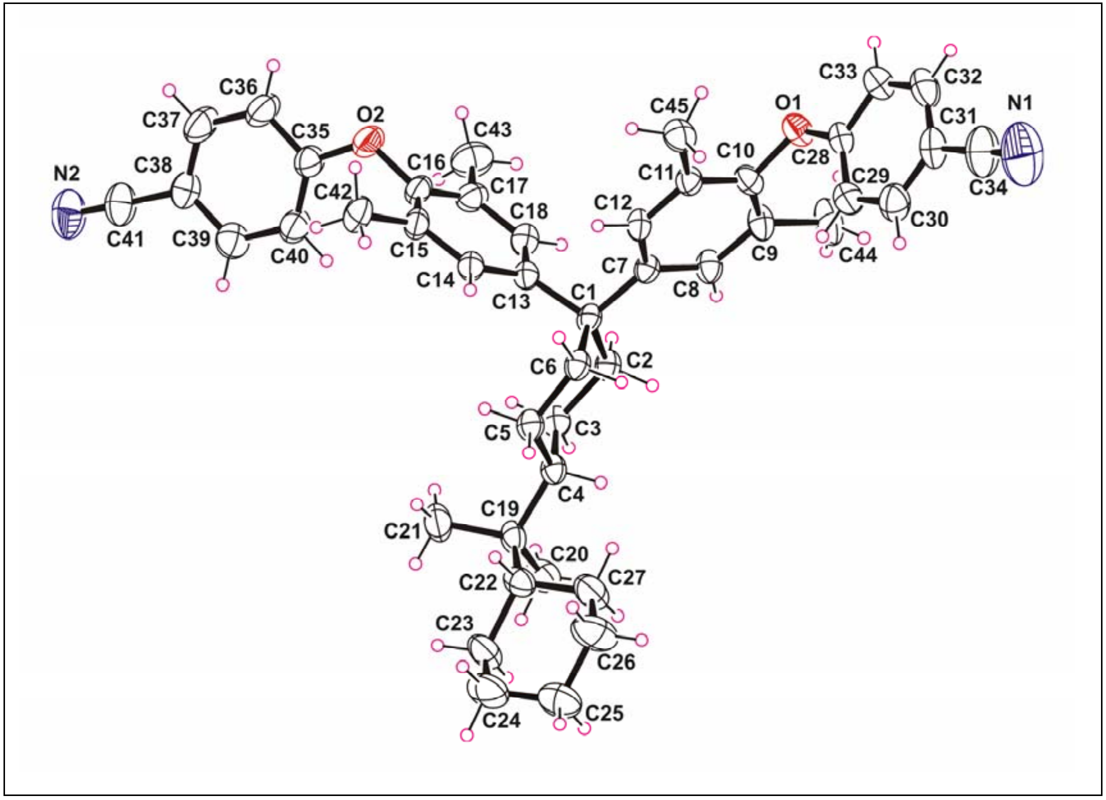


Figure 3.70: ORTEP diagram of 1,1-bis-[4-(4-cyanophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane

3.5 Conclusions

1. Six bisphenols viz. 1,1-bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane, 1,1-bis-[4-hydroxyphenyl-(4-phenylsulfonyl phenyl)]ethane, 1,1-bis-[4-hydroxyphenyl-(1-biphenyl)] ethane, 1,1-bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane , 1,1-bis-[4-hydroxy-(3,5-dimethyl phenyl)]-4-perhydrocumylcyclohexane and 1,1-bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene were synthesized starting from commercially available raw materials.
2. All the bisphenols were characterized by spectral techniques and purity was checked by HPLC.
3. The structural assignment of 1,1-bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene was completed along with the assignment for aliphatic ring protons with the help of 2D NMR spectrum.
4. The monomers containing 'cardo' groups namely perhydrocumyl cyclohexylidene group and octahydro-2(1H) naphthalidene group showed the presence of diastereotopic phenyl rings, which are magnetically non-equivalent.
5. Starting from these bisphenols, four new diamines viz. 1,1-bis-[4-(4-aminophenoxy) phenyl-1-(2-naphthyl)]ethane, 1,1-bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane , 1,1-bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane . 1,1-bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene , and two new diacids viz 1,1-bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane and 1,1-bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane were synthesized.
6. The diamine and diacid monomers were characterized by spectral techniques and spectroscopic analysis was supported by X-ray crystallographic data of the intermediates wherever suitable crystals could be obtained
7. Difunctional monomers are potentially useful for the synthesis of a host of high performance polymers.

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4.1 Introduction

Aromatic polyimides find applications as high performance polymers due to their excellent thermo-oxidative stability, electrical properties, high radiation and solvent resistance and high mechanical strength. However, they suffer from insolubility in common organic solvents and high softening temperatures that make their processing difficult and expensive. The most common technique for the fabrication of polyimides is forming the soluble precursor, a poly(amic acid), casting films and then thermally dehydrating into the final imide form. This process involving a soluble polymer precursor was pioneered by workers at Du Pont[1] in 1950's and to this date continues to be the primary route by which most polyimides are made. However, this process leads to other problems such as storage stability, inefficient cyclization , difficult removal of water and the formation of microvoids in the final material[2].

In the last few decades, many studies have been conducted to overcome these problems, majority of these studies involved three main structural modifications to tailor the properties:

1. Incorporation of groups such as hexafluoroisopropylidene [$-C(CF_3)_2-$] , –O- , $-SO_2-$ into the backbone to introduce kinks to the main chain which decrease the rigidity of the polymer backbone[3-6].
2. Incorporation of thermally stable and non-symmetrical linkages into the backbone[7-11].
3. Introduction of large polar / nonpolar pendant groups or flexible side chains in the polymer backbone [12-14] and hence disruption of symmetry and regularity.

Bulky substituents can impart significant increase in both Tg and thermo-oxidative stability while providing good solubility [15,16].Introduction of thermally stable 'cardo' groups or multicyclic structures is also a promising method for property modification in both polyimides and polyamides[17-20].

The present work reports synthesis and characterization of polyimides containing bulky naphthyl and biphenyl pendant groups and octahydro-2(1H)-naphthalydene and perhydrocumyl cyclohexylidene cardo groups.

A series of polyimides was synthesized by polycondensation of new ether containing diamines viz.

1. 1, 1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane (NABPDA)
2. 1, 1-bis–[4- (4-aminophenoxy) phenyl-1-biphenyl] ethane (BBHPDA)
3. 1, 1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene (DCHDA)
4. 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA),

with commercially available aromatic dianhydrides namely

1. 4,4'-oxydiphthalic anhydride (ODPA)
2. 3,3'4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)
3. 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA)
4. 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)
5. 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA)
6. 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA)

These polyimides were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy, X-ray diffraction analysis, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Optical properties of selected polyimide films were studied by UV-visible spectroscopy. Selected polyimide films were analyzed for dielectric constant. Gas permeability properties of selected polyimide films was studied.

4.2 Experimental

4.2.1 Materials

The four new diamines namely1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane (NABPDA), 1,1-bis–[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane (BBHPDA), 1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene (DCHDA), and 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA), were synthesized as described in **Chapter 3.** 4,4'-Oxydiphthalicanhydride (ODPA), 3,3',4,4'-hexafluoroisopropylidene diphthalic anhydride (6FDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA), 1,2,4,5-benzenetetracarboxylic dianhydrides (PMDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) all received from Aldrich, USA, 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA), from TCI, Japan, were sublimed before use. Chloroform, and methanol from S. D. Fine Chem. were distilled before use. N,N-Dimethylacetamide, N-methyl 2-pyrrolidone (NMP) and other solvents were purchased from S. D. Fine Chem. and were dried and distilled according to the reported procedures.[21]

4.2.2 Measurements

Inherent viscosity of polyimides was measured with 0.5 % (w/v) solution of polymer in either chloroform, N,N-dimethylacetamide, *m*-cresol or conc.H_2SO_4 at 30±0.1°C using an Ubbelohde suspended level viscometer on Schott Gerate CK-160 automatic viscometer.

Solubility of polyimides was determined at 3% (w/v) concentration in different solvents at room temperature or on heating.

Molecular weight of polyimides was measured on Thermofinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^5 A° to 50 A°), Detector - RI, room temperature. Polystyrene was used as the calibration standard. Polyimide sample (5 mg) was dissolved in 5 ml chloroform and filtered through 0.45 μ filter.

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

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

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

Thermogravimetric analysis was performed on TA Instrument TGA Q-5000 system at a heating rate of 20°C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC analysis was carried out on TA Instruments DSC Q10, at a heating rate of 20°C / minute in nitrogen atmosphere.

Optical properties of polyimide films (~20μ thickness) were determined using Shimadzu make UV-spectrophotometer model UV-161 PC.

Instron universal tester model 4204 with a load cell of 1 Kilo Newton was used to measure the stress-strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5mm/min was used. Measurements were carried out at room temperature using film specimens (10 mm wide, 5 cm long and ~50 μ thick) and an average of five individual measurements for each polymer was used.

4.2.2.1 Film preparation for measurement of gas permeability, mechanical and optical properties and dielectric constant

Polyimide films of 30-40 μm thickness, used for permeability studies were obtained by casting from chloroform solution for each polymer. Approximately 3 % (w/v) solution of polymer was prepared in chloroform and the solution was filtered through a 0.25 μm filter to remove particulates, if any. The clear polymer solution was poured into a clean glass disc (diameter 7.5 cm). Chloroform was evaporated slowly at room temperature. The films were removed and subsequently dried at 100°C for seven days under vacuum. Polyimide films used for determination of dielectric constant, mechanical properties and optical properties were cast similarly by dissolving appropriate quantities of polymer in chloroform.

The density of polyimide films of thickness 100 μm (which has been cast as described above using a 10 % (w/v) solution was determined by floatation method at 40 ± 0.1° C using aqueous potassium carbonate solution. Six samples of each polyimide were used for density determination and the obtained values were averaged and from the density values, specific free volume and fractional free volume (FFV) was calculated using Van Krevelen's method.[22]

4.2.2.2 Measurement of dielectric constant

The samples were made from polyimide circular films (~ 30-40 μm thick and 5 cm diameter) by vacuum deposition of gold powder in 1cm^2 area (the area of electrode). These films were then sandwiched between two electrodes of the instrument Solartron SI 1255 impedance analyzer with a dielectric interface 1296 in a parallel plate configuration.

A schematic representation of an impedance bridge used for measurement is shown in **Figure 4.1**. Essentially this is a modified form of Wheatstone bridge, where Z_1 and Z_2 are the fixed resistors with a known ratio, Z_3 is the standard impedance which consists of a series of variable capacitances and variable resistances. "DET" represents the null detector usually locks in amplifier. After the insertion of sample in the circuit the variable capacitance (C_3) and resistance R_3 standards were adjusted to obtain a zero voltage at the null detector. From this null detector condition, the real and imaginary component of the unknown impedance was calculated.

The measurements were carried out for a range of frequencies varying from 10 kHz to 1 MHz at room temperature. From the obtained capacitance values the dielectric constant was calculated using the following equation.

$$\varepsilon = C\, d \;/\; \varepsilon_0 A$$

Where ε is the dielectric constant ,C is the capacitance , d is the thickness of the film ε_0 is the permittivity of the free space (8.85×10^{-12} C^2/Nm^2) and A is the area of contact of the film with the electrode.

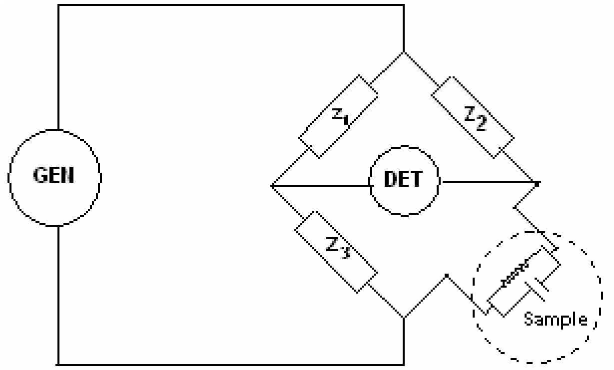


Figure 4.1: Schematic diagram of impedance- bridge circuit.

4.3 Synthesis of polyimides containing bulky pendant groups / cardo groups

A representative procedure for synthesis of polyimides is as follows:

A 100 ml three-necked round bottom flask equipped with a magnetic stirrer and a nitrogen inlet was charged with 1,1-bis-[4-{(4-aminophenoxy)phenyl}-1-(2-naphthyl)]ethane (0.60 g, 1.15 mmol) and N,N-dimethylacetamide (5 ml). When the diamine was completely dissolved in N, N-dimethylacetamide, 3,3', 4,4'- biphenyl tetra carboxylic dianhydride (0.34 g,1.15 mmol) was added in one portion. The reaction mixture was stirred at room temperature in nitrogen atmosphere affording a viscous poly (amic acid) solution. The solution was spread on a glass petri dish and dried at 100ºC for 1h in an oven to remove the solvent. The semidried poly (amic acid) film was sequentially heated at 150ºC for 30 min, at 200º C for 30 min and at 250ºC for 1h to ensure full imidization. By soaking in water, polyimide film was self stripped off from the glass surface.

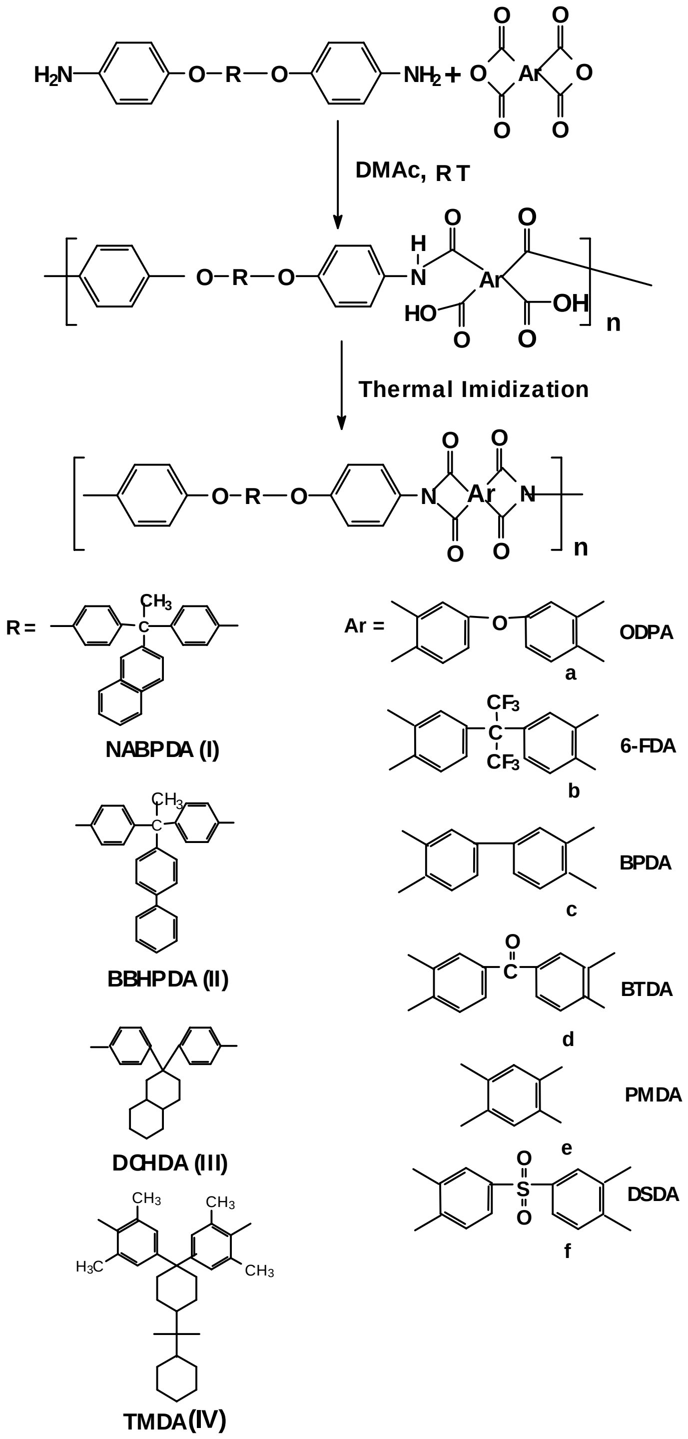
A similar procedure was followed for synthesis of other polyimides.

4.4 Results and Discussion

4.4.1 Synthesis and characterization of polyimides derived from diamine monomers containing bulky pendant group/ cardo group

Twenty four new polyimides containing bulky pendant groups/cardo groups were synthesized by the reaction of stoichiometric quantities of diamines and aromatic dianhydrides through conventional ring-opening polycondensation and subsequent thermal cyclodehydration as shown in Scheme 4.1. The results of polyimide synthesis are summarized in Table 4.1. The reaction mixture was homogenous throughout the course of reaction and gave viscous poly (amic acid)s, which were further converted to polyimides by thermal imidization as described in experimental section 4.3 . Inherent viscosity values of polyimides were in the range 0.40-1.62 dL/g indicating formation of medium to high molecular weight polymers.

Molecular weight of chloroform-soluble polyimide samples was determined by GPC. The number average molecular weight (Mn) of polyimides which were soluble in chloroform was in the range 37,900 -1,84,750 and weight average molecular weight (Mw) was in the range 95,100 - 4,47,830. 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.** Except for BTDA and PMDA-based polymers of the series, all polyimides could be cast into transparent and tough films from their solution in DMAc or chloroform.



Scheme 4.1: Synthesis of polyimides containing bulky pendant groups/cardo groups

Table 4.1: Synthesis of polyimides containing bulky pendant groups/cardo groups

Polyether-imide	Diamine	Dianhydride	Yield (%)	η_{inh} (dL/g)	Molecular Weight [e]		PDI Mw/Mn
					Mn	Mw	
PI-I a	NABPDA	ODPA	96	0.65[d]	39,300	1,12,800	2.9
PI-I b		6FDA	97	0.73[d]	95,150	2,17,900	2.3
PI-I c		BPDA	93	0.63[b]	-	-	-
PI-I d		BTDA	95	0.53[c]	-	-	-
PI-I e		PMDA	95	0.50[c]	-	-	-
PI-I f		DSDA	95	0.67[a]	-	-	-
PI-II a	BBHPDA	ODPA	97	0.60[d]	37,900	95,100	2.5
PI-II b		6FDA	98	0.62[d]	39,400	1,12,000	2.9
PI-II c		BPDA	95	0.50[d]	-	-	-
PI-II d		BTDA	93	0.48[a]	-	-	-
PI-II e		PMDA	92	0.45[c]	-	-	-
PI-II f		DSDA	93	0.55[a]	-	-	-
PI-III a	DCHDA	ODPA	92	0.60[d]	38,350	1,02,800	2.7
PI-III b		6FDA	95	0.68[d]	88,640	2,17,150	2.5
PI-III c		BPDA	93	0.52[b]	-	-	-
PI-III d		BTDA	92	0.62[b]	-	-	-
PI-III e		PMDA	93	0.40[c]	-	-	-
PI-III f		DSDA	95	0.60[a]	-	-	-
PI-IV a	TMDA	ODPA	98	1.32[d]	1,31,000	2,82,300	2.2
PI-IV b		6FDA	98	1.62[d]	1,84,750	4,47,830	2.4
PI-IV c		BPDA	97	1.23[d]	98,900	2,24,900	2.3
PI-IV d		BTDA	95	1.03[d]	58,000	1,54,700	2.7
PI-IV e		PMDA	95	0.50[b]	-	-	-
PI-IV f		DSDA	97	0.64[d]	39,600	99,900	2.5

a: η_{inh} of polyimides was measured at a concentration of 0.5 g /dl in DMAc at 30 ±0.1ºC.
b: η_{inh} of polyimides was measured at a concentration of 0.5 g / dl in *m*-cresol at 30 ±0.1ºC.
c: η_{inh} of polyimides was measured at a concentration of 0.5 g / dl in conc. H_2SO_4 30 ±0.1ºC.
d: η_{inh} of polyimides was measured at a concentration of 0.5g / dl in chloroform at 30 ±0.1ºC.
e: Measured by GPC in chloroform, polystyrene was used as the calibration standard

4.4.2 Structural Characterization

The formation of polyimides was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. A representative FTIR spectrum of polyimide film derived from TMDA and BPDA is shown in Figure 4.2

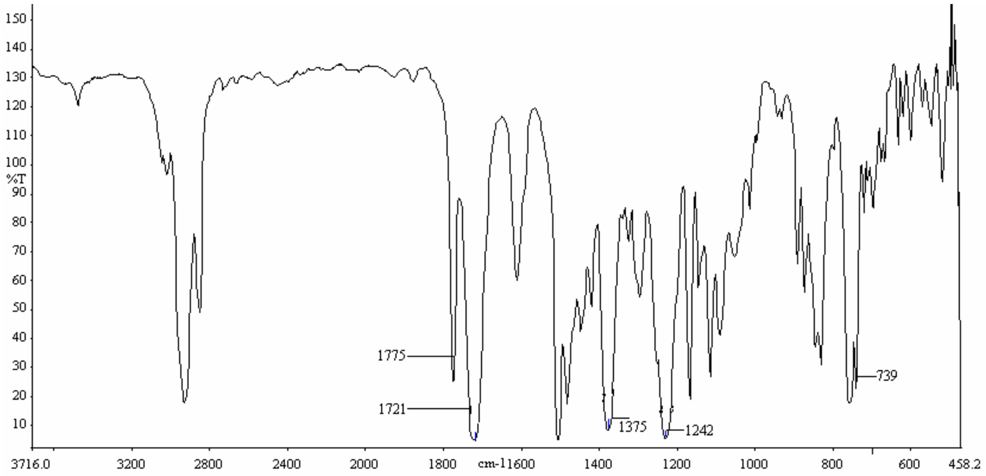


Figure 4.2: FT-IR spectrum of film of polyimide (PI-IVc) derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and BPDA

The absorption bands at 1775, 1721, 1375, and 739 cm^{-1} due to asymmetric C=O stretching, symmetric C=O stretching, C-N stretching and imide ring deformation, respectively confirmed the formation of imide linkage. The presence of band at 1242 cm^{-1} indicates presence of C-O-C linkage in the polymer backbone.

The structure of dianhydrides seems to affect the asymmetric C=O stretching frequency. Polyimide obtained from BPDA and 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane showed asymmetric C=O stretching bands at 1775 cm^{-1} (Figure 4.2), but in case of DSDA and TMDA based polyimides asymmetric C=O stretching band was observed at 1784 cm^{-1}. The observed shift arises from a decrease in electron density at the carbonyl carbon due to the electron withdrawing nature of -SO$_2$- linkage, which in turn increases the force constant of the C=O bond, leading to higher absorption frequency.

^{1}H NMR spectrum of polyimide derived from TMDA and dianhydride DSDA is reproduced in Figure 4.3

The protons 1 and 2 which appeared at 6.53 and 6.80 δ, ppm respectively, in case of monomer TMDA, (figure 3.38, chapter 3) were shifted to 7.28 and 6.83 δ, ppm due to –I effect of the two carbonyl groups of imide ring. Methyl protons 3,3’ appeared as two separate singlets at 2.07 and 2.14 δ, ppm and protons 4, 4’appeared as separate singlets at 6.92 and 7.10 δ ppm. The methyl protons 8 appeared as singlet at 0.64 δ, ppm. The cycloaliphatic protons appeared as multiplets in the range 0.75 to 2.74 δ, ppm. The protons a, a' of the dianhydride which are flanked by carbonyl group and sulfonyl group appeared downfield at 8.50 δ ppm as a singlet. Protons c, c' of dianhydride appeared at 8.41 δ ppm as doublet, due to the presence of sulfonyl group at the adjacent carbon, protons b, b' appeared at 8.11 δ ppm as a doublet.

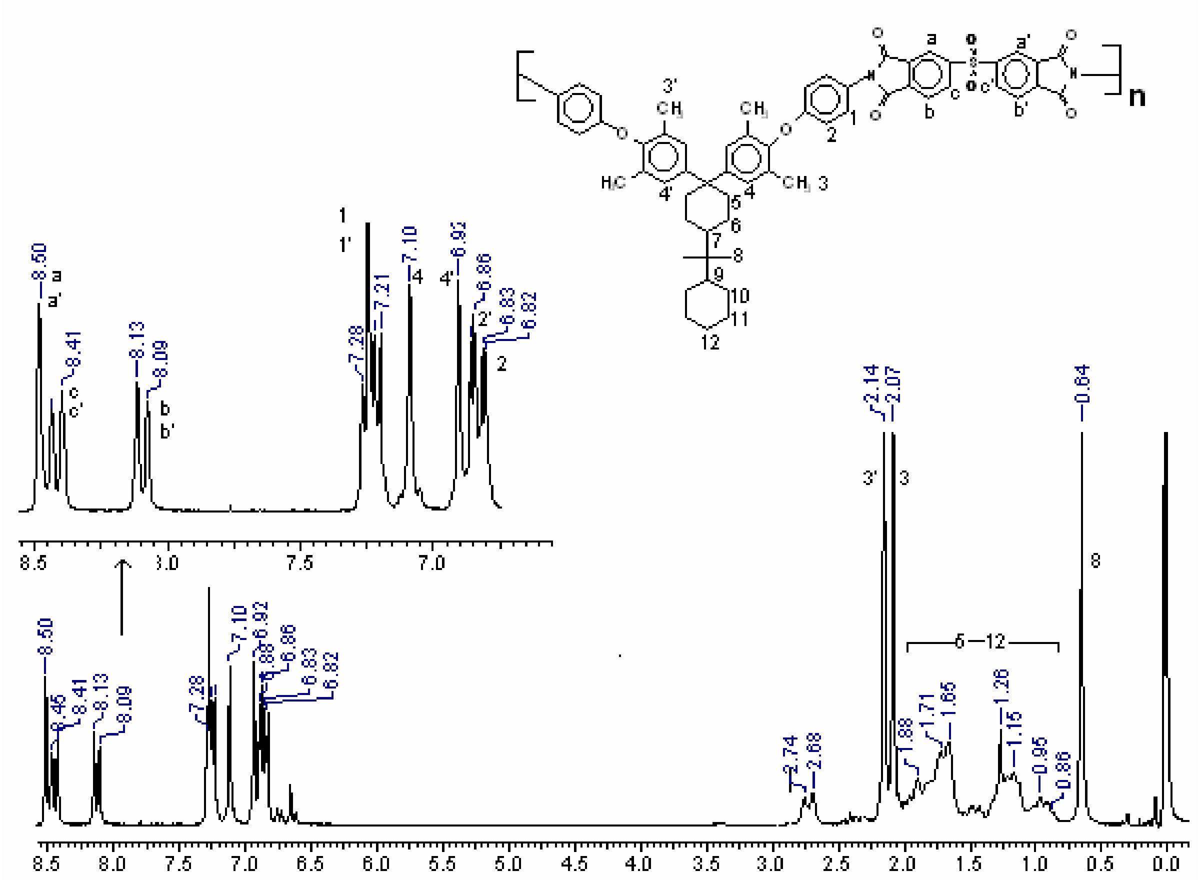


Figure: 4.3 ^{1}H NMR spectrum of polyimide (PI-IVf) derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and DSDA in $CDCl_3$

^{1}H NMR spectra of polyimides derived from NABPDA, BBHPDA and DCHBPDA with 6FDA are reproduced in Figure 4.4 to Figure 4.6 respectively, along with assignment of the protons.

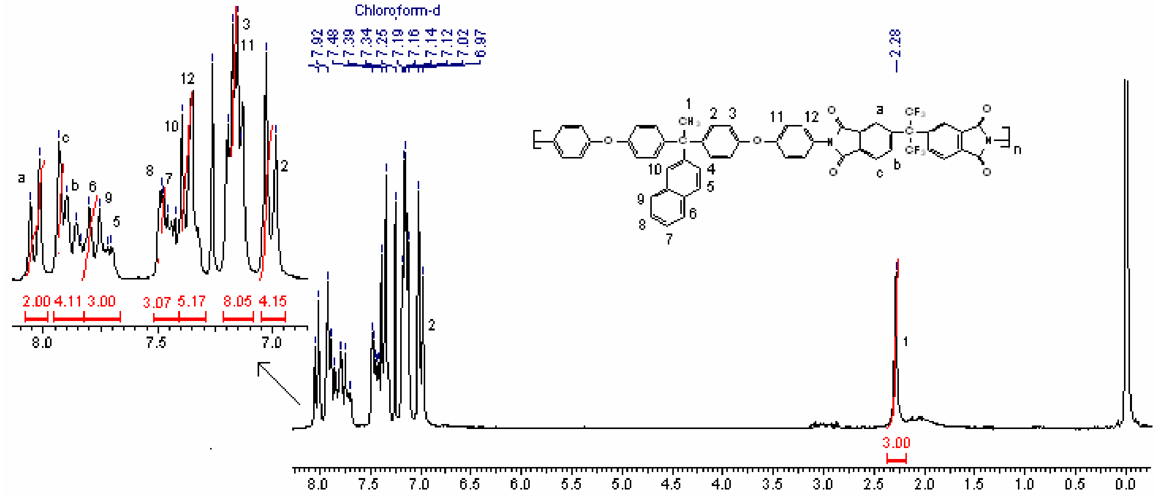


Figure 4.4 : ^{1}H NMR spectrum of polyimide (PI-Ib) obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane and 6FDA in $CDCl_3$

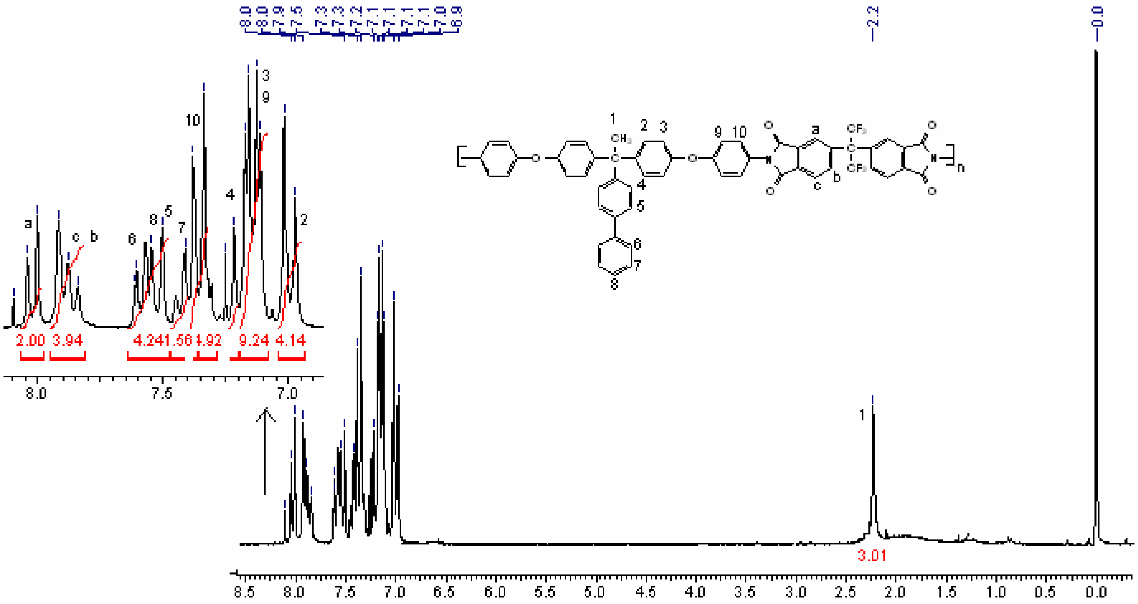


Figure 4.5: ^{1}H NMR spectrum of polyimide (PI-IIb) obtained from 1,1-bis–[4- (4-aminophenoxy) phenyl-1-biphenyl] ethane and 6FDA in $CDCl_3$

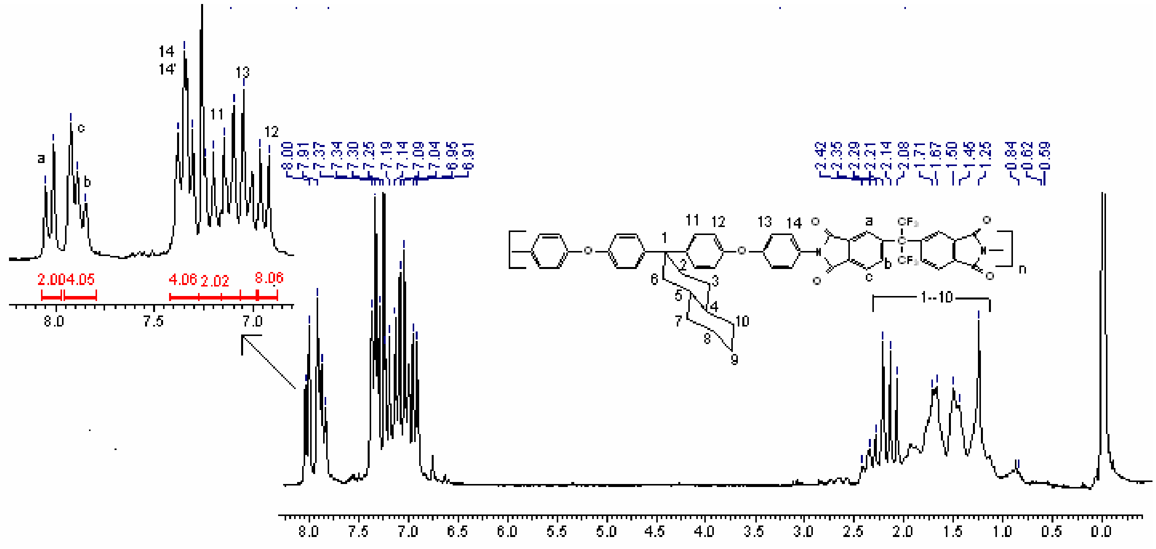


Figure 4.6: ^{1}H NMR spectrum of polyimide (PI-IIIb) obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene and 6FDA in $CDCl_3$

^{13}C NMR spectrum of polyimide obtained from TMDA and 6FDA is reproduced in Figure 4.7 along with assignments of carbon atoms. The carbonyl carbons j and k appeared at 166.36 and 166.22 δ ppm. Quaternary carbons 23,20 and 19 attached to nitrogen and oxygen atoms appeared at 157.84, 155.87 and 148.7 δ ppm respectively. Carbon c bearing fluorine atoms appeared as quartet centered around 124 δ ppm because of the heteronuclear ^{13}C-^{19}F coupling. Aliphatic carbon b bearing two CF_3 groups appeared at 64.26 δ ppm. Other aliphatic carbons of perhydrocumylcyclohexylidene cardo group appeared in the range 16.83 to 45.27 δ ppm. The spectroscopic data was in good agreement with the proposed structure

^{13}C NMR spectrum of polyimide obtained from BBHPDA and ODPA is reproduced in Figure 4.8 along with assignments of carbon atoms. The carbonyl carbons a and b appeared at 166.52 and 166.39 δ ppm. Quaternary carbons 10, 7 and 6 attached to nitrogen and oxygen atoms appeared at 127.31, 157.32 and 154.75 δ ppm, respectively. Carbon h attached to ether linkage in dianhydride moiety appeared at 161.20 δ ppm and quaternary carbons c,d appeared at 157.32 and 154.75 δ ppm. The spectroscopic data obtained for all the carbon atoms was in good agreement with the proposed structure

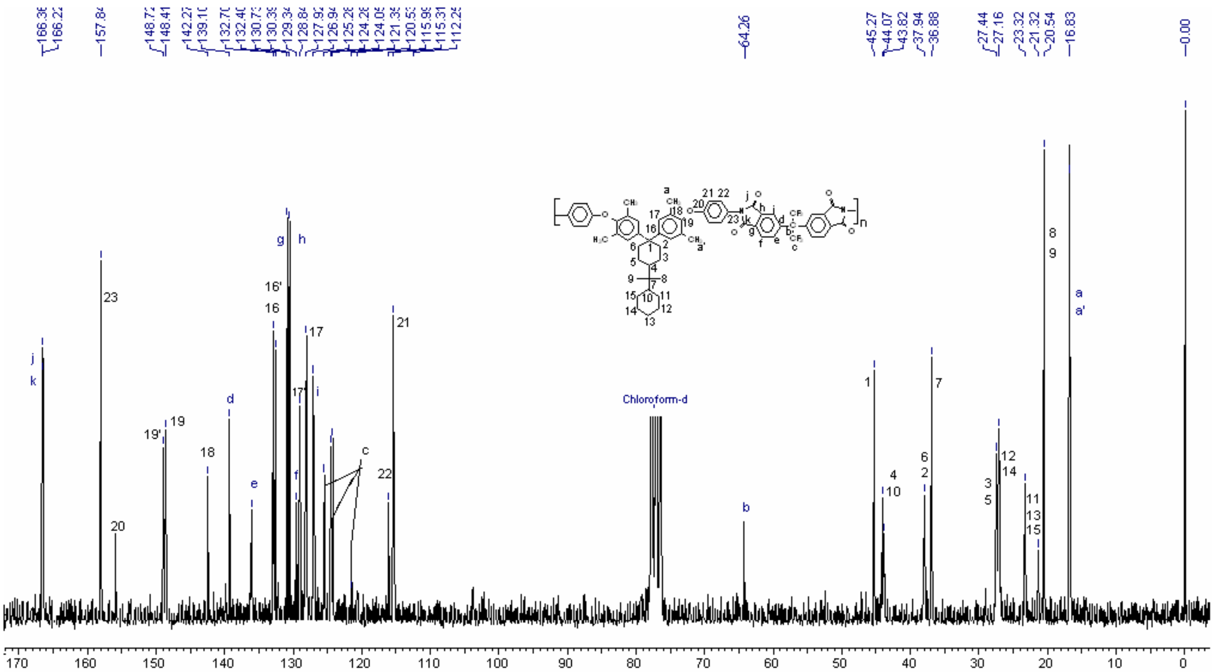


Figure 4.7: ^{13}C NMR spectrum of polyimide (PI-IV b) obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and 6FDA in $CDCl_3$

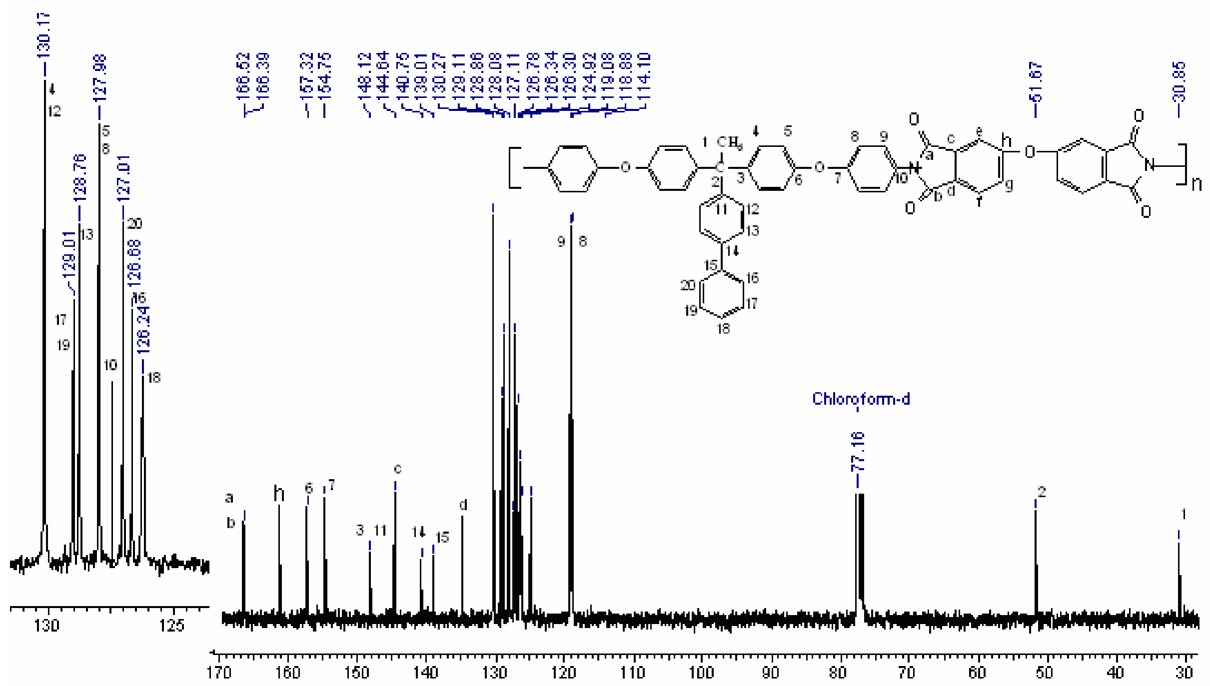


Figure 4.8: ^{13}C NMR spectrum of polyimide (PI-IIa) obtained from 1,1-bis–[4- (4-aminophenoxy) phenyl-1-biphenyl] ethane and ODPA in $CDCl_3$

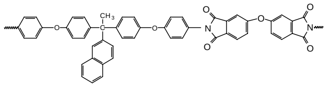
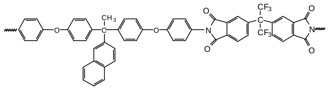
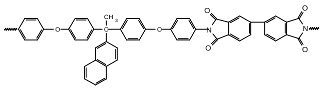
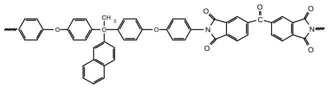
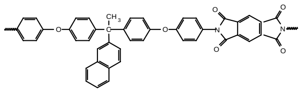
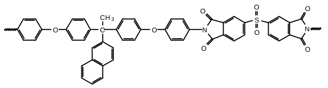
4.4.3 Properties of polyimides

4.4.3.1 Solubility of polyimides

Polyimides were tested for solubility at 3 % w/v concentrations in different solvents and data is summarized in **Tables 4.2, 4.3, 4.4, 4.5.**

Table 4.2 presents solubility data for polyimides derived from NABPDA and aromatic dianhydrides in several organic solvents. All polyimides, except PI-Id and PI-Ie derived from BTDA and PMDA, were soluble in NMP, *m*-cresol and pyridine at room temperature or upon heating. When the dianhydrides adopted were 6FDA and ODPA containing hexafluoro isopropylidene linkage and flexible ether linkage respectively, polyimides could be dissolved even in common organic solvent such as chloroform. The excellent solubility of polyimide derived from 6FDA could be attributed to the low cohesive energy provided by the fluorinated groups and the reduction in charge transfer complexes of conjugated aromatic system [23]. ODPA based polyimides exhibited good solubility owing to the presence of flexible ether linkage (-O-) present between the two phthalimide units.

Table 4.2: Solubility data of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane and aromatic dianhydrides

Polyimide		chloroform	NMP	DMAc	*m*-cresol	pyridine	THF
PI-I a		++	++	++	+	+	-
PI-I b		++	++	++	++	++	++
PI-I c		-	+	-	+	+	-
PI-I d		-	-	-	-	-	-
PI-I e		-	-	-	-	-	-
PI-I f		-	+	+	+	+	-

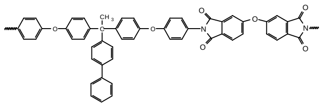
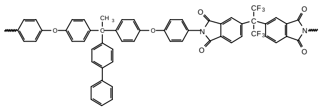
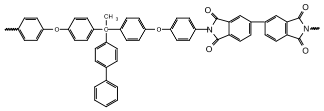
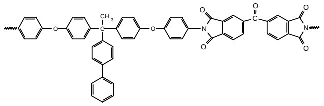
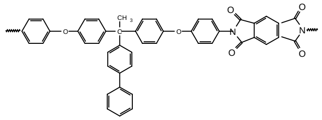
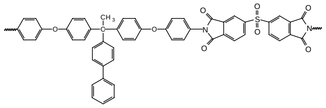
++ Soluble at room temperature, + soluble upon heating at 80ºC, - insoluble even upon heating

Table 4.3 presents solubility behavior of polyimides derived from BBHPDA and aromatic dianhydrides.

All the polyimides, except PI-IIe derived from PMDA, were found to be soluble in NMP, DMAc, *m*-cresol and pyridine at room temperature or on heating. Additionally polyimides based on 6FDA, ODPA and BPDA were soluble in common organic solvent such as chloroform.

It has been reported previously that analogous polyimide obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl]-1-phenylethane (containing pendent phenyl ring) and BPDA is soluble in NMP, m-cresol and pyridine upon heating[24a]. Better solubility of BBHPDA based polyimide was possibly due to the structural modification through incorporation of biphenyl pendant group and flexible ether linkage which increased the disorder in the chains and hindered dense chain staking, thereby reducing the interchain interactions to enhance solubility.

Table 4.3: Solubility behaviour of polyimides obtained from 1,1-bis–[4- (4-aminophenoxy) phenyl-1-biphenyl] ethane and aromatic dianhydrides

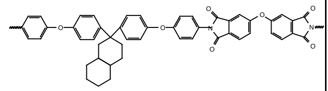
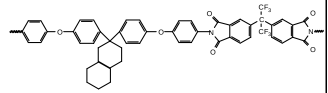
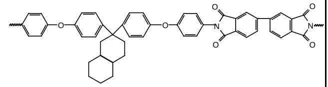
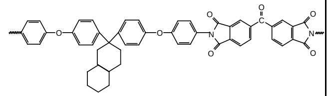
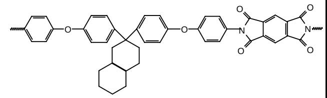
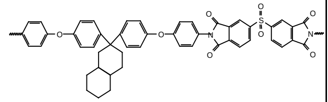
Polyimide		Chloroform	NMP	DMAc	*m*-cresol	Pyridine	THF
PI- II a		++	++	++	++	+	-
PI- II b		++	++	++	++	++	++
PI- II c		++	++	+	++	+	-
PI- II d		-	+	+	+	-	-
PI- II e		-	-	-	-	-	-
PI- II f		-	+	+	+	+	-

++ soluble at room temperature, + soluble on heating at 80ºC , - insoluble even on heating

Table 4.4 presents solubility data for the polyimides derived from DCHDA and commercially available dianhydrides tested at 3% w/v in various organic solvents.

All polyimides, except for PI-IIIe obtained from DCHDA and PMDA, were soluble in *m*-cresol at room temperature or on heating. When the dianhydrides used were ODPA and 6FDA, the polyimides obtained were soluble at room temperature in various organic solvents such as chloroform, NMP, DMAc, pyridine and THF whereas DSDA based polyimides were soluble in NMP and DMAc upon heating.

Table: 4.4 Solubility behaviour of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene and aromatic dianhydrides

Polyimide		Chloroform	NMP	DMAc	*m*-cresol	Pyridine	THF
PI- III a		++	++	++	++	++	++
PI- III b		++	++	++	++	++	++
PI- III c		-	-	-	+	-	-
PI- III d		-	-	-	+	-	-
PI- III e		-	-	-	-	-	-
PI- III f		-	+	+	+	-	-

++ soluble at room temperature, + soluble on heating at 80ºC, - insoluble even on heating

Table 4.5 summarizes the solubility data for polyimides derived from TMDA and aromatic dianhydrides tested at 3% w/v in various organic solvents.

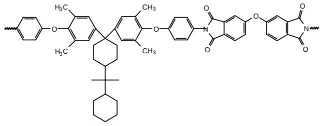
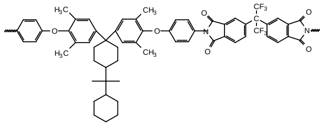
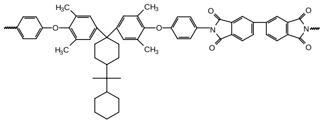
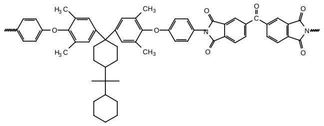
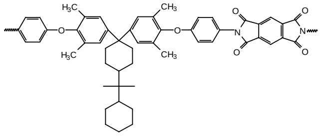
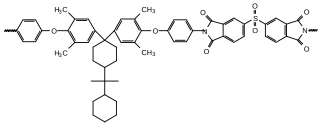
Except for polyimide based on TMDA and PMDA all polyimides based on TMDA were found to be soluble in the solvents tested namely chloroform, THF, NMP, DMAC, *m*-cresol and pyridine at room temperature. The good solubility of polyimides based on TMDA was apparently in part governed by modification in diamine structure by introduction of perhydrocumyl cyclohexylidene cardo group, incorporation of arylene ether units in the polymer backbone and substitution of tetra methyl groups along the polymer backbone. These modifications worked by inhibiting the dense chain packing of polymer chains also decreased the intermolecular forces between the polymer chains, consequently causing a decrease in crystallinity and increase in solubility.

Thus good solubility of these polyimides in common organic solvent make them potential candidates for practical applications in spin-coating or solvent casting processes.

In general, the solubility of polyimides depends on many parameters such as structure of diamines and dianhydrides used, method of synthesis of polyimides, packing of polyimide chains in bulk, or in other words crystallinity of polyimides and intermolecular interactions etc.

From the results presented in Tables 4.2, 4.3, 4.4 and 4.5 the organic-solvent solubilities of polyimides based on diamines namely 1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane , 1,1-bis-[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane ,1,1-bis-[4-(4-aminophenoxy)phenyl] octahydro-2(1H)-naphthalene and 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane may be explained by the incorporation flexible ether linkages and bulky pendant /cardo groups along polyimide backbone that inhibited the close packing of polymer chains. Therefore, diamines synthesized in the present work could be considered as useful monomers for preparation of organosoluble polyimides.

Table: 4.5 Solubility behavior of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides

Polyimide		Chloroform	NMP	DMAc	*m*-cresol	Pyridine	THF
PI-IV a		++	++	++	++	++	++
PI-IV b		++	++	++	++	++	++
PI-IV c		++	++	++	++	++	++
PI-IV d		++	++	++	++	++	++
PI-IV e		-	+	-	+	-	-
PI- IV f		++	++	++	++	++	++

++ soluble at room temperatue, + soluble upon heating at 80ºC , - insoluble even upon heating

4.4.3.2 X-Ray diffraction analysis

X-Ray diffraction patterns of polyimide films obtained from NABPDA, BBHPDA, DCHDA and TMDA with different dianhydrides are shown in Figures 4.9, 4.10, 4.11, 4.12, respectively. Bulky pendant groups in NABPDA and BBHPDA and cyclic cardo groups in TMDA and DCHDA prevented the close packing of polymer chains hence all the polyimides showed amorphous nature.

Polyimides derived from diamines NABPDA, BBHPDA, DCHDA and dianhydride PMDA were not soluble in common organic solvents, the films could not be cast. Furthermore these polymers could not be ground to fine, homogeneous powder (fine enough to pack the quartz window of the instrument) so X-ray analysis for these samples could not be done.

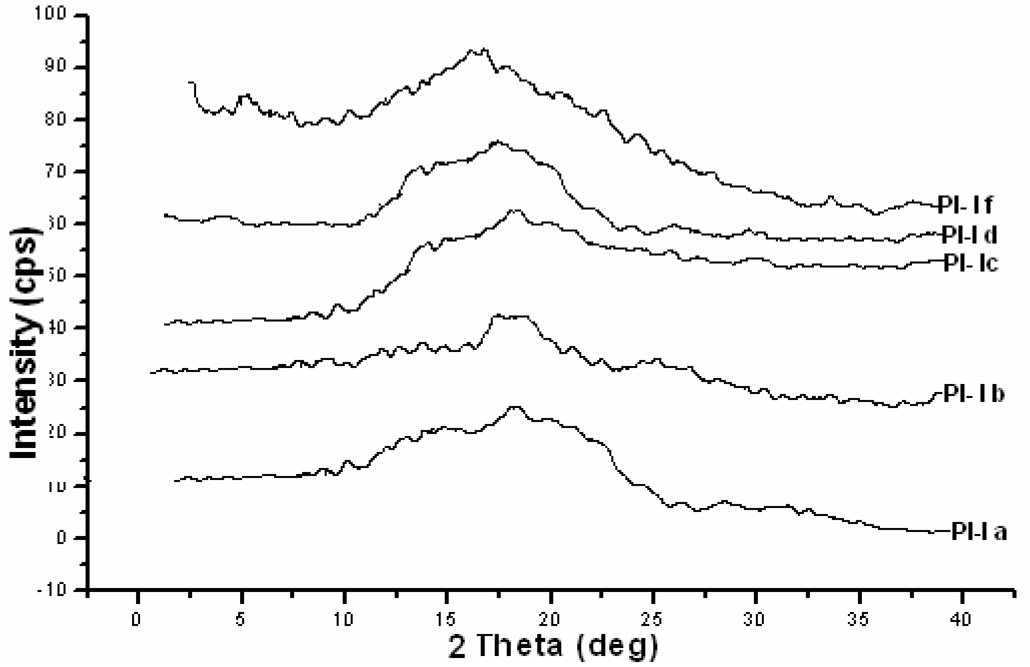


Figure 4.9: Wide angle X-ray diffractograms of polyimides obtained from 1, 1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane and aromatic dianhydrides

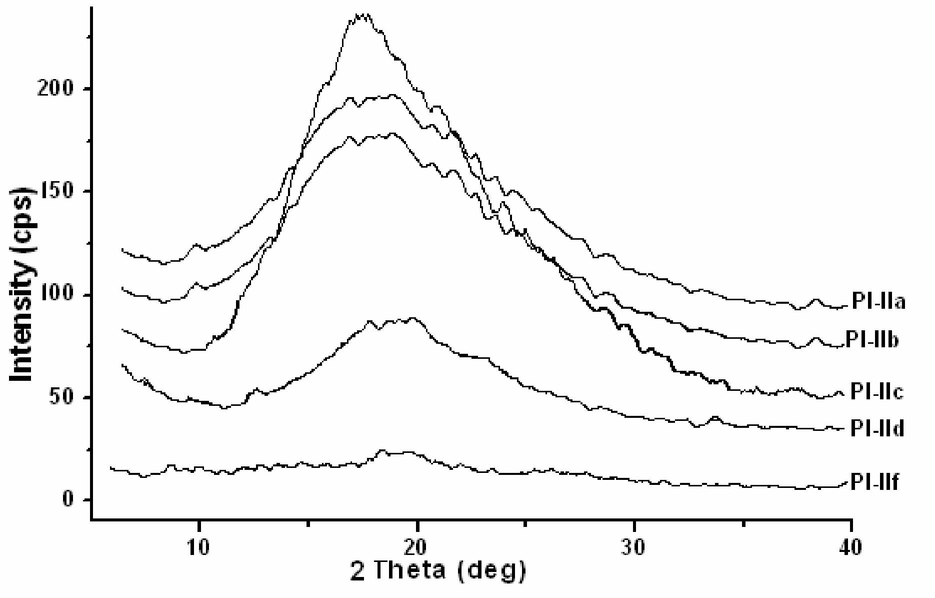


Figure 4.10: Wide angle X-ray diffractograms of polyimides obtained from 1,1-bis–[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane and aromatic dianhydrides

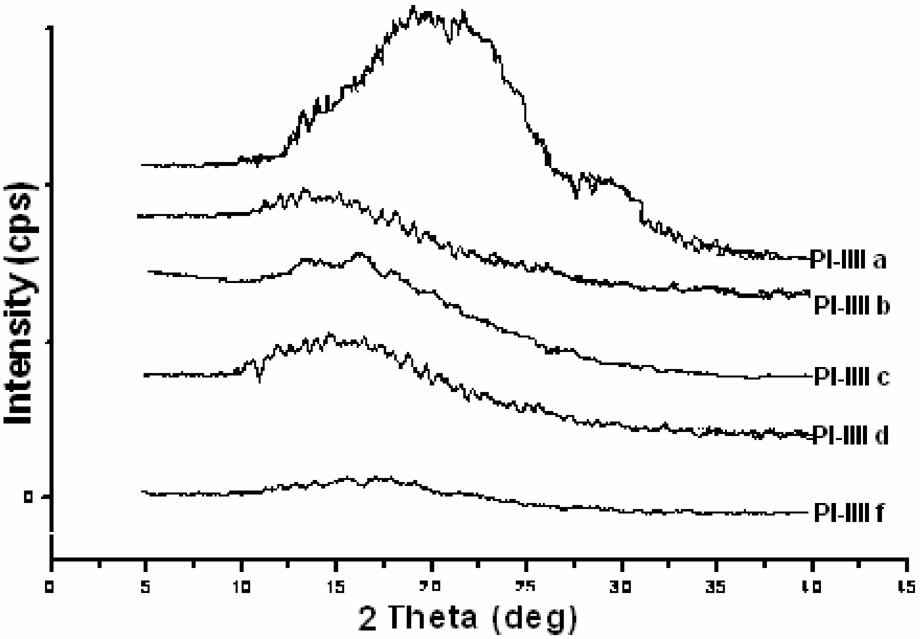


Figure 4.11: Wide angle X-ray diffractograms of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene and aromatic dianhydrides

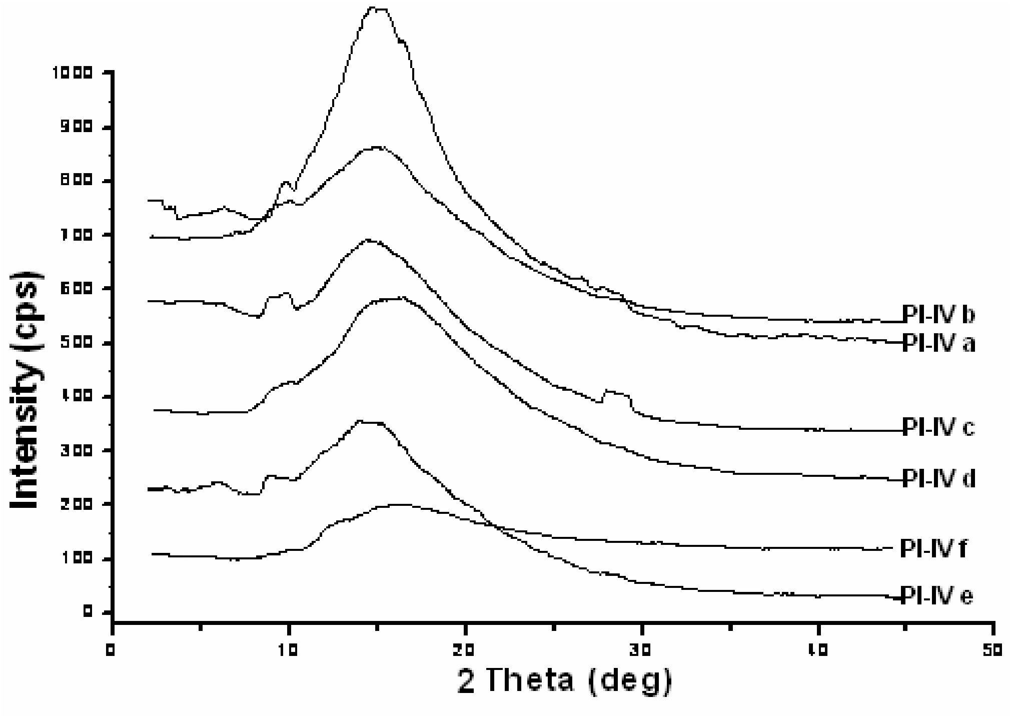


Figure 4.12: Wide angle X-ray diffractograms of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides

4.4.3.3 Thermal behavior of polyimides

Thermogravimetric analysis (TGA) of polyimides was performed at a heating rate of 20ºC/minute under nitrogen to provide information about their thermal stability . TG curves for polyimides based on NABPDA are shown in Figure 4.13. Initial decomposition temperatures (IDT), and decomposition temperature at 10 % weight loss (T_{10}) were calculated from the TG curves and the data is presented in Table 4.6.

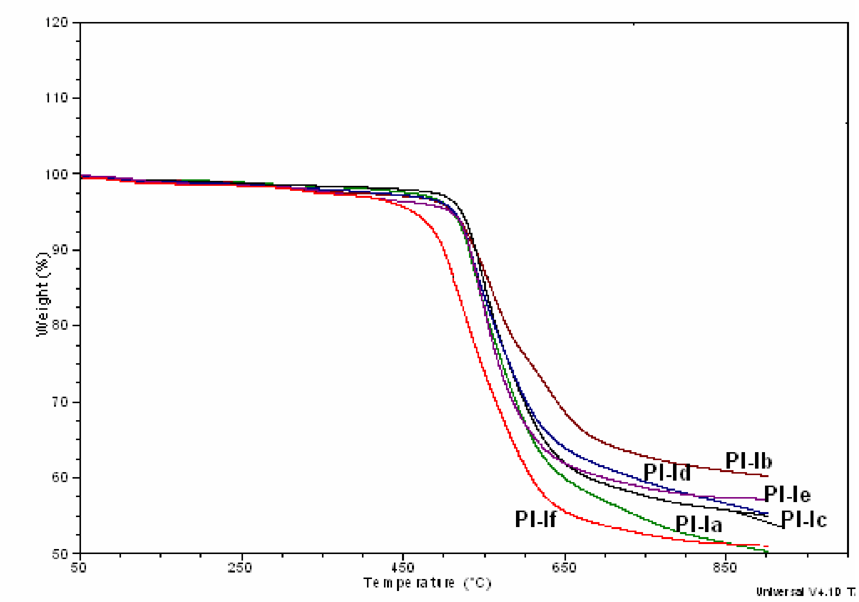
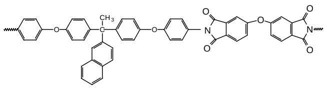
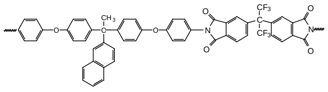
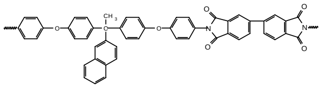
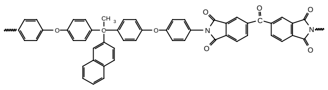
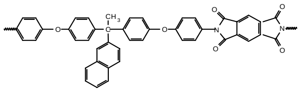
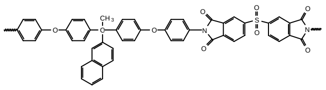


Figure 4.13: TG curves of polyimides (PI I a-I f) derived from 1,1-bis-[{4-(4-aminophenoxy) phenyl -1-(2-naphthyl)}] ethane and aromatic dianhydrides

Thermal degradation of polyimides based on NABPDA started in the range 482ºC-521ºC and temperature at 10% weight loss (T_{10}) were in the range 502ºC- 539ºC. All polyimides showed single stage decomposition.

Table 4.6: Thermal properties of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane and aromatic dianhydrides.

Polyimide		IDT (ºC)[a]	T_{10} (ºC)[a]	Tg (ºC)[b]
PI-I a		514	531	246
PI-I b		510	539	271
PI-I c		521	539	272
PI-I d		513	532	249
PI-I e		520	533	316
PI-I f		482	502	262

a: Measured by TGA at a heating rate of 20 ºC/min in nitrogen.
b: Measured on DSC at a heating rate of 20 ºC/min in nitrogen.

Glass transition temperature (Tg) of polyimides was determined by differential scanning calorimetery (DSC). DSC curves are shown in Figure 4.14. Tg values were obtained from the second heating scans of polyimide samples at a heating rate of 20 ºC /min. and glass transition temperatures (Tg) are reported in Table 4.6.

Tg of polyimides based on NABPDA was in the range 246-316ºC. Tg values of these polyimides depended on the structure of the dianhydride components and decreased with increasing flexibility of the polymer backbone. The highest value of Tg is 316ºC obtained for the polyimide derived from rigid PMDA and the lowest value 246ºC was obtained for ODPA-based polyimide owing to the presence of flexible ether linkage between the phthalimide units.

There is a large window between Tg and decomposition temperature which could be advantageous in the processing of these polymers.

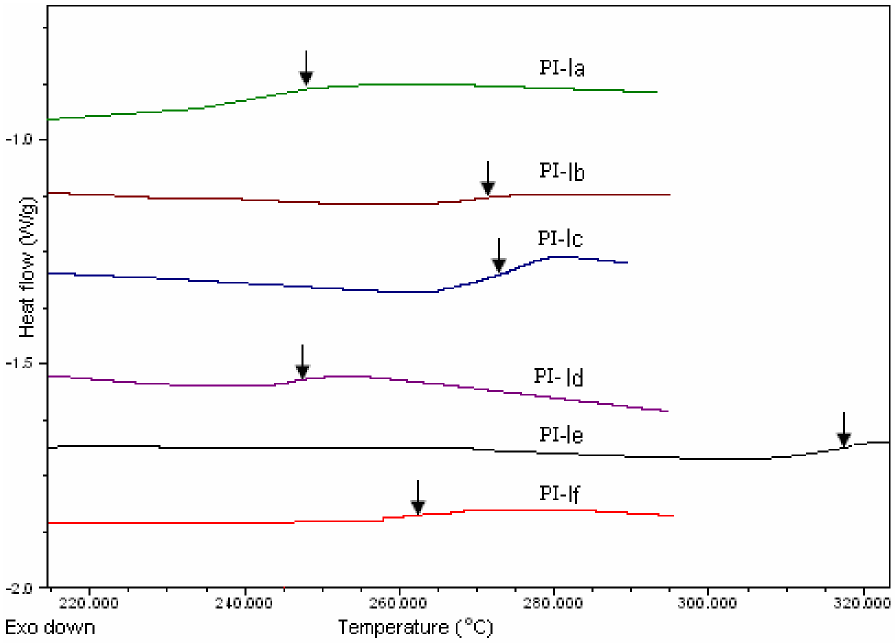


Figure 4.14 DSC curves of polyimides (PI Ia -If) derived from 1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane and aromatic dianhydrides

Figure 4.15 shows TG curves for polyimides obtained from diamine BBHPDA.

Table 4.7 presents the thermal properties of polyimides obtained from BBHPDA and aromatic dianhydrides.

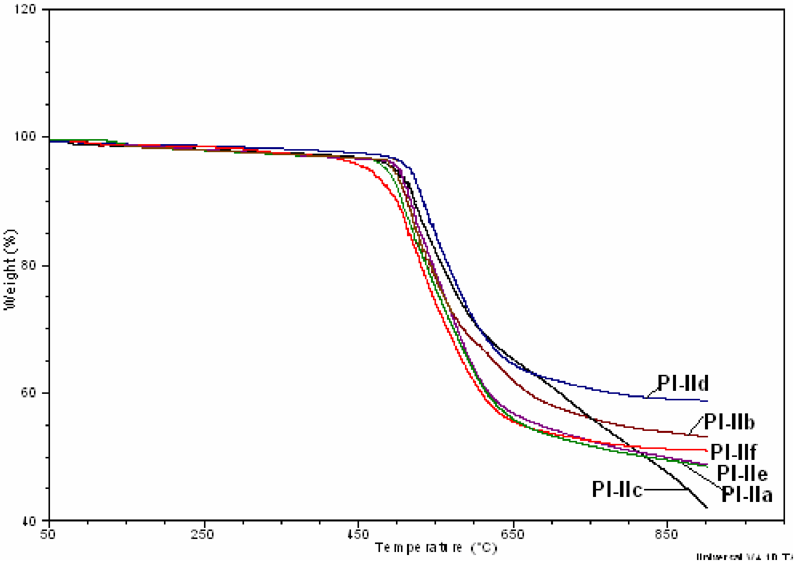
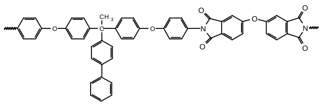
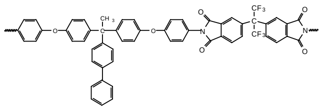
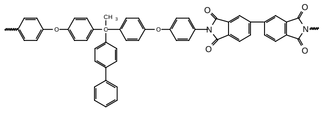
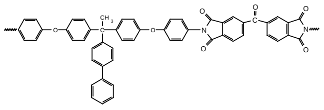
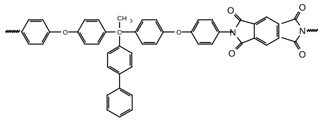
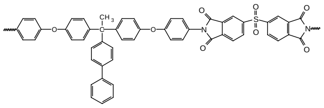


Figure 4.15: TG curves of polyimides (PI II a-II f) derived from 1,1-bis–[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane and aromatic dianhydrides

Table 4.7: Thermal properties of polyimides obtained from 1,1-bis–[4- (4-aminophenoxy) phenyl-1-biphenyl] ethane and aromatic dianhydrides.

Polyimide		IDT, °C[a]	T_{10}, °C[a]	Tg, °C[b]
PI-II a		480	511	254
PI-II b		500	519	271
PI-II c		500	521	274
PI-II d		513	533	258
PI-II e		538	542	311
PI-II f		488	507	272

a: Measured by TGA at a heating rate of 20 °C/min in nitrogen.
b: Measured on DSC at a heating rate of 20 °C/min in nitrogen.

TG curves showed that initial decomposition temperature (IDT) of polyimides based on BBHPDA was in the range 480-538 °C and temperature at 10 % wt loss (T_{10}) was in the range 507-542 °C, indicating their good thermal stability.

Figure 4.16 shows DSC curves for polyimides obtained from BBHPDA and aromatic dianhydrides. Glass transition temperature (Tg) of polyimides obtained from BBHPDA was in the range 254°C-311°C.

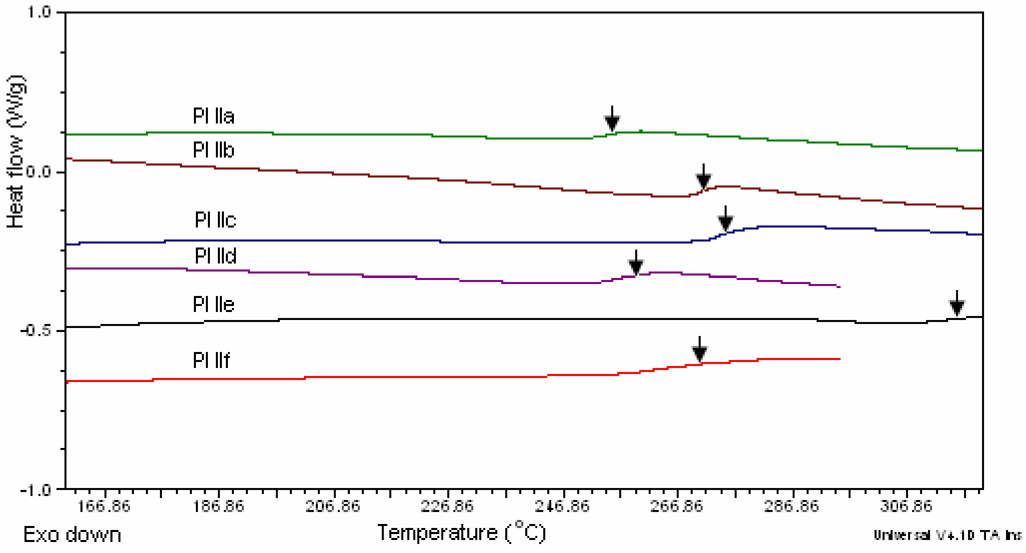


Figure 4.16 DSC curves of polyimides (PI IIa -II f) derived from 1,1-bis–[4-(4-aminophenoxy) phenyl-1-biphenyl] ethane and aromatic dianhydrides

Figure 4.17 shows TG curves of polyimides based on DCHDA. Table 4.8 presents thermal properties of polyimides obtained from DCHDA and aromatic dianhydrides. Thermogravimetric analysis revealed that all polyimides were stable up to 457°C indicating their good thermal stability. Degradation of polyimides based on DCHDA started in the range 457-502 °C (IDT) and temperature at 10% weight loss was in the range 473-504 °C.

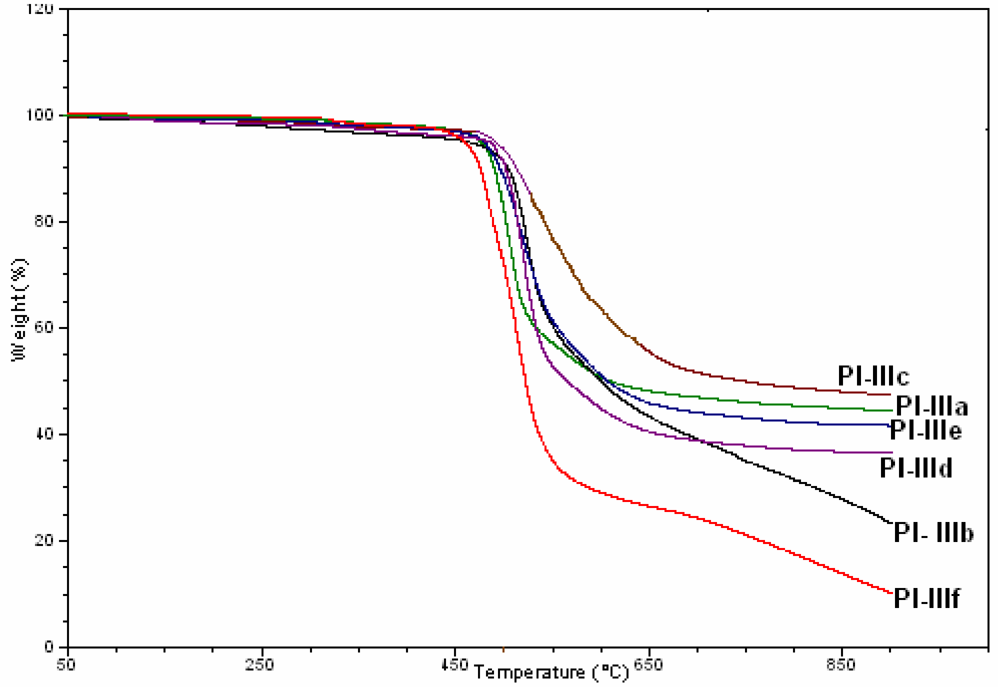
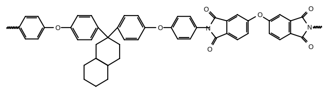
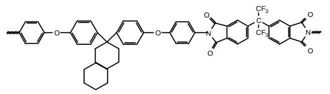
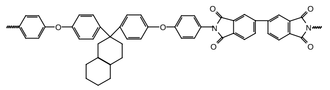
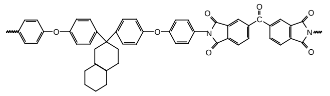
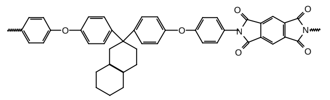
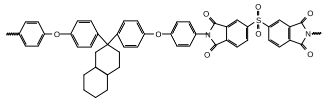


Figure 4.17: TG curves of polyimides (PI-IIIa to PI-IIIf) derived from1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene and aromatic dianhydrides

Table 4.8: Thermal properties of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene and aromatic dianhydrides

Polyimide		IDT, ºC[a]	T_{10}, ºC[a]	Tg, ºC[b]
PI-III a		**478**	**485**	**256**
PI-III b		**495**	**498**	**274**
PI-III c		**502**	**504**	**276**
PI-III d		**476**	**481**	**256**
PI-III e		**495**	**502**	**313**
PI-III f		**457**	**473**	**262**

a: Measured by TGA at a heating rate of 20 ºC/min in nitrogen.
b: Measured on DSC at a heating rate of 20 ºC/min in nitrogen.

Figure 4.18 shows DSC curves for polyimides based on diamine DCHDA and aromatic dianhydrides. Glass transition temperature (Tg) of polyimides obtained from diamine DCHDA was in the range 256ºC -313ºC. Tg of analogous polyimides obtained from diamine1,1-bis [4-(4-aminophenoxy)phenyl]cyclohexane (containing cyclohexylidene cardo group)[25] and aromatic dianhydrides was in the range 230-266ºC. Hence increasing the bulk of the cardo group by introduction of octahydro 2-(1H) naphthalydene unit possibly hindered the free rotation of polyimide chains and improved the glass transition temperature of polyimides.

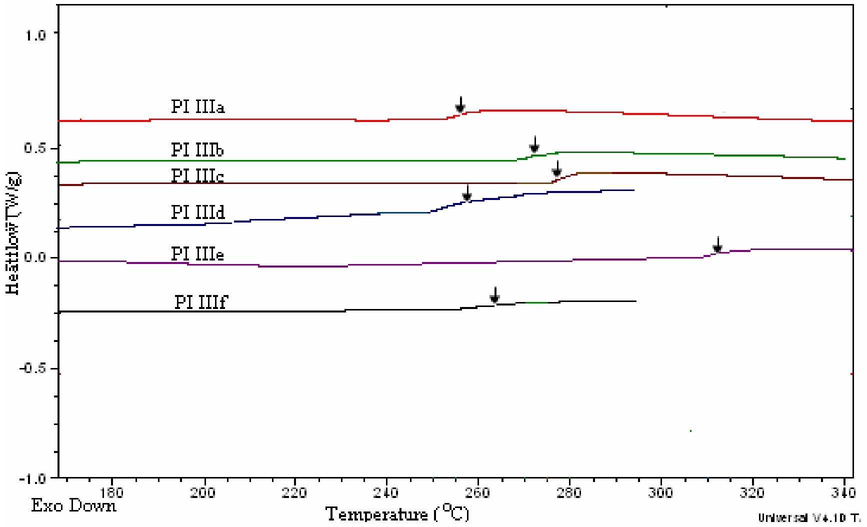


Figure 4.18 DSC curves of polyimides (PI IIIa- III f) derived from 1,1-bis-[4-(4-aminophenoxy) phenyl] octahydro-2(1H)-naphthalene and aromatic dianhydrides

TG curves of polyimides obtained from diamine TMDA and aromatic dianhydrides are shown in Figure 4.19 and Table 4.9 presents thermal properties of polyimides obtained from TMDA and aromatic dianhydrides.

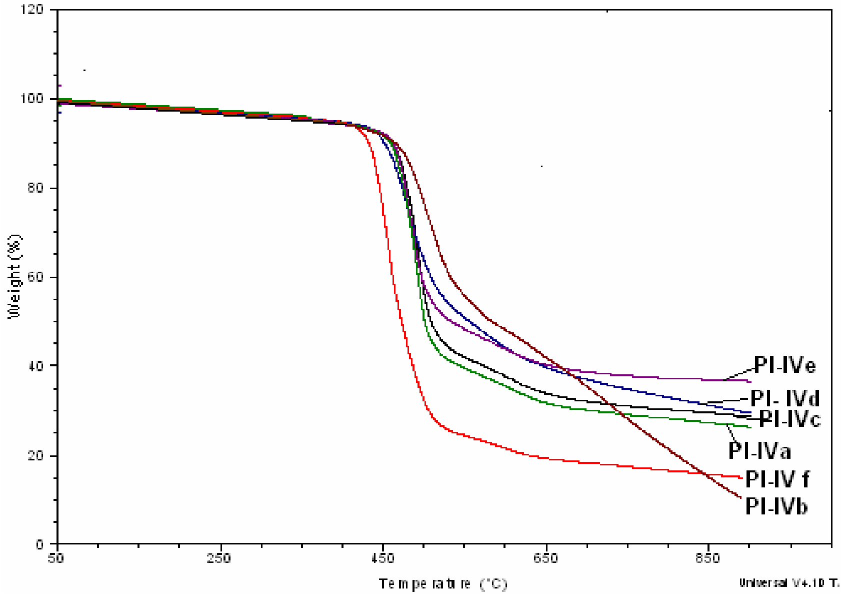
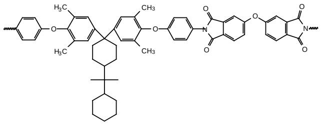
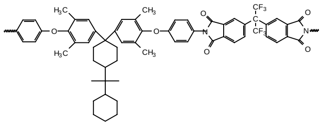
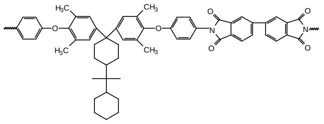
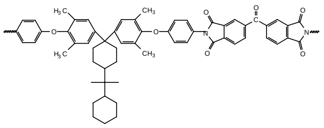
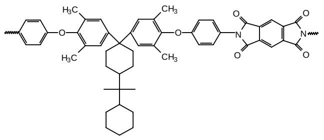
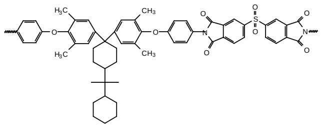


Figure 4.19: TG curves of polyimides (PI IV a-IV f) derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides

Table 4.9: Thermal properties of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides.

Polyimide		IDT(°C)[a]	T_{10} (°C)[a]	Tg (°C)[b]
PI-IV a		440	447	244
PI-IV b		435	450	268
PI-IV c		465	467	266
PI-IVd		450	455	267
PI-IV e		463	465	287
PI-IV f		430	435	280

a: Measured by TGA at a heating rate of 20 °C/min in nitrogen.
b: Measured on DSC at a heating rate of 20 °C/min in nitrogen.

Polyimides based on TMDA exhibited initial decomposition temperatures in the range 430-465 °C and temperatures at 10% weight loss were recorded in the range 435-467 °C. The corresponding polyimides based on diamine1,1-bis[4-(4-aminophenoxy)phenyl)]-4-perhydrocumyl cyclohexane[26] (containing perhydrocumyl cyclohexylidene cardo group with out four methyl groups along the backbone) and BPDA, ODPA and 6FDA showed temperatures at 10% weight loss as 480, 505 and 508°C respectively. Polyimide based on methyl substituted diamine TMDA showed comparatively lower thermal stability owing to the presence of aliphatic substituents.

Figure 4.20 shows DSC curves for polyimides based on TMDA. Glass transition temperature (Tg) of polyimides obtained from TMDA are in range 244-287ºC. Polyimides based on TMDA and aromatic dianhydrides BPDA, ODPA and 6FDA showed Tg at 266 ºC, 244 ºC and 268 ºC respectively. The corresponding polyimides based on 1,1-bis[4-(4-aminophenoxy)phenyl)]-4-per-hydrocumyl cyclohexane[26] (containing perhydrocumyl cyclohexylidene cardo group without four methyl groups along the backbone) and BPDA, ODPA and 6FDA showed Tg at 249ºC , 234 ºC and 260ºC respectively. Symmetrical substitution of four methyl groups ortho to ether linkage restricted the freedom of rotation and mobility of phenylene rings of the backbone around the ether bridge and hence improved the glass transition temperature.

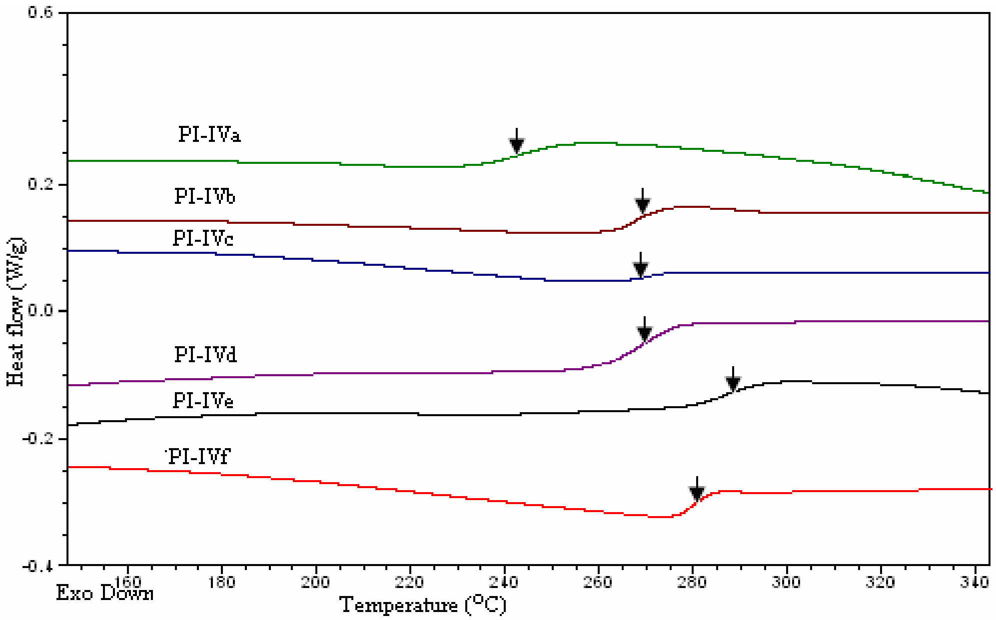


Figure 4.20 DSC curves of polyimides (PI IVa-IV f) derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides

4.4.3.4 Optical properties

Optical transparency of polyimide films is of special importance in some application such as flexible solar radiation protectors, optical waveguides for communication interconnects and in orientation films in liquid crystal display devices [27a,b].

However, most of the conventional polyimides are colored due to the formation of charge transfer complex between alternating electron donor (diamine) and electron acceptor (dianhydride) moieties. The fluorine containing monomers have gained particular importance in the synthesis of optically transparent polyimides since polymers obtained from them are highly soluble, colorless and thermally stable[28-32].Some alicyclic monomers have also been investigated for the synthesis of optically transparent polyimides[33a].

In the present study optical transparency of polyimide films having thickness of ~ 30-40 µm was measured by transmission UV-visible spectroscopy. Figure 4.21 shows UV-visible spectra of polyimides PI-IVa to PI-IVf obtained from TMDA and different aromatic dianhydride and Figure 4.22 shows UV- visible spectra of polyimides PI-Ia to PI-If obtained from NABPDA and different aromatic dianhydrides.

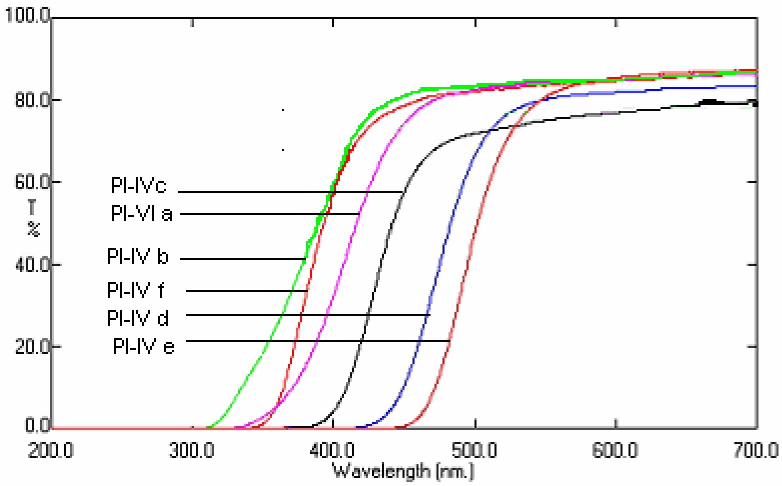


Figure 4.21: UV- visible spectra of polyimides PI-IVa to PI-IVf obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides

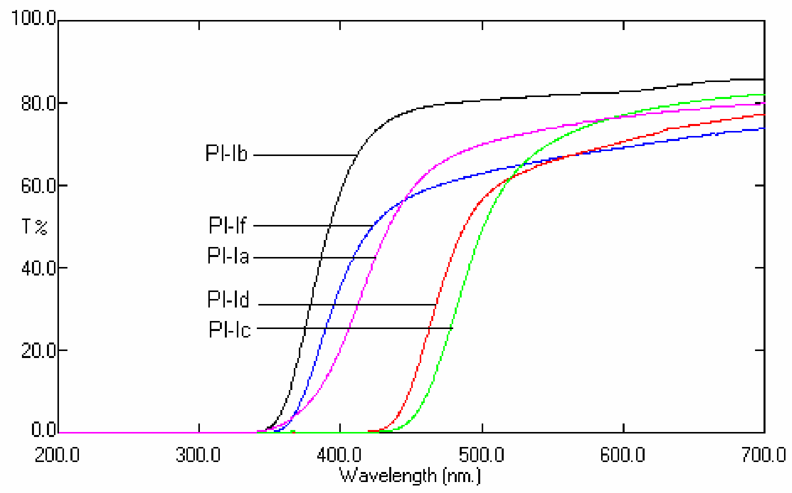


Figure 4.22: UV-visible spectra of polyimides PI-Ia to PI-If obtained from 1,1-bis-[4-(4-aminophenoxy) phenyl -1-(2-naphthyl)] ethane and different aromatic dianhydrides

The cutoff wavelength (absorption edge, λ_0), and % transmittance at 500 nm for polyimides are given in Table 4.10

Table 4.10 Cutoff wavelength (absorption edge, λ_0), and % transmittance at 500 nm of polyimides based on TMDA (PI IVa-f) and NABPDA (PI Ia-f)

Polyimide	Diamine	Dianhydride	λ_0 (nm)	% transmittance at 500 nm
PI-IVa	TMDA	ODPA	350	78
PI-IVb		6FDA	330	86
PI-IVc		BPDA	386	68
PI-IVd		BTDA	423	79
PI-IVe		PMDA	444	65
PI-IVf		DSDA	380	80
PI-I a	NABPDA	ODPA	348	68
PI-I b		6FDA	345	80
PI-I c		BPDA	425	52
PI-I d		BTDA	432	58
PI-I f		DSDA	352	63

In case of all polyimides, transmission of light started below 444 nm. The percentage transmittance was in the range of 65–86 % and 52 -80% for the polyimides based on TMDA and NABPDA respectively. The order of transparency could be elucidated from the cut off wave length (λ_0) and percentage transmittance at 500 nm and was found to be PMDA<BPDA<BTDA<DSDA≤ODPA<6FDA. These results were attributed to the ability of various aromatic dianhydrides to form charge transfer complexes (CTC) between alternating electron donors (diamine moieties) and electron acceptors (dianhydrides moieties).The trend obtained in cut of wavelengths and transparency of polyimides derived from various aromatic dianhydrides is in good agreement with the trend documented in the literature for different aromatic dianhydrides[33b,c,d].

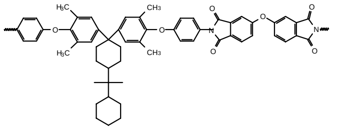
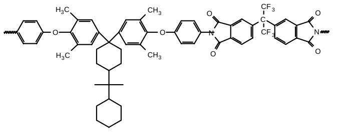
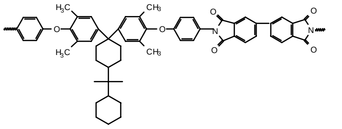
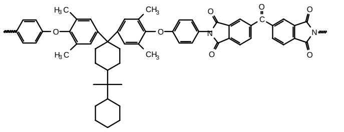
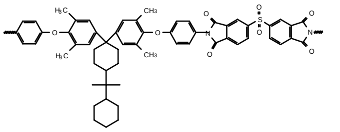
6FDA and ODPA-based polyimides produced fairly transparent and colorless films due to the presence of hexafluoro isopropylidene group and ether linkage respectively which led to reduction of intermolecular charge transfer complex formation.

Polyimides derived from TMDA and 6FDA gave the maximum transmittance of 86% at 500 nm. The higher optical transparency of TMDA based polyimides could be attributed to the presence of perhydrocumyl cyclohexylidene cardo group and four methyl groups along the polymer back bone which might hinder the packing of polymer chain and thus minimize the formation of charge transfer complexes.

4.4.3.5 Mechanical properties measurement

The mechanical properties of polyimide samples derived from TMDA and various aromatic dianhydrides were tested by an Instron Universal Tester**.** The mechanical properties of polyimides are summarized in **Table 4.11.**

Table 4.11: Mechanical properties of polyimides obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic dianhydrides

Polyimide		**Strength at break (MPa)[a]**	**Elongation at break (%)[a]**	**Initial Modulus (GPa)**
PI-IV a		87 (0.83)	11.27 (0.93)	2.12
PI-IV b		82(2.70)	8.12 (1.83)	1.72
PI-IV c		85(1.82)	11.51 (2.83)	1.90
PI-IV d		79(1.85)	6.28 (2.62)	1.72
PI-IV f		76(0.98)	6.02 (0.61)	1.64

a : Values in the brackets show the standard deviation of the measurement data obtained for four individual samples

The polyimide films possess tensile strength in the range 76-87 MPa, elongation at break in the range 6.02-11.51 % and initial modulus in the range 1.64-2.12 GPa indicating that these polyimide films were tough and flexible to be used as strong polymeric materials.

4.4.3.6 Gas permeability studies of polyimides

Gas separation using membrane technology is useful for a variety of applications, such as hydrogen recovery from reactor purge gas, nitrogen and oxygen enrichment, water vapor removal from air, stripping of carbon dioxide from natural gas, etc. Finding new membrane materials with high permeability and permselectivity has been an active research field for several years. Recent studies indicate that the packing density, the segmental motion of polymer chains and gas-polymer interactions are dominant factors that affect gas transport properties. High permeability is primarily related to high free volume, while significant increase in gas permselectivity may be achived by restricted segmental motion. On the basis of this one can design new polymers to combine two favorable factors, and synthesize polymers with both high gas permeability and high permselectivity.

Moreover, in some cases it is desirable for the membrane separation process to be operated at high temperature so that the purge streams from synthesis gas production can be regulated in composition and recycled without extensive cooling and reheating prior to recycling to the reactor. Therefore, it is necessary that polymers exihibit high glass transition temperature so that they can be used for the membrane separation applications at high temperatures.

4.4.3.6.1 Polyimides as gas separation membranes

Polymers with high glass transition temperature such as polyimides are of importance as gas separation membranes. Polyimides exhibit moderate permeability coefficients, high selectivity, excellent thermal stability and film formability, making them attractive for this application.[34] Recent studies demonstrated that both permeability and selectivity might be enhanced by the incorporation of bulky groups[35] or cardo groups[36] in polymeric membranes to simultaneously decrease the chain packing efficiency and hinder torsional mobility[37]. There have been many studies on structurally modified polyimides in order to enhance gas permeability and selectivity.[38-42] Many studies in this field indicated that the following structural modifications are required in order to enhance the selectivity and permeability of polyimides.[43]

1. The backbone chains must be stiffened by inhibiting their intersegmental (rotational) mobility.
2. Intersegmental packing of the polymer chains must be simultaneously prevented

3. Interchain interactions must be weakened and if possible, eliminated.

Polyimides containing perhydrocumyl cyclohexylidene cardo group showed high glass transition temperature. Introduction of four methyl group along the back bone and perhydrocumyl cyclohexylidene cardo group has resulted in improved solubility of polyimides PI-IVa-f. There are several reports on gas permeability studies of polyimides and copolyimides based on the dianhydrides 6FDA and ODPA[44 a,b].

Polyimides PI-IVa and PI-IVb based on ODPA and 6FDA were obtained with considerable viscosity to be transformed into dense film form. The films were strong enough to withstand the pressure during permeation analysis. Thus, these polyimides were potentially good candidates for gas permeation analysis.

4.4.3.6.2 Measurement of gas permeability

In the present work, the variable volume method was used to determine permeability of helium, nitrogen, oxygen, methane and carbon dioxide.[28] The purity of the gases used was minimum 99.9 %. The permeability measurements were carried out at 35±0.1°C and upstream pressures of 10 Kg/cm^2 while maintaining permeate side at ambient pressure. The schematic diagram of permeation apparatus is given in **Figure 4.23**

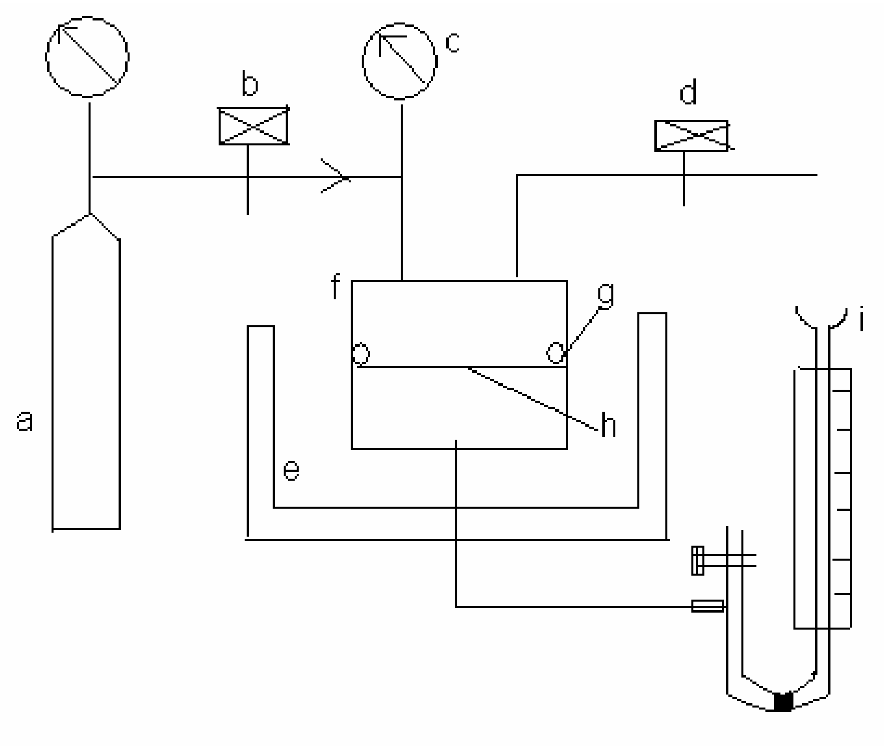


Figure 4.23: Schematic diagram for gas permeability measurement
(a: Gas cylinder; b: Inlet valve; c: Pressure gauge; d: Outlet valve; e: Thermostat; f: Permeation cell; g: 'O' ring; h: Membrane; i: Calibrated flow meter).

The permeation cell was opened and circular coupon (size: 49 mm) of membrane was mounted in the cell. An O-ring was placed on the top of 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.

The amount of gas permeated per unit time was recorded after a certain period of time. The readings were continued till enough data was generated to ensure the equilibrium had reached (depends on the gas used and membrane mounted in the cell). The initial and final pressure on the gauge was also recorded while taking the readings. The gas permeability was calculated for each reading using the equation given below and the consistent data was averaged.

At the end of the experiment, cell was depressurized and disconnected from the cylinder.

$$p_{avg} = (p_{\text{int}} + p_{final})/2$$

$$\Delta p = p_{avg} - p_{ambient}$$

$$Permeability(P) = \frac{14.7 \bullet dis\text{tan}ce \bullet flow\ meter\ const. \bullet thickness}{76 \bullet area\ of\ the\ membrane \bullet \Delta p \bullet time} \text{........(1)}$$

$$selectivity\,\alpha_{(A/B)} = P_A / P_B$$

Δp was recorded in psi, P is the gas permeability in barrer

From the permeability coefficients obtained by **equation (1)**, the ideal separation factor for different pairs of gases was calculated.

4.4.3.6.3 Gas permeability analysis

In the present work permeability studies of five gases viz, He, N_2, O_2, CO_2, and CH_4 for polyimides derived from TMDA- 6FDA (PI-IV b), and TMDA- ODPA (PI-IV a) were carried out. The physical and thermal properties of polyimides are listed in **Table 4.12**.

Table 4.12: Physical properties of polyimides governing gas permeation analysis

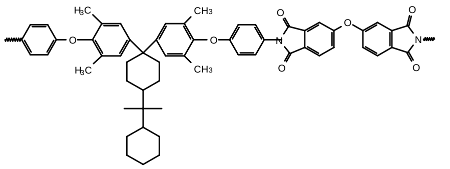
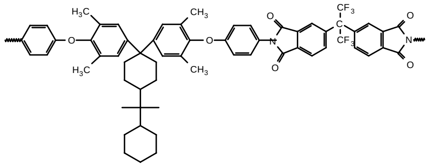
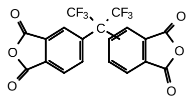
Polyimide	Tg (^{o}C)	Density (g/cm^3)	V $_f$ (FFV)	d-spacing (A^o)
 PI-IV a	244	1.1858	0.334	5.3010
 PI-IV b	268	1.2210	0.357	5.8280

Table 4.13 presents data obtained from the literature for gas permeability studies of polyimides based on 6FDA and ODPA[44a].

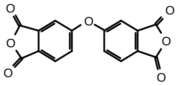
Table 4.13: Data obtained from literature for polyimides containing dianhydrides 6FDA and ODPA

Dianhydride	Diamine	Density	FFV (V$_f$)	d-spacing	P(CO$_2$)	α (CO$_2$/CH$_4$)
6FDA	IPDA	1.363	0.161	5.67	20.4	50.4
ODPA		1.275	0.146	5.55	2.50	42.0
6FDA	BAPF	1.440	0.173	5.93	18.9	45.7
ODPA		1.38	0.165	5.77	3.56	41.0

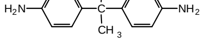
6FDA



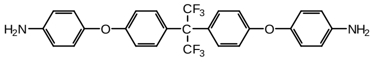
ODPA



IPDA



BAPF



TMDA was expected to offer high free volume because of the four methyl substitution ortho to the –C-O- bond of flexible ether group which would severely restrict the rotational motion of phenylene rings. Therefore, TMDA based polyimides were expected to show both high permeability due to high free volume and high selectivity due to low interchain rotation ability. The effect of alkyl substitution has been investigated previously.[45]

Some aromatic polyimides that contain –$C(CF_3)_2$– groups in their dianhydride moieties have been found considerably more gas-selective (particularly to CO_2 relative to CH_4) than other polymers with comparable permeabilities[42],[46]. It has also been found that aromatic polyimides that contain -$C(CF_3)_2$- groups in dianhydride moiety as well as in the diamine moieties exhibit both high selectivity and permeability. Introduction of -$C(CF_3)_2$- groups has following effects[47];

1. The chain stiffness increased because bulky 6F groups inhibit intersegmental mobility. Selectivity is thereby enhanced since the greater chain stiffness enables polyimide matrics to better discriminate between permeating molecules of different sizes. Thus, in other words, it enhances the "molecular sieving" ability of the polymers.
2. Chain packing is inhibited due to presence of bulky -$C(CF_3)_2$- groups resulting into increased permeability.
3. Introduction of bulky -$C(CF_3)_2$- groups weakens the formation of charge transfer complexes, reduces the chain packing and thereby increases permeability.

For the above mentioned facts polyimides obtained from TMDA-6FDA and TMDA-ODPA were selected for gas permeability measurements.

As anticipated, due to the presence of –$C(CF_3)_2$- group in 6FDA the Tg and d-spacing of PI-IVb is higher than PI-IVa obtained from ODPA which contained ether linkage(-O-) . Though the FFV of PI-IVb is higher than PI-IVa, the density of PI-IVb is still found to be much higher due to the presence of bulky –$C(CF_3)_2$- group. These results are also supported with the data given in Table 4.13 for polyimides[44a] which compares the physical properties and permeabilities of polyimides containing dianhydrides 6FDA and ODPA. The replacement of –O- linkage in PI-IVa with –$C(CF_3)_2$- in PI-IVb elevated the permeability of various gases by 2 -3 times in magnitude. Though an increase in permeability is expected in 6FDA based polyimide the trend in selectivity is not monotonous. Only He based selectivities were decreased while other selectivities remained practically similar or slightly increased e.g. in case of α (CO_2/ CH_4) **(Table 4.14).**

Table 4.14: Permeability coefficients (P)[a] and selectivities (α)[b] of polyimides PI IVa and PI-IV b

Permeability	PI-IV a	PI-IV b
P(He)	**25.4**	**50**
P(N_2)	**0.35**	**1.11**
P(O_2)	**1.71**	**5.04**
P(CH_4)	**0.16**	**0.45**
P(CO_2)	**6.1**	**19.7**
α (He/N_2)	**72**	**45**
α (He/CH_4)	**151**	**112**
α (O_2/N_2)	**4.9**	**4.5**
α (CO_2/N_2)	**17**	**17**
α(CO_2/ CH_4)	**36**	**44**

a: expressed in barrer, b: ratio of pure gas permeability.

The –$C(CF_3)_2$- group is anticipated to increase diffusivity as observed in the case of non interacting gases (He/N_2) resulting in decrease in He based selectivity [47] (Table 4.14). This group also might be responsible for elevating solubility of some gases like CO_2 and thus solubility selectivity. This may be compensating diffusivity selectivity, and hence overall result is only slight variation in selectivity.[42]

Thus comparatively high permeabilities without sacrificing much of selectivities were obtained for polyimide PI-IVb, and hence the utility of these polyimide as membrane materials for gas separation can be envisaged.

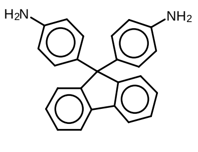
4.4.3.7 Dielectric properties of polyimides.

Polyimides have been identified as having excellent potential for use in electronic devices. The wide range of applications of polyimides in this field include: substrate films for flex circuits, interlayer dielectrics in integrated circuits, junction protective coatings, conductive coatings, adhesives, and as base materials for photosensitive formulations for electronic applications, etc.[48-50].

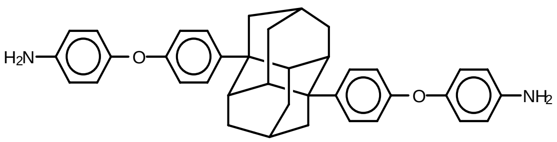
Low dielectric constant materials are necessary for minimizing crosstalks and maximize signal propagation speed in microelectronic devices. Hence the development of polyimides with increasingly lower dielectric constant has been the focus of several recent investigations[51-53].

Among the strategies used to lower dielectric constant in polyimides are: (1) incorporating diamine and dianhydride reactants which minimize polarizability (2) incorporating diamine and dianhydride reactants which impart a high degree of free volume; (3) incorporating fluorine atoms into the molecular structure of the polyimides[54].

The incorporation of fluorine can affect the dielectric constant in several ways like (a) by increasing the free volume (b) by reducing the number of polarizable groups in unit volume. (c) greater fluorine content also increases the hydrophobicity of the polymer .The diminished moisture content results in decreasing the bulk dielectric constant at lower frequencies[55]. A correlation of high free volume with low dielectric constant has previously been found in polyimides [55, 56]. Studies have been made by incorporating cardo structures like DAPF and cage like structures like diamentane[57,58] in the diamine used for preparation of polyimides.



DAPF



1,6 –Bis [4-(4-aminopheoxy)phenyl]diamentane

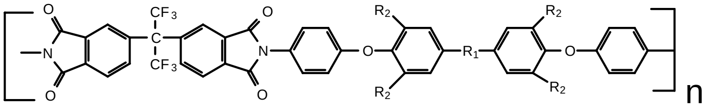
In present study, dielectric constant of selected polyimides derived from 6FDA and various diamines namely BBHPDA , TMDA and DCHDA was determined.

The dielectric constant measurements were carried out with a solartron SI 1255 impedance analyzer with a dielectric interface 1296 in a parallel plate configuration. The gold coated polyimide films were placed in an evacuated chamber and connected to a frequency generator .The impedance analyzer software was used to obtain dielectric constant (ε’).

Table 4.15 presents the physical properties and the dielectric constant measured at different frequencies:

Table 4.15 Physical properties and dielectric constants of polyimides.

Polyimide	Density(g/cm^3)	V_f (FFV)	Dielectric constant (ε’) at different frequencies		
			10 KHz	100 KHz	1 MHz
PI- II b	1.2589	0.3813	4.3665	3.8401	3.8012
PI-III b	1.2061	0.4019	4.1895	3.6366	3.5122
PI- IV b	1.2210	0.3570	4.4543	3.7319	3.6210



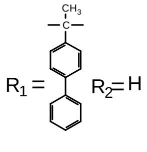
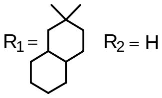
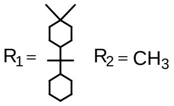
PI- II b	PI-III b	PI- IV b
		

Figure 4.24 shows the representative plot of dielectric constant (ε') against frequency for PI-III b. As the frequency was increased dielectric constant (ε') decreased and attained a constant value. In case of sample PI III b initially at 10 KHz dielectric constant (ε') was around 4.1895 which decreased as the frequency was increased; and attained the constant value 3.5122 at 1MHz.

The synthesized polyimides showed dielectric constants in the range 3.5122 – 3.8012 at 1MHz therefore the application of these materials in microelectronics and related fields are foreseen.

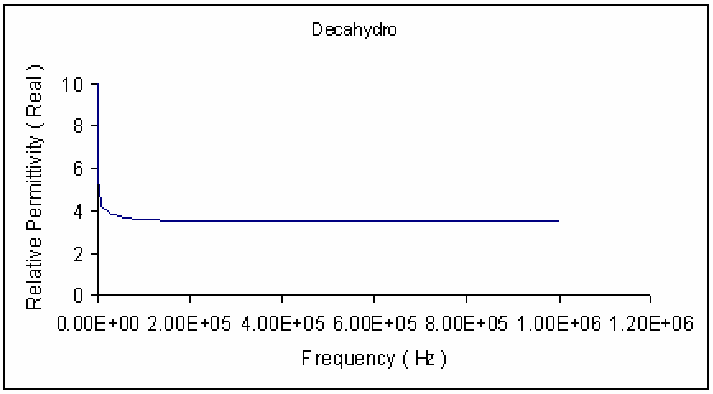


Figure 4.24 : Representative plot of dielectric constant (ε') vs frequency for PI-III b

4.5 Conclusions

1. Twenty four new polyimides containing bulky pendant groups or cardo groups and arylene ether linkages were synthesized by conventional two step polycondensation .
2. Inherent viscosity of polyimides were in range 0.40-1.62 dL/g indicating formation of medium to high molecular weight polymers.
3. Polyimides showed good solubility in aprotic polar solvents like NMP, DMAc etc. TMDA-based polyimides were soluble in aprotic polar solvents as well as in common organic solvents and better solubility behavior of these polyimides could be attributed to the presence of perhydrocumylcyclohexylidene cardo group, flexible ether linkages and four methyl substituents along the backbone.
4. Tough, transparent and flexible films could be cast from the solution of these polyimides in chloroform or DMAc.
5. Wide angle X-Ray diffraction patterns of the films showed that polyimides were amorphous in nature.
6. Tg and IDT values of polyimides were in the range 240-316°C and 430-538°C, respectively.
7. Optical transparency of the selected polyimide films was measured by transmission UV-visible spectroscopy. In case of polyimides, transmission of light started below 450 nm. The percentage transmittance was in the range of 65-86 % and 52-80% for polyimides based on TMDA and NABPDA, respectively. The order of transparency with respect to dianhydrides was found to be PMDA<BPDA<BTDA<DSDA≤ODPA<6FDA.
8. The mechanical properties of polyimide films derived from TMDA and various aromatic dianhydrides were tested by an Instron Universal Tester**.** The polyimide films possess tensile strength in the range 76-87 MPa, elongation at break in the range 6.02-11.51 % and initial modulus in the range 1.64-2.12 GPa indicating that these polyimide films were tough and flexible to be used as strong polymeric materials.
9. The gas permeability studies of polyimide films derived from TMDA and 6FDA and TMDA and ODPA revealed that the replacement of –O- linkage with $–C(CF_3)_2$- increased the permeability of various gases by 2 -3 times in magnitude.

Though an increase in permeability is expected in 6FDA based polyimide the trend in selectivity is not monotonous. Only He based selectivities were decreased while other selectivities remained practically similar or slightly increased {e.g. in case of α(CO_2/ CH_4) Table 4.14}.

10. Polyimides based on the dianhydride 6FDA, i.e PI-IIb, PI-IIIb and PI-IVb showed dielectric constants with in the range 3.5122 – 3.8012 at 1 MHz.

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Chapter 5A Synthesis and characterization of polyetheramides (PEAs)

5A.1 Introduction

Aromatic polyamides are characterized by their excellent balance of thermal and mechanical properties, which make them useful as high-performance materials for advanced technologies[1-3]. However, infusibility and limited solubility of aramids in common organic solvents restrict their widespread applications[4]. The major factors that account for low solubility of aromatic polyamides are molecular order, chain stiffness provided by high density of aromatic rings and strong interchain attractive forces (mainly hydrogen bonding), that enhance effective molecular packing. Therefore, many efforts have been focused to enhance their processability and solubility by the chemical modification of their structure by several methods, such as

(1) Introduction of bulky side groups.
(2) Incorporation of flexible groups into the polyamide backbone.
(3) Use of *meta*-oriented or asymmetrically substituted monomers[5-9] providing kinks to the polymer backbone.

These modifications work by breaking the chain symmetry and regularity and by destroying hydrogen bonds and generally lead to better solubility and slightly lower transition temperatures [10]. Previous studies have reported that incorporation of bulky groups viz. phenyl ring , diphenyl methylene linkage, 2,5-di-*t*-butyl phenylene ring etc. and cardo groups such as cyclododecylidene, adamantane or *t*-butyl cyclohexylidene results in polymers with enhanced solubility/processability and good thermal stability[11-26].

This chapter presents synthesis and characterization of new polyamides containing bulky pendent groups such as naphthyl and biphenyl or cardo groups such as octahydro-2(1H)-naphthalidene and perhydrocumyl cyclohexylidene groups.

A series of polyamides was synthesized by polycondensation of aromatic diamines containing bulky pendant group or cardo groups namely

1. 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)]ethane (NABPDA)
2. 1,1-bis–[4-(4-aminophenoxy)phenyl-1-biphenyl]ethane (BBHPDA)

3. 1,1-bis-[4-(4-aminophenoxy)phenyl]octahydro-2(1H)-naphthalene (DCHDA) and
4. 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA)

with commercially available aromatic diacids viz.

1. isophthalic acid
2. terephthalic acid
3. 4,4'-oxybisbenzoic acid,
4. 4,4'-(hexafluoro isopropylidene) bis (benzoic acid) and
5. biphenyl-4,4'-dicaboxylic acid.

Polyamides were characterized by inherent viscosity measurements, solubility tests, FT-IR, ^{1}H NMR, and ^{13}CNMR spectroscopy, X-ray diffraction analysis, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Selected polyamide films were tested for mechanical properties.

5A.2 Experimental

5A.2.1 Materials

1,1-Bis-[4-{(4-aminophenoxy)phenyl}-1-(2-naphthyl)]ethane (NABPDA), 1,1-bis–[4-{(4-aminophenoxy)phenyl}-1-biphenyl]ethane (BBHPDA), 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA) and 1,1-bis-{4-(4-aminophenoxy)phenyl}octahydro-2(1H)-naphthalene (DCHDA) were synthesized as described in **Chapter 3.** Commercially available diacids namely, isophthalic acid, terephthalic acid, 4,4'-oxybisbenzoic acid, biphenyl-4,4'-dicaboxylic acid, 4,4'-(hexafluoro isopropylidene) bis (benzoic acid) all received from Aldrich, USA were purified by reported procedures before use[27]. N-Methyl-2-pyrrolidone, pyridine and other solvents were purchased from S. D. Fine Chem., India and were dried and distilled according to the reported procedure[27]. Lithium chloride was dried at 150°C under reduced pressure for 12 h before use. Triphenyl phosphite received from Aldrich, USA was distilled under reduced pressure prior to use.

5A.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in N,N-dimethylacetamide at 30±0.1°C using an Ubbelohde suspended level viscometer on Schott Gerate CK-160 automatic viscometer.

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

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 DMSO d_6 as a solvent.

Solubility of polyamides was determined at 3% (w/v) concentration in different solvents at room temperature or on heating.

X-Ray diffraction patterns of polyamides were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2° / minute. Dried polymer films or powder was used for X-ray measurements.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 thermal analyzer system at a heating rate of 20°C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC measurements were carried out on TA Instrument *DSC* Q10, at a heating rate of 20°C / minute in nitrogen atmosphere.

An Instron universal tester model 4204 with a load cell of 1 Kilo Newton was used to measure the stress-strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5mm/min were used. Measurements were carried out at room temperature using film specimens (10 mm wide, 5 cm long and ~ 50 micron thick) five measurements were taken for each polymer sample.

5A.2.2.1 Film preparation for testing of mechanical properties

Polyamide films of ~ 50 μm thickness, used for testing of mechanical property were obtained by casting from DMAc solution. The solution of polyamide sample 5% (w/v) was prepared in DMAc and the solution was filtered through a 0.25 μ filter to remove particulates if any. The clear polymer solution was poured onto a clean glass dish (diameter 7.5 cm). DMAc was evaporated slowly at 100 °C. The films were removed and were subsequently dried at 100°C for seven days under reduced pressure.

5A.3 Synthesis of polyamides from diamine monomers containing bulky pendant group/ cardo group and commercially available diacids

A representative procedure for the synthesis of polyamide PA-IVa is described below.

A 100 ml three-necked round bottom flask equipped with a magnetic stirrer bar and a nitrogen inlet was charged with 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (0.50 g, 0.80 mmol), isophthalic acid (0.13g , 0.80 mmol) and triphenyl phosphite (0.54 g, 1.80 mmol) NMP (5 ml), pyridine (1.3 ml) and LiCl (0.35g) were added to it. The reaction mixture was stirred at 130°C for 6 h under nitrogen atmosphere. After cooling, the reaction mixture was poured into excess of methanol with constant stirring producing a white precipitate that was filtered and washed repeatedly with hot water and methanol. The precipitate was filtered and dried under reduced pressure to afford PA-IVa (95 % yield).

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

5A.4 Results and Discussion

5A.4.1. Synthesis and characterization of polyamides derived from diamine monomers containing bulky pendant group/ cardo group.

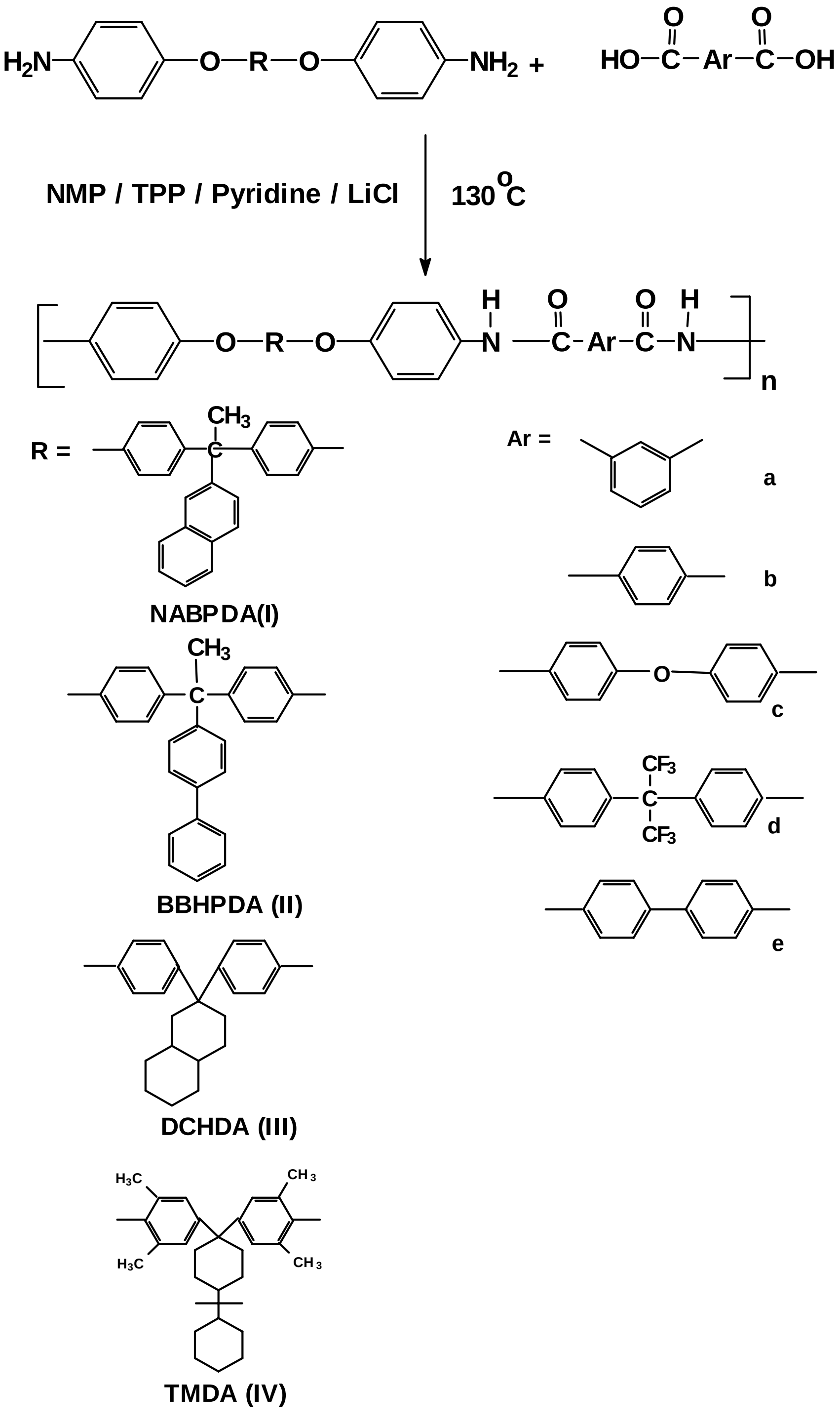
Phosphorylation polycondensation reaction has been applied extensively to polyamide synthesis since 1975, when Yamazaki, Matsuomoto and Higashi[28,29] reported this reaction. This technique employs triphenyl phosphite (TPP) and pyridine as condensing agents to synthesize polyamides directly from aromatic diamines and aromatic or aliphatic dicarboxylic acids. The reaction proceeds through formation of N-phosphonium salts of pyridine, followed by aminolysis. The advantages of direct polycondensation method over low temperature solution method are (1) the polymerization is carried out at moderate temperature without removing the side product (2) this method avoids tedious acid chloride preparation and storage step.

Studies have been carried out to optimize the reaction conditions in order to increase the molecular weight of polymers obtained *via* phosphorylation polycondensation.[29] Major factors governing molecular weight of the obtained polymers are (1) concentration of metal salts whose presence is known to increase the solvating power of aprotic solvents such as DMAc, NMP, etc. (2) temperature of the reaction (3) nature of aprotic solvent used and solvent to pyridine ratio (4) concentration of monomer and (5) molar ratio of TPP to monomer.

Twenty new polyamides were synthesized by the reaction of stoichiometric quantities of diamines and commercially available aromatic diacids by phosphorylation polycondensation. (**Scheme 5A.1) .** The ratio of monomer to TPP was 1: 2.2. Solvent NMP and pyridine were used in 4:1 (w/w) ratio and 7 wt % LiCl based on total solvent was taken.

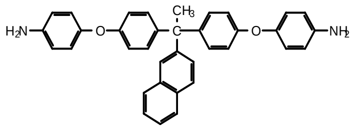
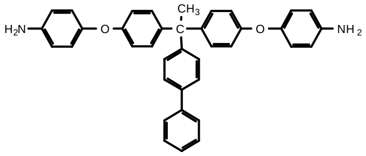
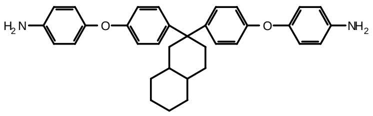
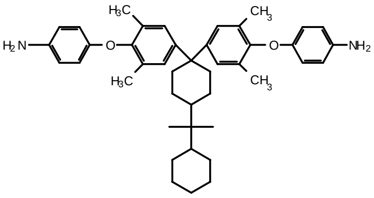
The reaction mixtures were homogeneous throughout the course of the reaction and produced polyamides in 85-97 % yields. The results of polyamide synthesis are summarized in **Table 5A.1.**

Inherent viscosities of polyamides were in the range 0.50 to 0.82 dL/g. indicating formation of medium to high molecular weight polymers. Polyamides could be cast into transparent tough films from their solution in DMAc.



Scheme 5A.1 Synthesis of polyamides from diamines containing bulky pendant groups/cardo groups and aromatic diacids

Table 5A.1: Synthesis of polyamides from diamines containing bulky pendant group/cardo group and aromatic diacids.

Polyamide	**Diamine**	**Diacid**	**Yield (%)**	**η_{inh} (dl/g)[a]**
PA-I a	NABPDA 	Isophthalic acid	93	0.65
PA-I b		Terephthalic acid	95	0.50
PA-I c		4,4’-Oxybisbenzoic acid	90	0.63
PA-I d		4,4’-(Hexafluoro isopropylidene) bis (benzoic acid)	92	0.50
PA-I e		Biphenyl-4,4’-dicarboxylic acid	87	0.70
PA-II a	BBHPDA 	Isophthalic acid	93	0.82
PA-II b		Terephthalic acid	91	0.80
PA-II c		4,4’-Oxybisbenzoic acid	93	0.65
PA-II d		4,4’-(Hexafluoro isopropylidene) bis (benzoic acid)	96	0.70
PA-II e		Biphenyl-4,4’-dicarboxylic acid	86	0.80
PA-III a	DCHDA 	Isophthalic acid	95	0.50
PA-III b		Terephthalic acid	97	0.52
PA-III c		4,4’-Oxybisbenzoic acid	87	0.62
PA-III d		4,4’-(Hexafluoro isopropylidene) bis (benzoic acid)	92	0.62
PA-III e		Biphenyl-4,4’-dicarboxylic acid	85	0.70
PA-IV a	TMDA 	Isophthalic acid	95	0.80
PA-IV b		Terephthalic acid	90	0.70
PA-IV c		4,4’-Oxybisbenzoic acid	92	0.52
PA-IV d		4,4’-(Hexafluoro isopropylidene) bis (benzoic acid)	90	0.65
PA-IV e		Biphenyl-4,4’-dicarboxylic acid	87	0.70

a: η_{inh} of polyamides was measured at a concentration of 0.5 g/ dL in DMAc at 30 ±0.1ºC.

5A.4.2 Structural Characterization

Polyamides were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

A representative FT-IR spectrum of polyamide film obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and 4,4’-(hexafluoro isopropylidene) bis (benzoic acid) is shown in **Figure 5A.1**

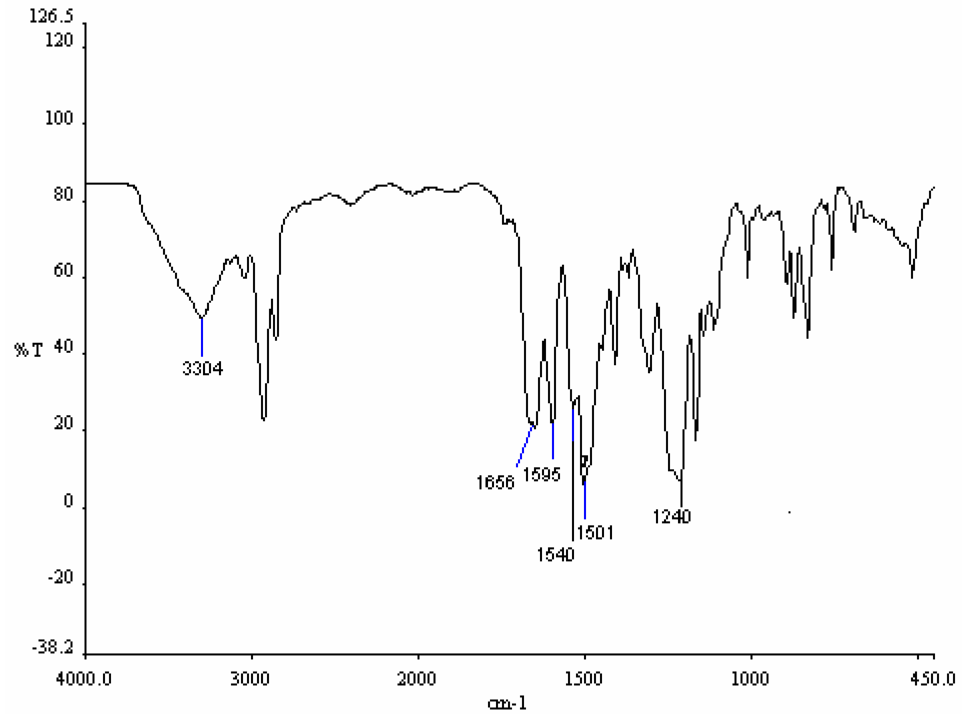


Figure 5A.1: FTIR spectrum of polyamide obtained from1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and 4,4’-(hexafluoro isopropylidene) bis (benzoic acid)

Absorption band at 3304 cm^{-1} is attributed to the N-H stretching which is consistent with the secondary amide character of polyamide. The amide-I band associated with stretching vibration of carbonyl group, appeared at 1656 cm^{-1}. Lowering of carbonyl frequency can be attributed to the involvement of -NH- group in hydrogen bonding or in resonating structure of amide linkage. The amide- II band, ascribed to the coupling of the –N-H bending and –C-N stretching of -C-N-H group, appeared at 1540 cm^{-1}. Band at 1240 cm^{-1} indicates the presence of C-O-C linkage along the polymer backbone

^{1}H NMR spectrum of polyamide obtained from TMDA and 4,4'-(hexafluoro isopropylidene) bis (benzoic acid) in DMSO d_6 is shown in **Figure 5A.2**

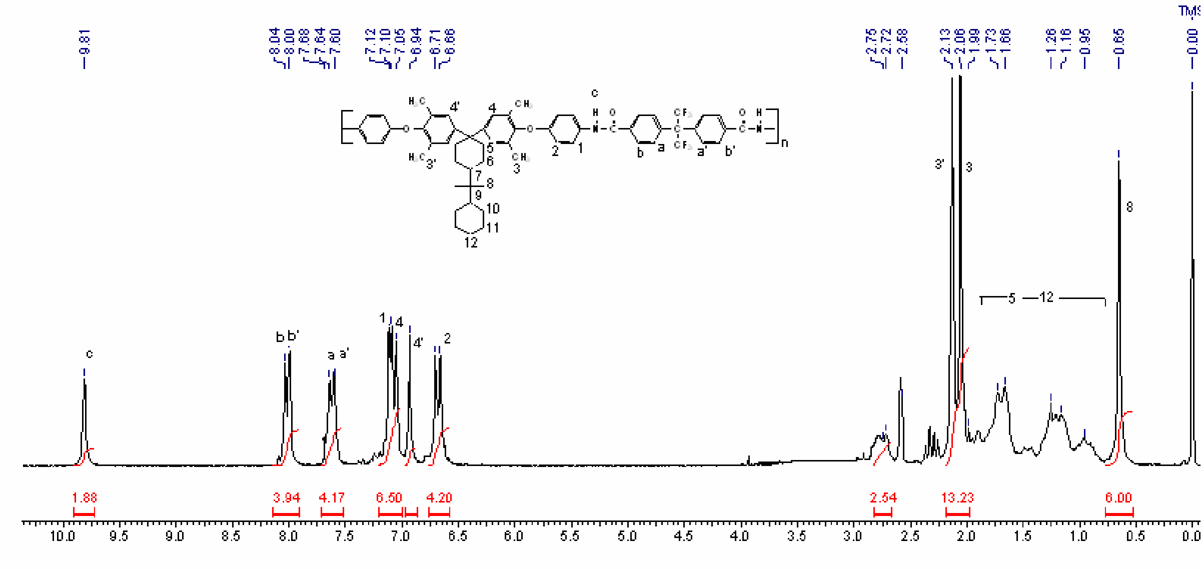


Figure 5A.2: ^{1}H NMR spectrum of polyamide obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and 4,4'-(hexafluoro isopropylidene) bis (benzoic acid) in DMSO-d_6

A singlet at 9.81 δ ppm corresponds to proton c of -NH linkage. Protons b,b' ortho to carbonyl group appeared as doublet at 8.02 δ ppm. Protons a, a' ortho to the carbon attached to –C(CF_3)- group appeared as doublet at 7.62 δ, ppm. Protons 1and 2 which appeared at 6.53 and 6.80 δ, ppm in monomer diamine (Figure 3.38, Chapter3) were shifted to 6.68 and 7.11 δ, ppm after polymerization due to –I effect of carbonyl group of the amide linkage. Methyl protons ortho to ether linkage showed two separate singlets at 2.13 and 2.06 δ ppm. The alicyclic protons appeared as multiplet in the range 0.80 -1.80 δ ppm. Protons 8 of methyl group showed a singlet at 0.65 δ ppm.

^{13}C NMR spectrum of polyamide derived from TMDA and 4,4'-(hexafluoro isopropylidene) bis (benzoic acid) is reproduced in Figure 5A.3 Carbon 23 attached to –NH- group which appeared at 148 δ ppm in the monomer diamine (Figure 3.40, Chapter 3) was shifted to 154.08 due to –I effect of carbonyl group adjacent to –NH- in the amide linkage. Hexa-fluoro isopropylidene group showed the characteristic quartet centered at

125.61 δ ppm due to ^{13}C-^{19}F heteronuclear coupling, and a peak at 64.26 δ ppm for the quaternary carbon attached to –$C(CF_3)_2$ group.

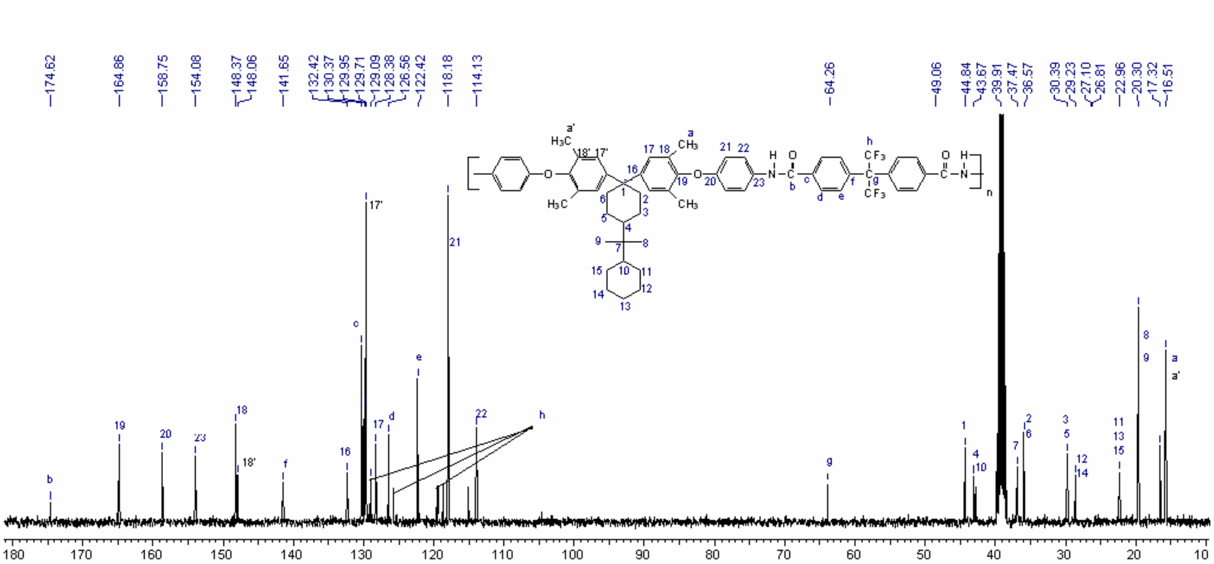


Figure 5A.3: ^{13}C NMR spectrum of polyamide obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and 4,4’-(hexafluoro isopropylidene) bis (benzoic acid) in DMSO-d_6

5A.4.3 Properties of Polyamides

5A.4.3.1 Solubility behavior of polyamides

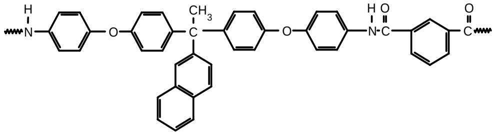
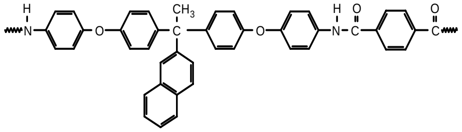
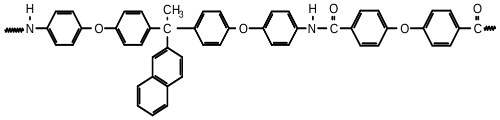
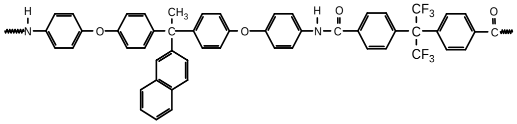
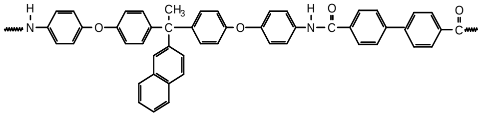
The solubility behaviour of aromatic polyamides was tested at 3% w/v in various solvents. The results are summarized in **Table 5A.2.**

All polyamides were soluble at room temperature in amide-type polar aprotic solvent such as DMAC, DMF and NMP. In addition polyamide obtained from NABPDA and hexafluoroisopropylidene (6F) group containing diacid (PA-Id), *m*-oriented isophthalic acid (PA-Ia) and flexibilizing ether containing diacid (PA-Ic) dissolved in solvents such as *m*-cresol and DMSO at room temperature or on heating.

Polyamide obtained from NABPDA and terephthalic acid (PA-Ib) and NABPDA and biphenyl-4,4'-dicarboxylic acid (PA-Ie) exhibited slightly lower solubility in various organic solvents because of their symmetrical *p*-oriented structure and rigid biphenylene segments.

In general polyamides based on NABPDA showed better solubility than conventional polyamides apparently due in part to the presence of packing-disruptive naphthyl pendant units in the polymer backbone and flexible ether linkage which resulted in increased interchain distances and decreased intermolecular interactions.

Table 5A.2 Solubility behaviour of polyamides derived from 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)]ethane and aromatic diacids

Polyamides		NMP	DMAc	DMF	DMSO	m-cresol	THF	$CHCl_3$
PA-I a		++	++	++	+	+	--	--
PA-I b		++	++	++	+	--	--	--
PA-I c		++	++	++	+	+	--	--
PA-I d		++	++	++	++	++	++	--
PA-I e		++	++	++	--	--	--	--

++ Soluble, + soluble on heating at 60°C, -- insoluble.

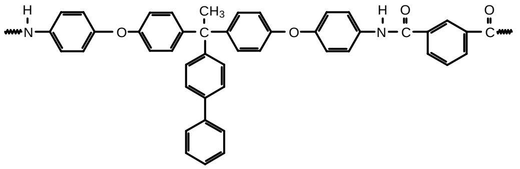
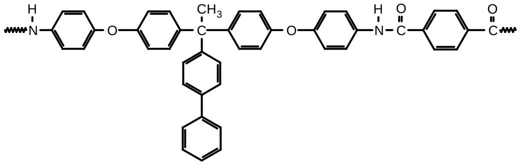
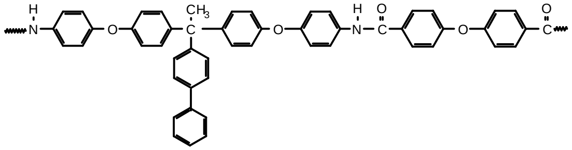
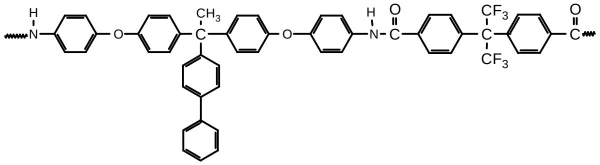
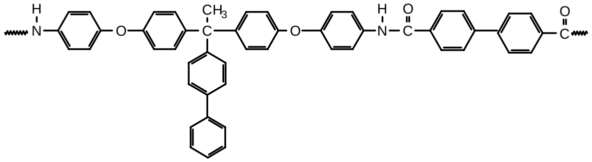
Table 5A.3 presents solubility data for polyamides derived from BBHPDA and aromatic diacids tested at 3% (wt/v) concentration in various organic solvents.

All polyamides except for polyamides PA-IIb and PA-IIe were found to be soluble at room temperature in polar aprotic solvent such as DMF, DMAc, NMP and in *m*-cresol and DMSO.

These results demonstrated that BBHPDA based polyamides exhibited good solubility in organic solvents which is possibly governed by the structural modification through the incorporation of biphenyl pendant group and flexible ether linkage which disrupted the close packing of polymer chains.

PA-IIb and PA-IIe derived from BBHPDA and terephthalic acid and BBHPDA and biphenyl-4,4'-dicarboxylic acid, respectively exhibited slightly lower solubility in various organic solvents. Lower solubility of these two polymers may indicate close packing ability and rigidity due to the presence of *p*-oriented terephthalic acid segments and rigid rod like 4,4' biphenylene segments.

Table 5A.3 Solubility data obtained for the polyamides derived from and 1,1-bis–[4-{(4-aminophenoxy)phenyl}-1-biphenyl]ethane aromatic diacids

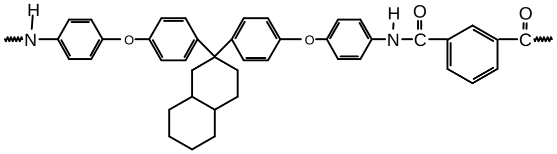
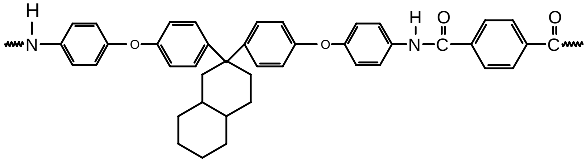
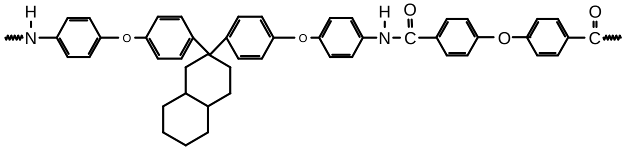
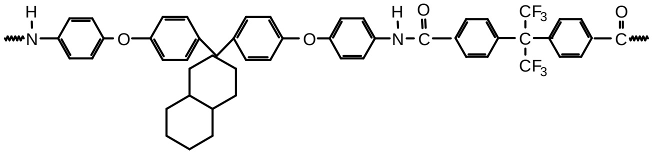
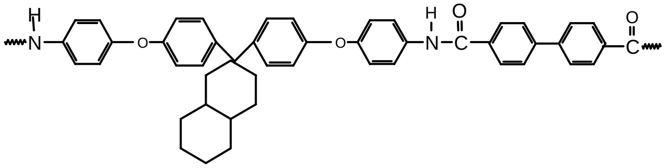
Polyamides		NMP	DMAc	DMF	DMSO	m-cresol	THF	$CHCl_3$
PA-II a		++	++	++	++	++	--	--
PA-II b		++	++	++	+	--	--	--
PA-II c		++	++	++	++	++	--	--
PA-II d		++	++	++	++	++	++	--
PA-II e		++	++	++	--	--	--	--

++ Soluble, + soluble on heating at 60°C , -- insoluble

Table 5A.4 summarizes the solubility data obtained for polyamides derived from DCHDA and aromatic diacids. Polyamides derived from DCHDA were soluble in aprotic polar solvents such as DMAC, DMF and NMP and also in *m*-cresol and DMSO at room temperature or on heating except the polyamide PA-IIIb and PA-IIIe obtained from terephthalic acid and biphenyl-4,4'-dicarboxylic acid respectively.

These results demonstrated that polyamides bearing octaydro-2(1H) naphthalydene cardo group showed good solubility in organic solvent possibly due to the presence of octaydro-2(1H) naphthalidene cardo group, which probably disturbed the dense chain packing of polymer chains. Additional factors contributing to the enhanced solubility was the characteristic amorphous nature caused by the introduction of cardo units and flexible ether linkage; consequently the solvent molecules could easily penetrate to solubilize the polymer chains.

Table 5A.4 Solubility data obtained for the polyamides derived from 1,1-bis-{4-(4-aminophenoxy)phenyl}octahydro-2(1H)-naphthalene and aromatic diacids.

Polyamides		NMP	DMAc	DMF	DMSO	m-cresol	THF	$CHCl_3$
PA-III a		++	++	++	+	+	--	--
PA-III b		++	++	++	+	--	--	--
PA-III c		++	++	++	+	+	--	--
PA-III d		++	++	++	++	++	++	--
PA- III e		++	++	++	--	--	--	--

++ Soluble, + soluble on heating at 60ºC , -- insoluble

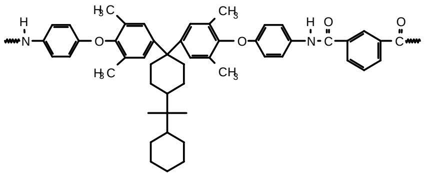
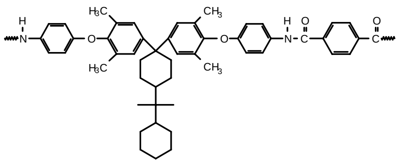
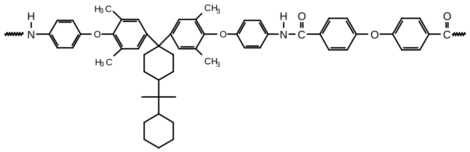
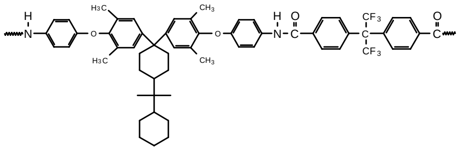
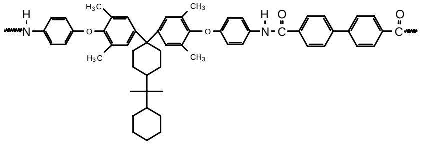
Table 5A.5 presents solubility data obtained for polyamides derived from TMDA and aromatic diacids tested at 3% w/v in various organic solvents.

All polyamides derived from TMDA and aromatic diacids were soluble in polar aprotic solvent such as NMP, DMAc and DMF as well as in solvents such as m-cresol and THF at room temperature or upon heating.

The good solubility of TMDA based polyamides was in part governed by the structural modification through the incorporation of perhydrocumyl cyclohexylidene group and flexible ether linkage which disrupted the close packing of polymer chains. In addition, substitution of methyl groups on phenylene rings in the backbone also inhibited close packing of the polymer chains and contributed to enhance the solubility of polyamides effectively, these results are in good agreement with previous reports.[30a,b,c]

In the present study it was observed that incorporation of bulky pendant group / cardo group and flexible ether linkage in polyamides resulted in inhibiting the close packing of the polymer chains and weaker intermolecular interactions, and therefore enhanced the solubility.

Table 5A.5 Solubility data obtained for the polyamides derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic diacids.

Polyamides		NMP	DMAc	DMF	DMSO	m-cresol	THF	$CHCl_3$
PA-IV a		++	++	++	--	+	++	--
PA-IV b		++	++	++	--	+	+	--
PA-IV c		++	++	++	--	+	++	--
PA-IV d		++	++	++	--	+	++	--
PA-IV e		++	++	++	--	+	+	--

++ Soluble, + soluble on heating at 60ºC , -- insoluble

5A.4.3.2 X-Ray diffraction analysis

X-Ray diffraction patterns of polyamide films obtained from NABPDA, BBHPDA, and TMDA and DCHDA with different diacids are shown in Figure 5A.4-Figure 5A.7 respectively.

Broad amorphous halos were observed in wide angle X-ray diffractograms of polyamides. Introduction of aromatic bulky pendant groups namely naphthyl group in NABPDA and biphenyl group in BBHPDA may have disrupted the chain regularity and packing leading to amorphous polyamides. Similarly introduction of cardo groups namely octahydro2-(1H) naphthalydene group in DCHDA and perhydrocumyl cyclohexylidene cardo group in TMDA inhibited the close packing of the chains producing amorphous polyamides.

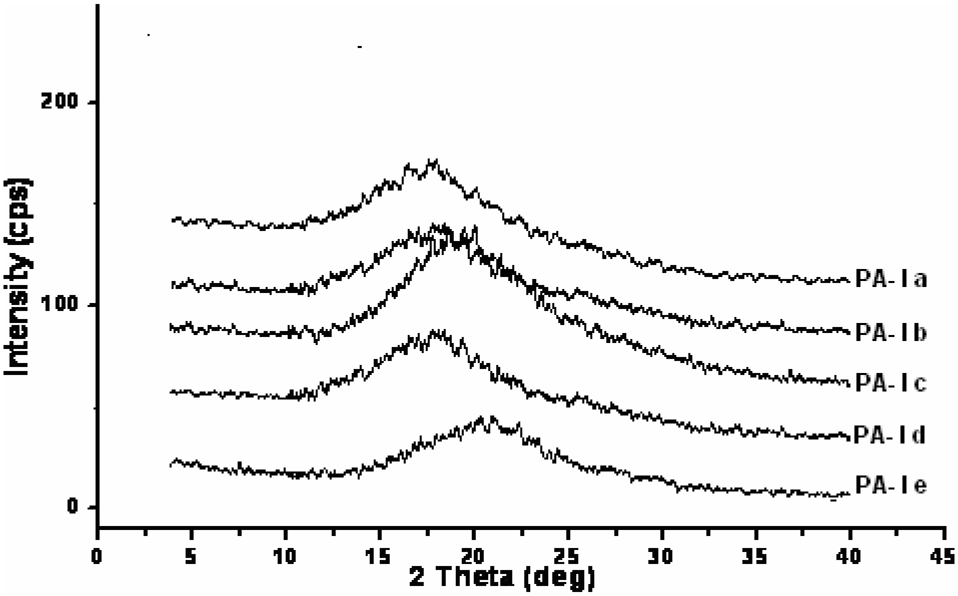


Figure 5A.4: Wide angle X-ray diffractograms of polyamides obtained from 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)]ethane and aromatic diacids (PA-Ia to PA-Ie)

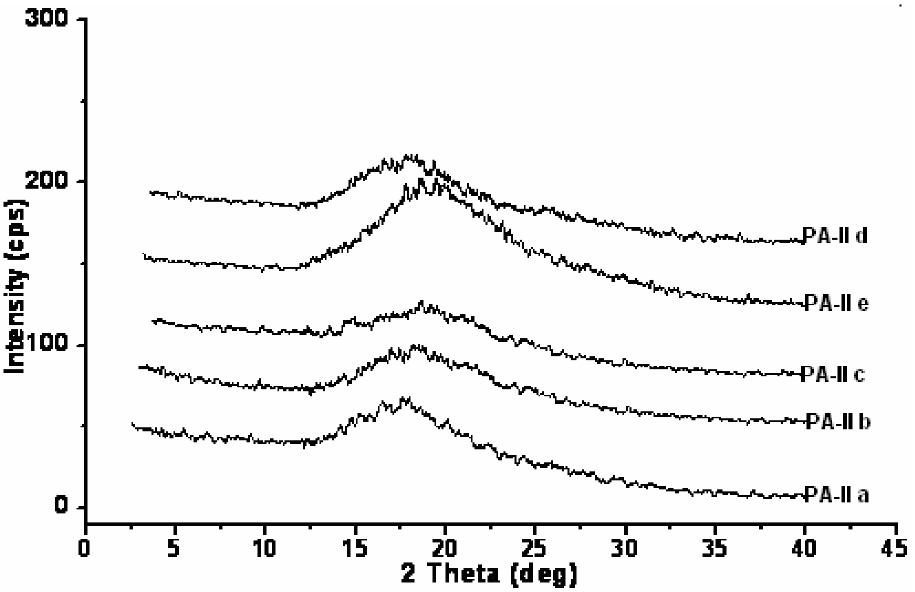


Figure 5A.5: Wide angle X-ray diffractograms of polyamides obtained from1,1-bis–[4-(4-aminophenoxy)phenyl-1-biphenyl]ethane and aromatic diacids (PA-IIa to PA II e)

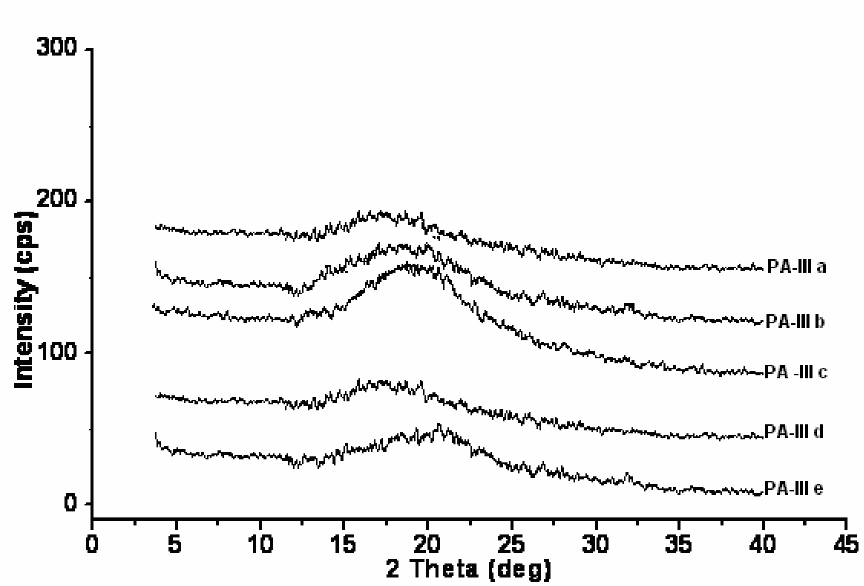


Figure 5A.6: Wide angle X-ray diffractograms of polyamides obtained from 1,1-bis-[4-(4-aminophenoxy)phenyl]octahydro-2(1H)-naphthalene (DCHDA) and aromatic diacids (PA-IIIa to PA III e)

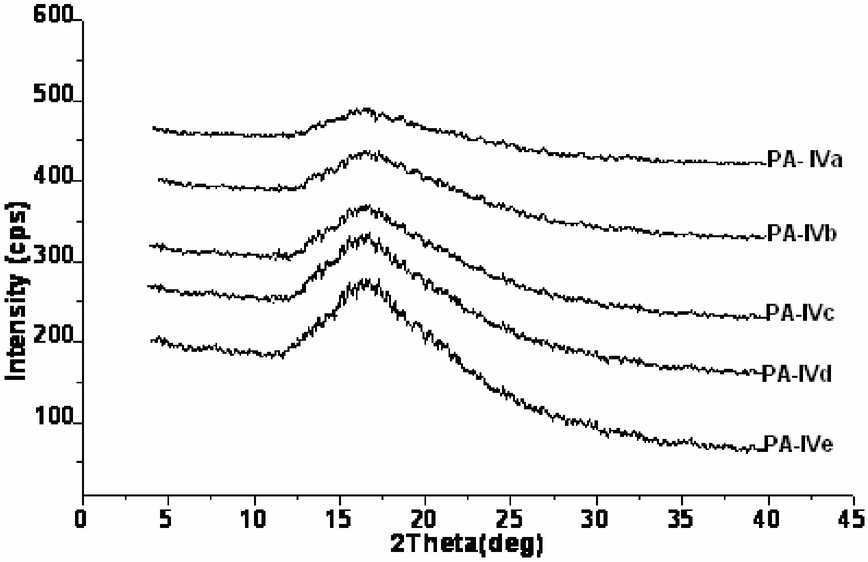


Figure 5A.7: Wide angle X-ray diffractograms of polyamides obtained from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic diacids (PA-IVa to PA IVe)

5A.4.3.3 Thermal behaviour of polyamides

Thermal stability of polyamides based on NABPDA was evaluated by thermogravimetric analysis (TGA) at a heating rate of 20°C/minute in inert atmosphere. TG curves for polyamides based on NABPDA are presented in **Figures 5A.8**. The initial decomposition temperature (IDT) and the decomposition temperature at 10% weight loss (T_{10}) was calculated from the TG curves and data is presented in **Tables 5A.6**

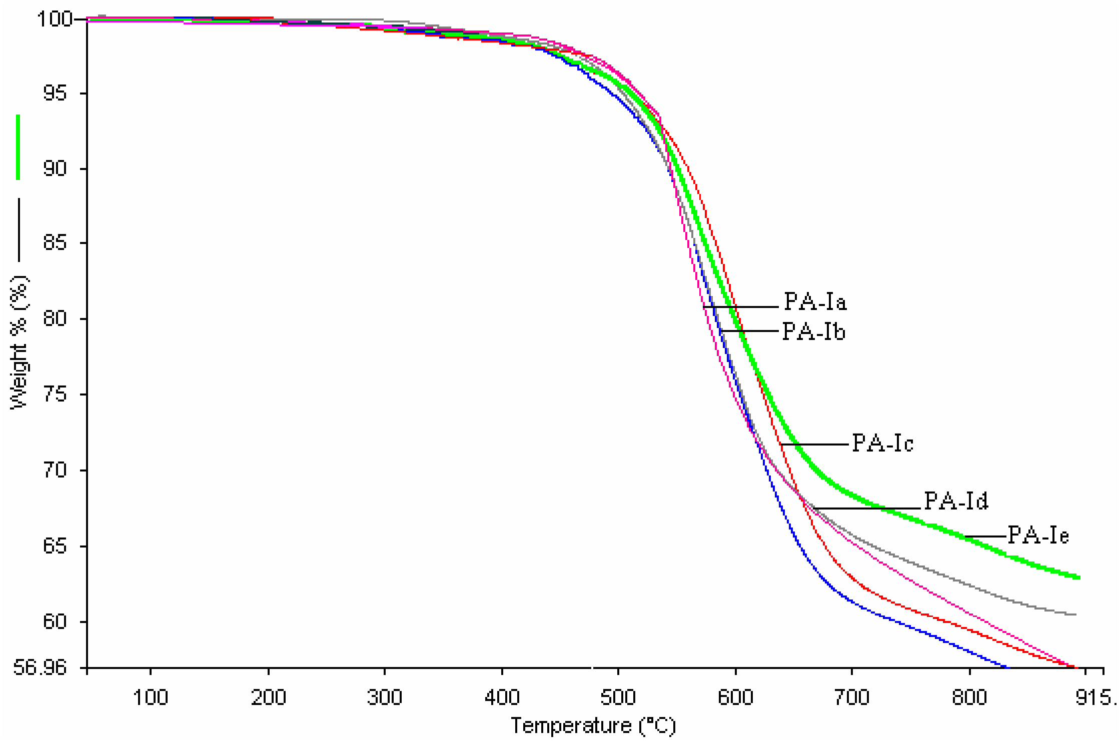
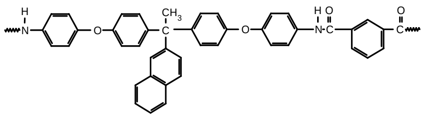
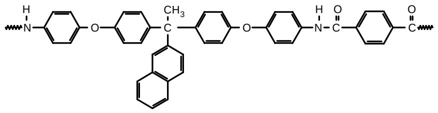
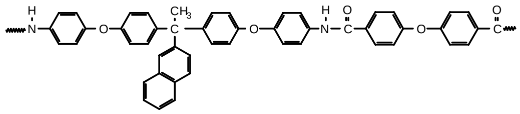
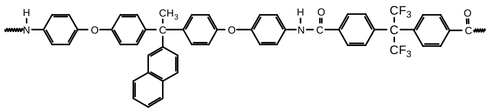
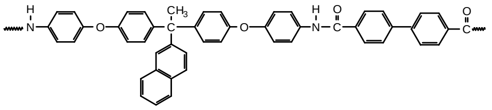


Figure 5A.8: TG curves of polamides (PA I a – PA I e) derived from 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)]ethane and aromatic diacids

All polyamides obtained from NABPDA were stable up to 520°C indicating their good thermal stability. Polyamides exhibited single stage decomposition starting in the range 520°C-522°C. Temperature at 10% weight loss was in the range 540°C-548°C.

Table 5A.6: Thermal properties of polyamides obtained from 1,1-bis-[4-(4-aminophenoxy)phenyl-1-(2-naphthyl)]ethane and aromatic diacids

Polyamide		IDT(°C) [a]	T_{10} (°C) [a]	Tg(°C) [b]
PA-I a		**520**	**540**	**248**
PA-I b		**521**	**545**	**255**
PA-I c		**520**	**548**	**248**
PA-I d		**522**	**542**	**258**
PA-I e		**522**	**542**	**267**

a: Measured by TGA at a heating rate of 20 °C/min in nitrogen.
b: Measured on DSC at a heating rate of 20 °C/min.

Glass transition temperature (Tg) of polyamides based on NABPDA was obtained by differential scanning calorimetery (DSC). Tg values were obtained from the second heating scans of polyamide samples at a heating rate of 20°C /minute. Glass transition temperature (Tg) of polyamides based on NABPDA are given in **Table 5A.6**

Figure 5A.9 shows DSC curves of polyamides based on the diamine NABPDA and aromatic diacids. Tg values of polyamides based on NABPDA were in the range 248°C - 267°C . The Tg values decreased in the same order as that of increase in flexibility of the polymer backbone depending on the flexibility of diacid segment. Hence the highest Tg 267°C was obtained for the polyamide obtained from NABPDA and biphenyl-4,4'-dicaboxylic acid due to the presence of the rigid biphenyl segments and symmetric orientation of *p*-phenylene units in the backbone. The lowest Tg was obtained for polyamide based on 4,4'-oxybisbenzoic acid and the order of decrease in Tg of polyamides based on various diacids was as follows; Biphenyl-4,4’-dicarboxylic acid > 4,4’-(hexafluoro isopropylidene) bisbenzoic acid >terephthalic acid > isophthalic acid ≥ 4,4’-oxybisbenzoic acid.

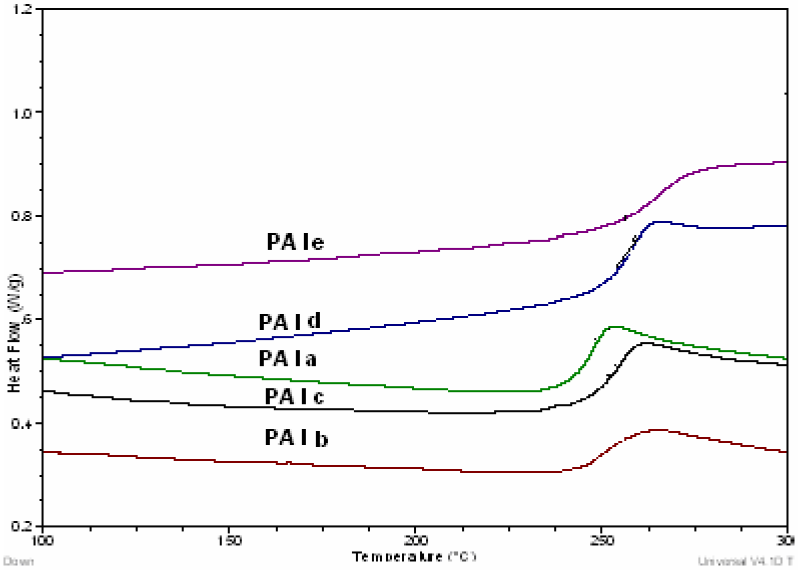


Figure 5A.9 : DSC curves of polyamides (PA Ia-PA Ie) derived from 1,1-bis-[{4-(4-aminophenoxy)phenyl-1-(2-naphthyl)}]ethane and aromatic diacids

Figure 5A.10 presents TG curves of polyamides obtained from diamine BBHPDA and aromatic diacids. **Table 5A.7** presents thermal properties of polyamides obtained from the diamine BBHPDA and aromatic diacids. These polyamides were stable up to 496°C indicating their good thermal stability. Initial decomposition temperature (IDT) of the polyamides was in the range 496°C to 506°C. All polyamides showed single stage decomposition and the temperature at 10 % weight loss (T_{10}) was in the range 533°C -548°C.

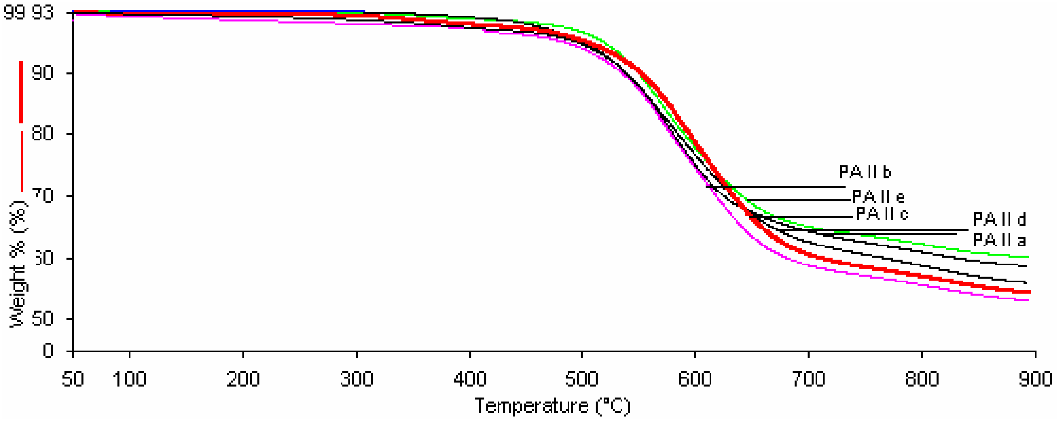
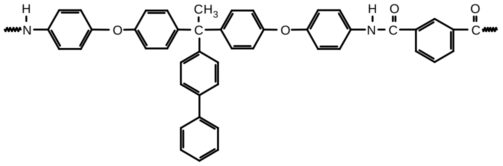
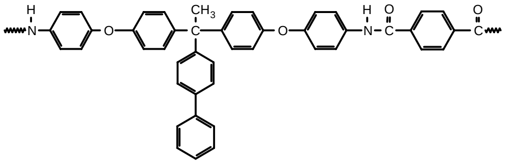
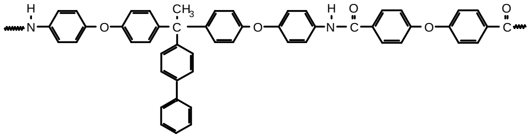
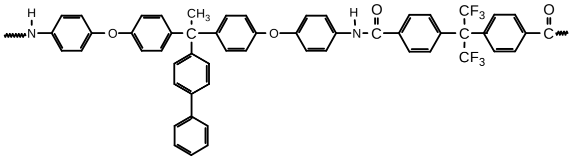
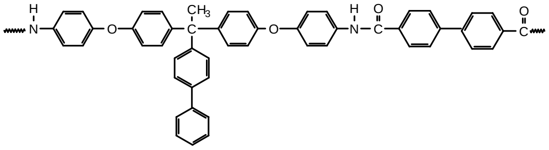


Figure 5A.10:Thermogravimetric curves of polyamides (PA II a – PA II e) derived from 1,1-bis–[4-(4-aminophenoxy)phenyl-1-biphenyl]ethane and aromatic diacids.

Table 5A.7 Thermal properties of polyamides obtained from1,1-bis–[4-{(4-aminophenoxy)phenyl}-1-biphenyl]ethane and aromatic diacids

Polyamide		IDT ºC^a	T$_{10}$ ºC^a	Tg ºC^b
PA-II a		498	539	257
PA-II b		506	533	272
PA-II c		502	539	255
PA-II d		498	541	272
PA-II e		496	548	278

a: Measured by TGA at a heating rate of 20 ºC/min in nitrogen.
b: Measured on DSC at a heating rate of 20 ºC/min in nitrogen.

Figure 5A.11 presents the DSC curves of polyamide obtained from diamines BBHPDA and aromatic diacids.

Polyamides based on BBHPDA and aromatic diacids showed glass transition temperature (Tg) in the range 255 -278ºC. It was observed that corresponding polyamides obtained from 1,1-bis[4-(4-amino phenoxy)phenyl]-1-phenylethane (which contained pendant phenyl ring) and aromatic diacids[31] possess Tg in the range 210ºC-268ºC. Hence introduction of biphenyl pendant group improved glass transition temperatures possibly due to increased rigidity and hindered rotation of the polymer chains.

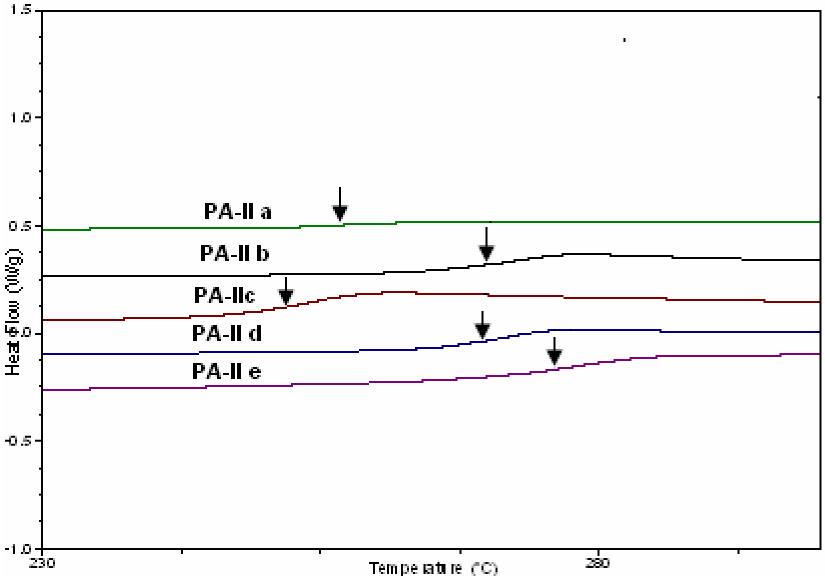


Figure 5A. 11 : DSC curves of polyamides (PA II a-PA II e) derived from from1,1-bis–[4-{(4-aminophenoxy)phenyl}-1-biphenyl]ethane and aromatic diacids.

Figure 5A.12 shows TG curves of polyamides obtained from diamines DCHDA. **Table 5A.8** presents thermal properties of polyamides obtained from diamine DCHDA and aromatic diacids. TG curves revealed that polyamides do not show any decomposition below 488°C. Decomposition of polyamides started in the range 488-507°C.Temperature at 10 % weight loss (T_{10}) was in the range 492°C -511°C.

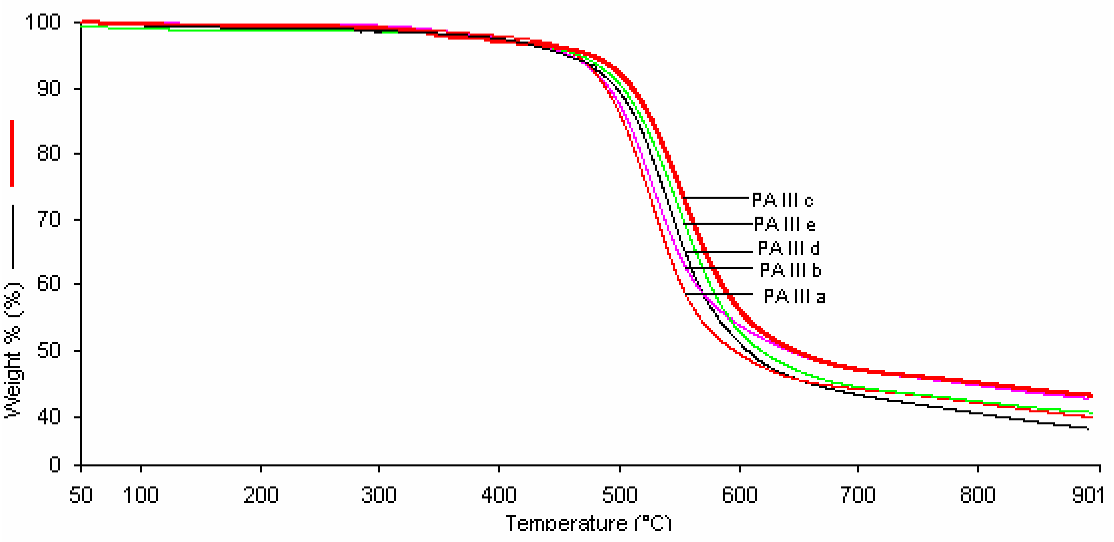
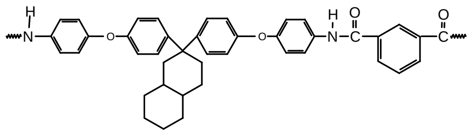
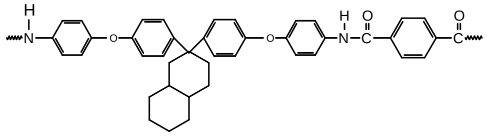
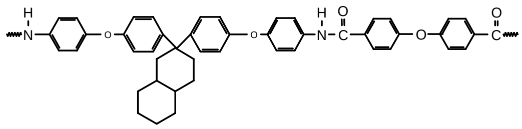
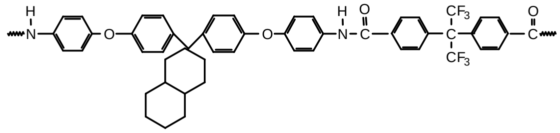
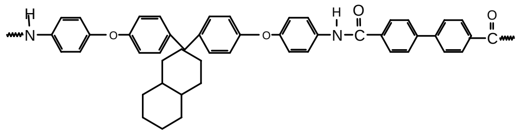


Figure 5A.12: Thermogravimetric curves of polyamides (PA IIIa – PA IIIe) derived from1,1-bis-[4-(4-aminophenoxy)phenyl]octahydro-2(1H)-naphthalene and aromatic diacids

Table 5A.8 Thermal properties of polyamides obtained from diamine 1,1-bis-[4-(4-aminophenoxy)phenyl]octahydro-2(1H)-naphthalene and aromatic diacids.

Polyamide		IDT (°C)[a]	T_{10} (°C)[a]	Tg (°C)[b]
PA-III a		496	499	268
PA-III b		496	499	272
PA-III c		488	492	266
PA-III d		496	498	281
PA-III e		507	511	301

a: Measured by TGA at a heating rate of 20 °C/min in nitrogen.
b: Measured on DSC at a heating rate of 20 °C/min.

Figure 5A.13 shows the DSC curves of polyamides obtained from DCHDA and aromatic diacids. Polyamides based on DCHDA and aromatic diacids showed Tg in the range 266°C -301°C.

It has been reported that analogous polyamides obtained from diamine 1,1-bis[4-(4-aminophenoxy)phenyl]cyclohexane[32] showed Tg in the range 195°C-243°C which is lower than the Tg of polyamides obtained from DCHDA. Hence introduction of octahydro-2(1H) naphthalidene cardo group improved the glass transition temperature of polyamides possibly due to restricted rotation of the polyamide chains.

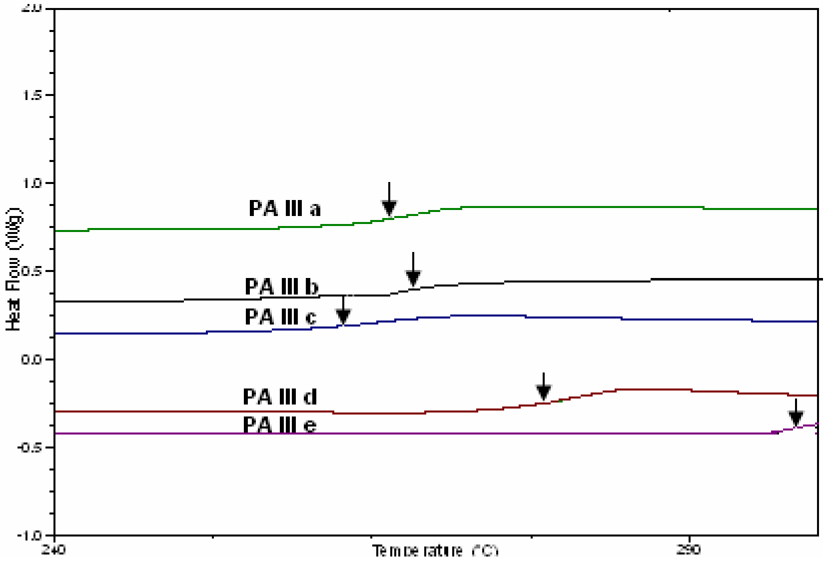


Figure 5A.13: DSC curves of polyamides (PA III a-PA III e) derived from 1,1-bis-[4-(4-aminophenoxy)phenyl]octahydro-2(1H)-naphthalene and aromatic diacids

Figure 5A.12 presents TG curves of polyamides obtained from diamines TMDA and aromatic diacids. **Table 5A.9** presents thermal properties of polyamides obtained from TMDA and aromatic diacids. Polyimides exhibited single stage decomposition starting in the range 378-491°C and temperature at 10 % weight loss (T_{10}) are in the range 384°C-498°C.

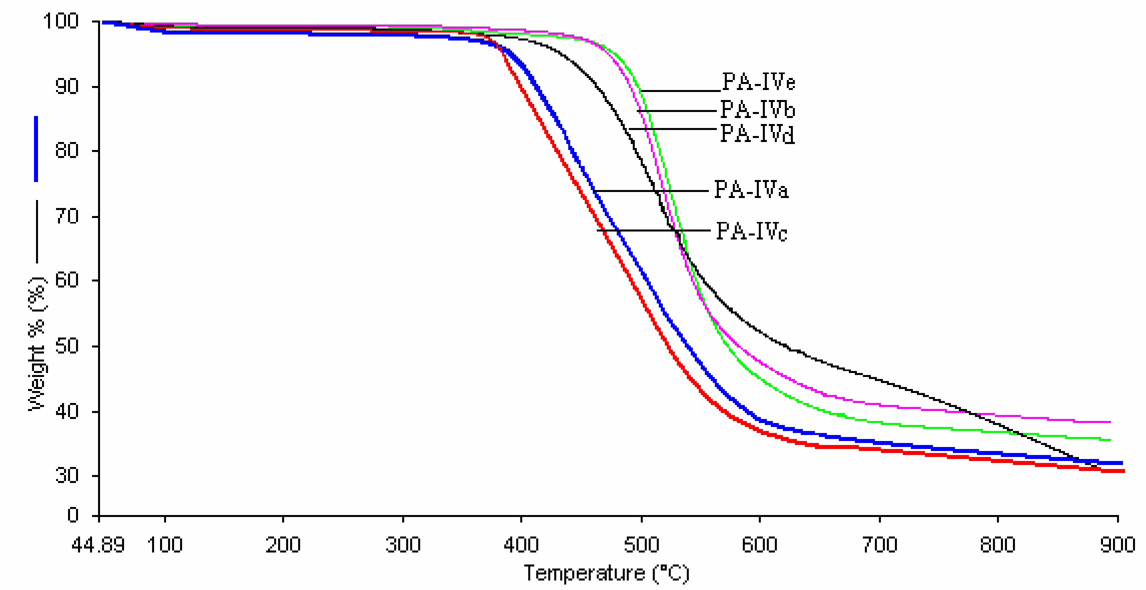
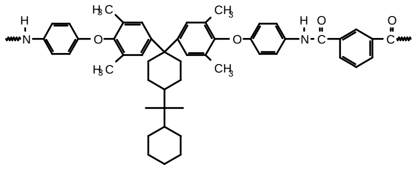
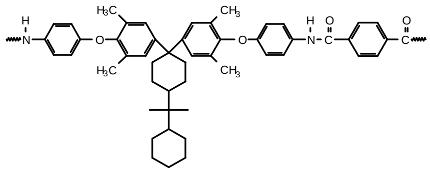
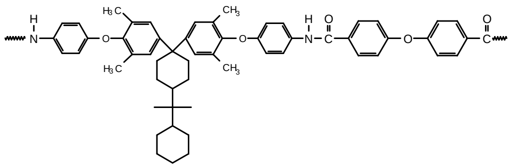
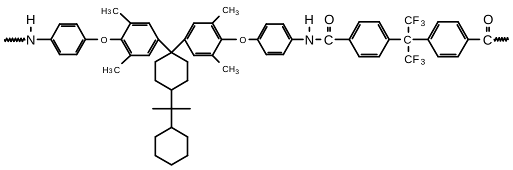
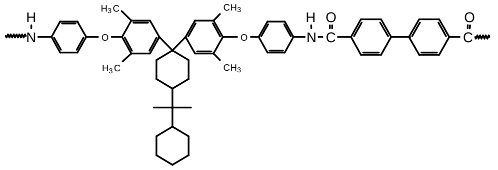


Figure 5A.14: Thermogravimetric curves of polyamides (PA IVa – PA IVe) derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexaneand aromatic diacids.

Table 5A.9 Thermal properties of polyamides obtained from the diamine 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic diacids

Polyamide		IDT,°C^a	T_{10},°C^a	Tg,°C^b
PA-IV a		393	414	266
PA-IV b		487	490	267
PA-IV c		378	384	264
PA-IV d		453	455	267
PA-IV e		491	498	288

a: Measured by TGA at a heating rate of 20 °C/min in nitrogen.
b: Measured on DSC at a heating rate of 20 °C/min in nitrogen.

Figure 5A.15 shows DSC curves of polyamides obtained from TMDA and aromatic diacids. Tg values for polyamides based on TMDA are in the range 264-288 °C. *m*-Oriented isophthalic acid based polyamide exhibited the lowest Tg 264 °C and polyamide obtained from biphenyl-4,4'-dicaboxylic acid exhibited the highest Tg 288 °C due to the presence of its rigid structure and symmetric orientation of *p*-phenylene units in the backbone.

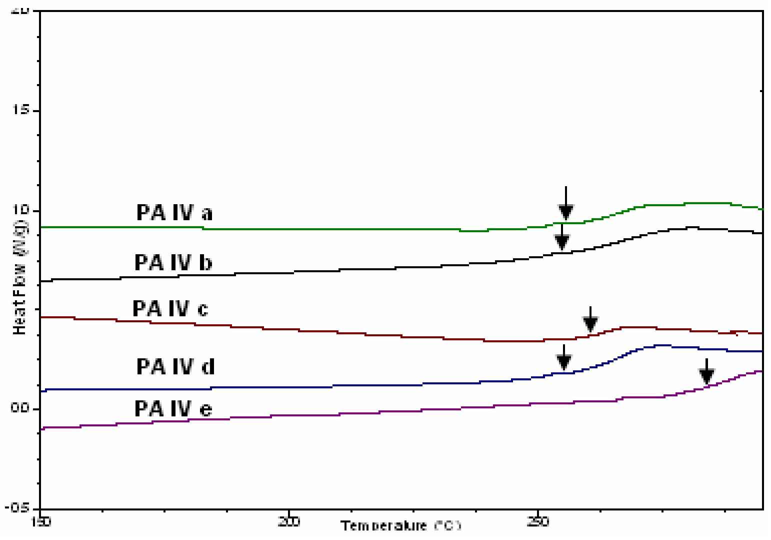
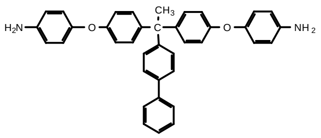
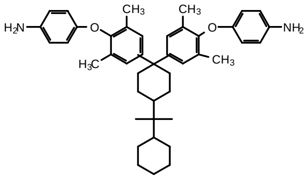


Figure 5A.15 : DSC curves of polyamides (PA IV a -PA IV e) derived from 1,1-bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane and aromatic diacids

5A.4.3.4 Mechanical properties measurement

The mechanical properties of polyamide samples of two series viz (1) polyamides derived from diamine TMDA containing perhydrocumyl cyclohexylidene cardo group and aromatic diacids, (2) polyamides derived from diamine BBHPDA containing biphenyl pendent group and aromatic diacids were tested by an Instron universal tester and the data is given in Table 5A.10

Table 5A.10 Mechanical properties of polyamides

Polyether amide	**Diamine**	**Diacid**	**Strength at break (MPa)**[a]	**Elongation at break (%)**[a]	**Modulus (GPa)**
PA-II a		Isophthalic acid	75(1.50)	10(1.48)	2.07
PA-II b		Terphthalic acid	71(1.70)	6(1.30)	2.18
PA-II c		4,4'-Oxybisbenzoic acid	67(1.44)	7(0.70)	1.70
PA-II d		4,4'-(Hexafluoroisopropylidene) bis (benzoic acid)	69(2.30)	8(1.90)	2.17
PA-II e		Biphenyl-4,4'-dicarboxylic acid	61(0.60)	8(2.20)	1.90
PA-IVa		Isophthalic acid	57(0.90)	6(0.76)	2.10
PA-IVb		Terphthalic acid	58(0.80)	5(0.50)	1.80
PA-IVc		4,4'Oxybisbenzoic acid	52(0.90)	6(0.52)	1.30
PA-IVd		4,4'-(Hexafluoroisopropylidene) bis (benzoic acid)	62(1.93)	6(1.72)	1.40
PA-IVe		Biphenyl-4,4'-dicaboxylic acid	57(1.70)	6(1.48)	2.10

a : Values in the brackets show the standard deviation of the measurement data obtained for four individual samples

Polyamides based on BBHPDA possess tensile strength in the range 61-75 MPa and % elongation in the range 6-10 % and modulus in the range 1.70-2.17 GPa. Polyamides based on TMDA possess tensile strength in the range 52-62 MPa and % elongation in the range 5-6 % and modulus in the range 1.30-2.10 GPa. This demonstrated that these polyimide films were tough and flexible and could be considered as strong polymeric materials.

5A.5 Conclusions

1. Twenty new polyamides containing bulky pendant groups or cardo groups were synthesized by phosphorylation polycondensation.
2. Inherent viscosity of polyamides were in the range 0.50-0.82 dL/g indicating formation of medium to high molecular weight polymers.
3. Polyamides showed good solubility in aprotic polar solvents like NMP, DMAc etc. TMDA-based polyamides were soluble in aprotic polar solvents as well as in common organic solvents such as THF. Better solubility behavior of TMDA based polyamides could be attributed to the presence of perhydrocumylcyclohexylidene cardo group, flexible ether linkages and four methyl substituents along the backbone.
4. Tough, transparent and flexible films could be cast from the solution of these polyamides in DMAc.
5. Wide angle X-ray diffraction patterns of polyamide films showed their amorphous nature.
6. IDT and T_{10} values of the polyamides were in the range 378-522 ^{o}C and 384-549 ^{o}C, respectively indicating good thermal stability. Tg was in the range 248-288 ^{o}C.
7. Mechanical properties of polyamide films obtained from the diamines BBHPDA and TMDA were studied. Polyamide based on BBHPDA possess tensile strength in the range 61-75 MPa and % elongation in the range 6-10 % and modulus in the range 1.70-2.17 GPa. Polyamide based on TMDA possess tensile strength in the range 52-62 MPa and % elongation in the range 5-6 % and modulus in the range 1.30-2.10 GPa indicating that these polyimide films were tough and flexible and could be considered as strong polymeric materials.

5 B.1 Introduction

In recent years many efforts have been centered to enhance the processability and solubility of polyamides by chemical modification of their structure. These structural modifications can be brought about by either synthesizing new diamines or by synthesizing new diacids which eventually make the backbone of the polymer. Previous studies have reported that incorporation of cardo groups such as cyclododecylidene[11,12], adamentane[13,14], tricyclo[5.2.1.0]decane[15,16,] *tert*-butylcyclohexylidene[17] into the backbone of polyamides results in polymers with enhanced solubility retaining high thermal stability.

The synthesis and characterization of polyamides starting from new cardo diacid namely 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane (PCPDA) is reported in the present work.

Polyamides were synthesized by phosphorylation polycondensation of diacid PCPDA with commercially available diamines namely *m*-phenylene diamine, *p*-phenylene diamine and benzidine.

5 B. 2 Experimental

5B.2.1 Materials

1,1–Bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane (PCPDA) was synthesized as described **Chapter 3.** Commercially available diamines viz. *m*-phenylene diamine, *p*-phenylene diamine and benzidine received from Aldrich, USA were purified by reported prodcedure before use[28]. N-Methyl 2-pyrrolidinone and pyridine from S. D. Fine Chem., India were dried and distilled according to the reported procedure.[28] Lithium chloride was dried at 150^{o}C under reduced pressure for 12 h before use. Triphenyl phosphite received from Aldrich ,USA was distilled under reduced pressure prior to use.

5B.2.2 Measurements

Inherent viscosity of polymers was measured with 0.5 % (w/v) solution of polymer in N,N-dimethylacetamide at 30±0.1^{o}C using an Ubbelohde suspended level viscometer.

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

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 spectrum and 50, 100 or 125 MHz for ^{13}C spectrum measurements using DMSO d_6 as a solvent.

Solubility of aromatic polyamides was determined at 3 wt % (w/v) concentration in different solvents at room temperature or on heating.

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

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 thermal analyzer system at a heating rate of 20°C / minute under nitrogen atmosphere. Sample weight taken was ~5 mg.

DSC was carried out on TA Instruments *DSC* Q10, at a heating rate of 20°C / minute in nitrogen atmosphere.

5B.3 Synthesis of polyamides starting from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and commercially available diamines

A representative procedure for the synthesis of polyamide PA-V b is as follows :

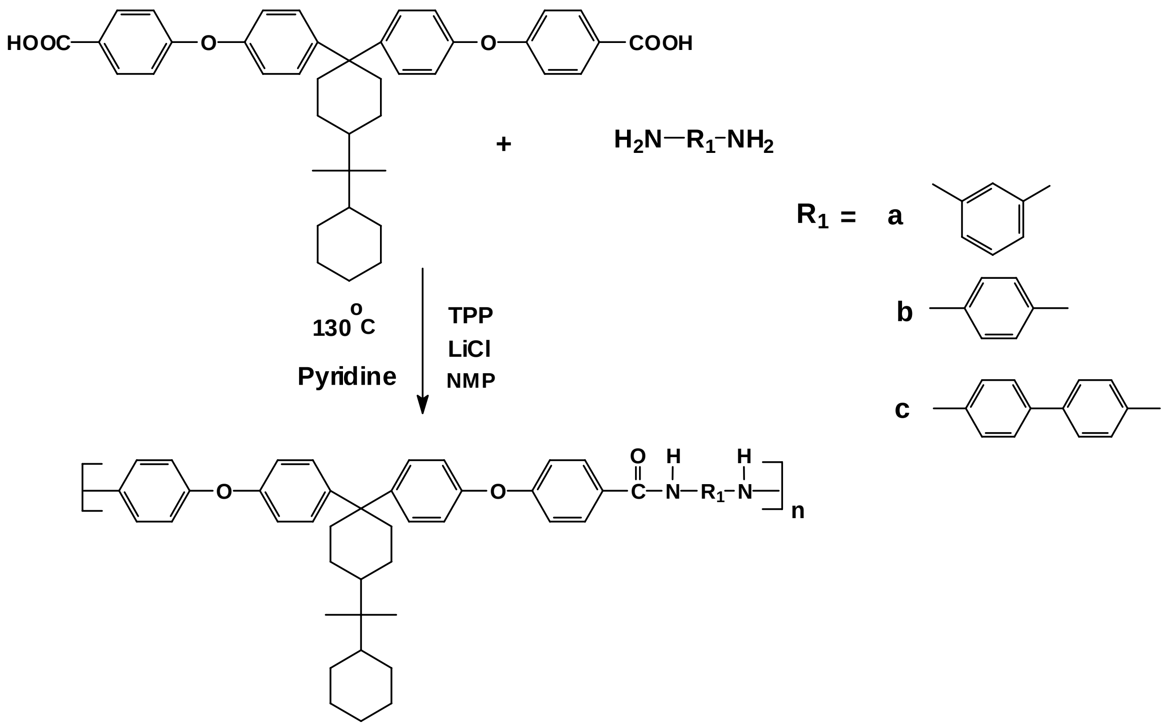
A100 ml three-necked round bottom flask equipped with a magnetic stirrer bar and a nitrogen inlet was charged with PCPDA, (0.35 g, 0.71 mmol) , *p*-phenylene diamine (0.08 g, 0.74 m mol) and triphenyl phosphite (0.536 g ,1.6 mmol). NMP (5 mL), pyridine (1.3 mL) and LiCl (0.35 g) were added to it. The reaction mixture was stirred at 130^{o}C for 6 h under nitrogen atmosphere. After cooling, the reaction mixture was poured into excess of methanol with constant stirring, producing a white precipitate that was washed repeatedly with hot water and methanol. The precipitate was filtered and dried under reduced pressure to afford PA-Vb.

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

5B.4 Results and Discussion

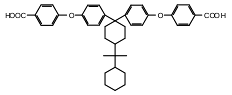
5B.4.1. Synthesis and characterization of polyamides derived from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and aromatic diamines

Polyamides were obtained by the reaction of stoichiometric quantities of PCPDA and commercially available aromatic diamines by phosphorylation polycondensation. Scheme **5B.1** outlines synthesis of polyamides starting from PCPDA and aromatic diamines. The reaction mixtures were homogeneous throughout the course of the reaction and gave polyamides with yields in the range 93-95%. The results are summarized in **Table 5B.1.** Inherent viscosities of the polyamides were in the range of 0.45 to 0.55 dL/g indicating formation of medium molecular weight polymers.



Scheme 5B.1: Synthesis of polyamides starting from1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and aromatic diamines

Table 5B.1: Synthesis of polyamides starting from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and aromatic diamines.

Polyamide	Diacid	Diamine	Yield (%)	η_{inh} (dl/g)[a]
PA-V a		*m*-Phenylene diamine	93	0.51
PA-V b		*p*-Phenylene diamine	95	0.45
PA-V c		Benzidine	95	0.55

5B.4.2 Structural Characterization

Polyamides were characterized by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. A representative FTIR spectrum of polyamide film derived from PCPDA and *m*-phenylene diamine is shown in **Figure 5B.1**

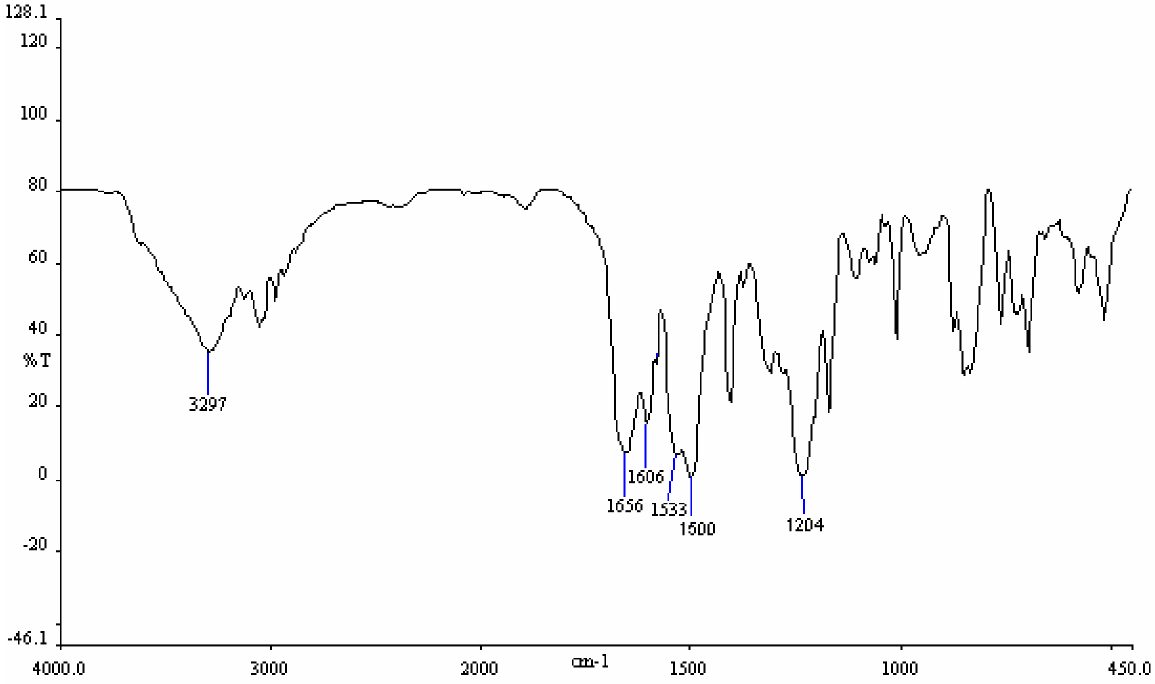


Figure 5B.1 IR spectrum of polyamide obtained from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and m-phenylene diamine.

Absorption band at 3297 cm^{-1} is attributed to the N-H stretching which is consistent with the secondary amide character of polyamide. The amide-I band, associated with stretching vibration of carbonyl group appeared at 1656 cm^{-1}. Lowering of carbonyl frequency can be attributed to the involvement of -NH- group in hydrogen bonding or in resonating structure of amide linkage. The amide- II band , ascribed to the coupling of the –N-H bending and –C-N stretching of -C-N-H group, appeared at 1533 cm^{-1}. Band at 1204 cm^{-1} indicates the presence of C-O-C linkage along the polymer backbone

^{1}H NMR spectrum of polyamide derived from PCPDA and *m*-phenylene diamine is reproduced in **Figure 5B.2**

A singlet at 10 δ, ppm corresponds to -NH proton of amide linkage. The protons 15 ortho to carbonyl group appeared at 7.97 δ, ppm due to –I effect of carbonyl group attached to the adjacent carbon atom. Protons 13 and 14 ortho to ether group appeared at 6.96 δ ppm as doublet of doublet. Protons 12 and 12' meta to –O- linkage appeared as two separate doublets at 7.51 and 7.22 δ ppm. The protons of *m*-phenylene diamine segment 18 and19 make a multiplet centered at 7.20 δ ppm and proton 17 flanked by amide linkages appeared up field as a singlet at 6.86 δ, ppm. Aliphatic protons 1 of perhydrocumyl cyclohexylidene cardo group appeared as doublet at 2.75 δ ppm. Protons 2-11 appeared as multiplets in the region 0.70 to 2.00 δ ppm. Methyl protons 4 and 5 appeared as singlet at 0.60 δ ppm.

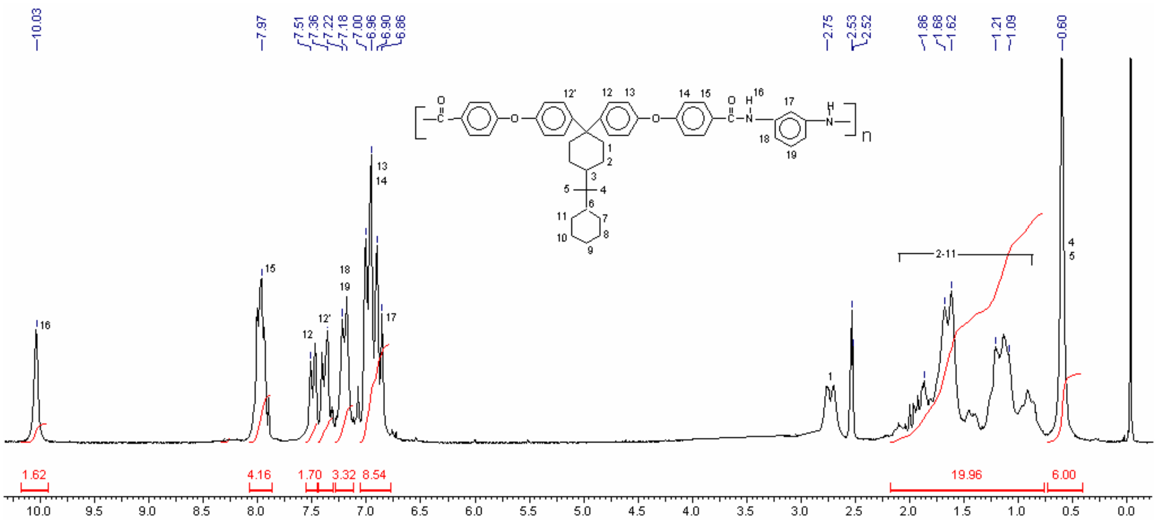


Figure 5B.2: ^{1}H NMR spectrum of polyamide derived from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and *m*-phenylene diamine in DMSOd$_{6}$.

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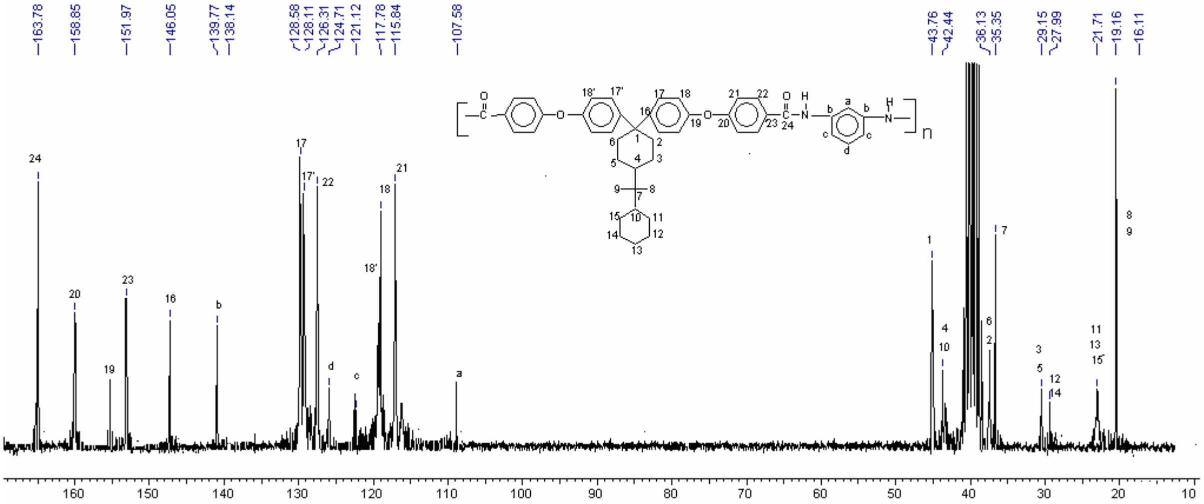

Figure 5B.3 : ^{13}C NMR of spectrum of polyamide derived from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and *m*-phenylene diamine in DMSOd$_6$.

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Figure 5B.3 presents ^{13}C NMR spectrum of polyamide derived from PCPDA and *m*-phenylene diamine. The carbonyl carbon 24 appeared downfield at 163.78 δ ppm .The carbons 19 and 20 adjacent to ether linkage appeared at 158.85 and 154 δ ppm. Carbon 23 adjacent to carbonyl group appeared at 151.97 δ ppm. Since the two phenyl rings attached to perhydrocumyl cyclohexylidene group are magnetically nonequivalent the carbons 17, 17'and 18, 18'make two different peaks at 128.58 and 128.11δ ppm and 117.5and 117.78 δ ppm respectively. Carbons 21 and 22 appeared at 126.31 and 115.84 δ ppm .The carbons 'c' and 'd' of m-phenylenediamine, appeared at 121.3, 124.7 δ ppm. Carbon 'b' which is attached to -CONH- linkage appeared at 139.77 δ ppm and carbon 'a' appeared up field at 107.58 δ ppm due to the presence of two –CONH- amide linkages on the carbons adjacent to it.

5B.4.3 Properties of Polyamides

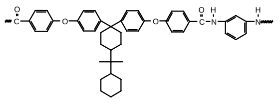
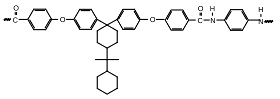
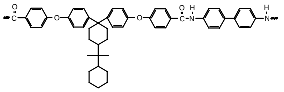
5B.4.3.1 Solubility of polyamides

Polyamides were tested for solubility at 3 % w/v in different solvents and data is summarized in **Table 5B.2** All polyamides were soluble in polar aprotic solvents such as NMP, DMAc, DMF at room temperature or on heating

Additionally polyamide based on PCPDA and *m*-phenylene diamine (PA-Va) was soluble upon heating in DMSO, *m*-cresol and THF. Polyamide based on PCPDA and *p*-phenylene diamine (PA-Vb) was found to be soluble upon heating in DMSO.

These results showed that polyamides bearing perhydrocumyl cyclohexylidene group exhibited good solubility in organic solvents owing to the presence of perhydrocumyl cyclohexylidene group. The single crystal X-ray study of DCNPCPBP (Figure 3.63: ORTEP diagram of DCNPCPBP, Chapter 3) had revealed that the inner aromatic rings are attached nearly orthogonal to bridged carbon C-1. Therefore, the resulting polyamides would have a periodically twisted polymer backbone which probably disturbed the dense packing of polymer chains, consequently the solvent molecules could easily solubilize the polyamide chains.

Table 5B.2: Solubility behaviour of polyamides obtained from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and commercially available aromatic diamines.

Polyamides		NMP	DMAc	DMF	DMSO	*m* -cresol	THF
PA-V a		++	++	++	+	+	+
PA-V b		++	++	++	+	--	--
PA-V c		++	++	+	--	--	--

++ Soluble, + soluble on heating at 60°C, -- insoluble.

5B.4.3.2 X-Ray diffraction analysis

X-Ray diffraction patterns of polyamide films obtained from PCPDA, and aromatic diamines are shown in Figure 5B.7. The diffraction patterns showed only broad amorphous halos for all polyamides. It indicates that introduction of cardo groups namely perhydrocumyl cyclohexylidene group inhibited the close packing of the chains leading to amorphous polyamides.

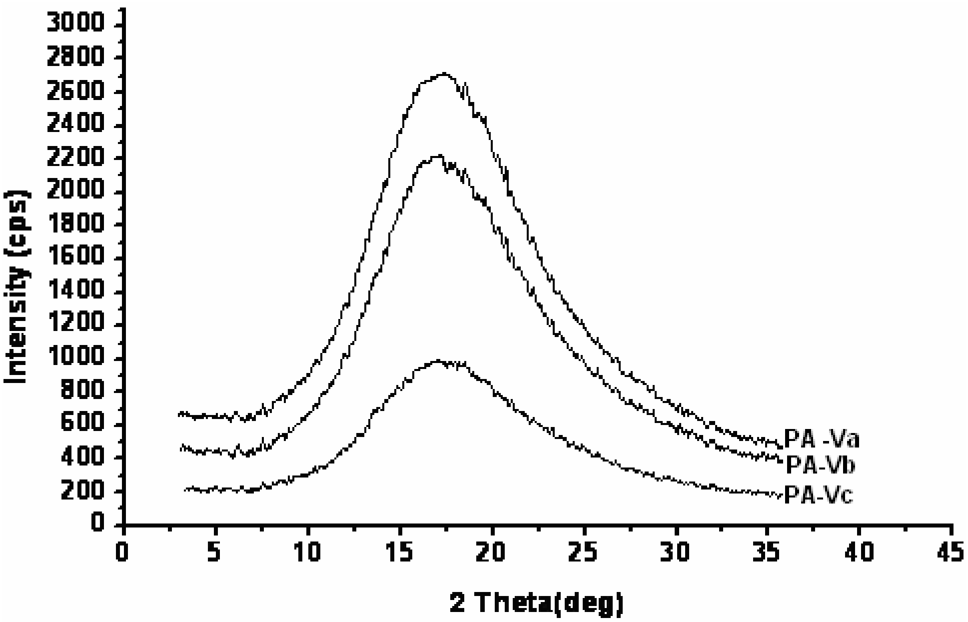


Figure 5B.4: Wide angle X-ray diffractograms of polyamides obtained from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and different aromatic diamines.

5B.4.3.3 Thermal behaviour of polyamides

In the present study, thermal stability of polyamides was studied by thermogravimetric analysis (TGA) at a heating rate of 20°C/minute under nitrogen. Thermogravimetric curves are given in Figure 5B.5.The initial decomposition temperature (IDT) and the decomposition temperature at 10% weight loss (T_{10}) and the glass transition temperatures (Tg) for polyamides are presented in Table 5B.3. DSC curves are shown in **Figure 5B.6.**

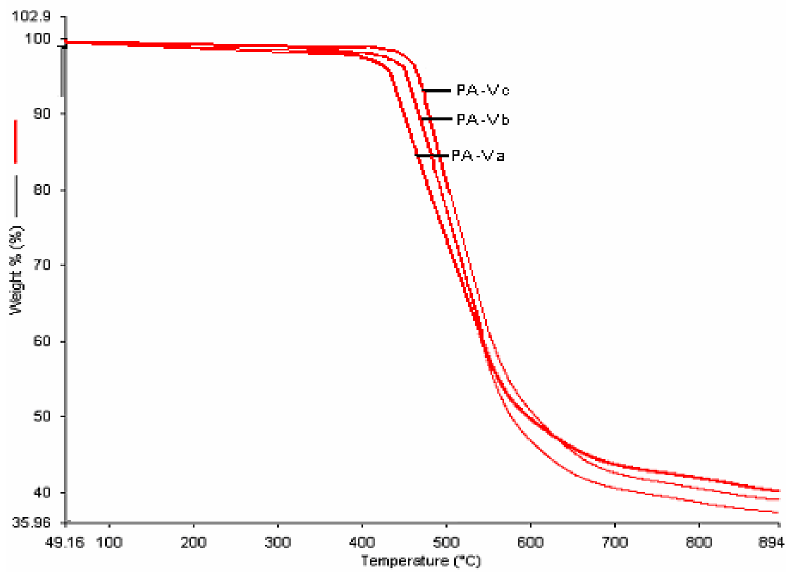
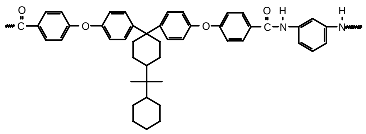
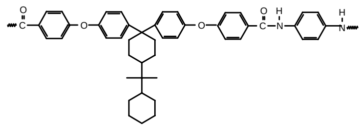
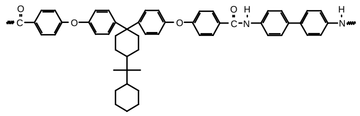


Figure 5B.5: TG curves of polyamides obtained from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and aromatic diamies.

All polyamides were stable upto 382 °C and showed single stage decomposition starting in the range 382 °C- 480 °C. Temperature at 10% weight loss was in the range 455 °C - 495 °C indicating their good thermal stability.

Polyamide obtained from PCPDA and m-phenylene diamine exhibited the lowest glass transition temperature (Tg) of 227 °C due to the presence of *m*-oriented phenylene segments and polyamide obtained from benzidine showed the highest Tg of 305 °C as expected from its rigid and symmetrical *p*-oriented structure.

Table 5B.3: Thermal properties of polyamides obtained from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and aromatic diamines.

Polyamide		IDT °C	T_{10}°C	Tg °C
PA-V a		382	455	227
PA-V b		478	490	245
PA-V c		480	495	305

a: Measured on DSC at a heating rate of 20 °C/min in nitrogen.

b: Measured by TGA at a heating rate of 20 °C/min in nitrogen.

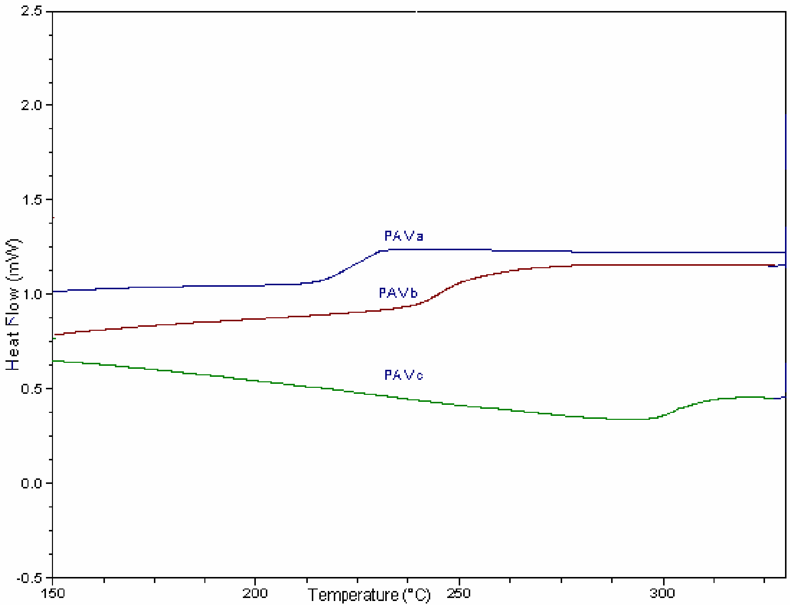


Figure 5B.6: DSC curves of polyamides obtained from 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane and aromatic diamines.

5B.5 Conclusions

1. Three new polyamides containing cardo group were synthesized by phosphorylation polycondensation starting from new diacid 1,1–bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane (PCPDA) and aromatic diamines.
2. Inherent viscosity of polyamides was in the range 0.45-0.55 dL/g indicating formation of medium molecular weight polymers.
3. Polyamides were soluble in aprotic polar solvents like NMP, DMAc and DMF. Tough, transparent and flexible films could be cast from solution of these polyamides in DMAc.
4. Wide angle X-ray diffraction patterns of polyamide films showed their amorphous nature.
5. IDT and T_{10} values of the polyamides were in the range 382-480 ^{o}C and 455-495 ^{o}C, respectively indicating good thermal stability. Tg was in the range 227-305^{o}C.

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Chapter 6 Synthesis and characterization of polyesters

6.1 Introduction

Aromatic polyesters are an important class of high performance polymers which possess high thermal stability and good mechanical properties and are, therefore, applied widely in aviation, automobile and electronic industries.[1,2] However, most aromatic polyesters encounter processing difficulties due to their high glass transition or melting temperatures coupled with insolubility in common organic solvents.[3,4] Therefore, development of aromatic polyesters for use at high temperature with improved processability is an important goal. Several approaches have been adapted[5-35] to improve solubility and processability of aromatic polyesters. These include :

(1) Insertion of flexible spacers in the backbone;

(2) Incorporation of bent or ‘crankshaft’ units along the backbone;

(3) Appending of bulky side groups or flexible side chains.

Incorporation of bulky pendant groups along the polymer backbone has been demonstrated to improve solubility of polyesters. This is due to disturbance in dense chain packing of the polymer chains by bulky pendant groups which, in turn, increase the free volume. Bulky pendant groups also decrease the molecular mobility, so that overall observable effect is an increase of glass transition temperature and an improvement of solubility at the same time.

The objective of the present work was to synthesize polyesters and copolyesters based on a diphenol containing phenyl sulfonyl phenyl pendant group, namely, 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane (DPSBP), with isophthaloyl chloride andterephthaloyl chloride, and to investigate the effect of introduction of bulky pendant group on properties of polyesters and co polyesters.

Polyesters were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The mechanical properties of selected polyesters were determined.

6.2 Experimental

6.2.1 Materials

1,1-Bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane, was synthesized as described in **Chapter 3.** Bisphenol-A (BPA) and benzyltriethyl ammonium chloride (BTEAC) (Aldrich) were used as received. Dichloromethane (S.D.Fine Chemicals) was dried and distilled over calcium hydride. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were prepared by standard methods and purified by distillation under reduced pressure.[36] Other solvents were purified according to standard procedures.[37]

.

6.2.2 Measurements

Inherent viscosity (η_{inh}) of polyesters was measured on 0.5 % (w/v) solution of polyester in chloroform or phenol/tetrachloroethane (60/40,w/w) mixture at 30 ± 0.1^{o}C using an Ubbelohde suspended level viscometer on Schott Gerate CK-160 automatic viscometer.

Solubility of aromatic polyesters was determined at 3 % (w/v) concentration in different solvents at room temperature or on heating.

Molecular weight of polyesters was measured on Thermofinnigan make gel permeation chromatograph (GPC), using the following conditions: Column - polystyrene-divinylbenzene (10^{5}A^{o} to 50A^{o}), Detector-RI, room temperature. Polystyrene was used as the calibration standard. Polyester sample (5 mg) was dissolved in 5 ml chloroform and filtered through 0.45 μ filter.

FTIR spectra were recorded using polyester films on a Perkin Elmer Spectrum GX spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker 200 or 500 MHz spectrophotometer using $CDCl_3$ as solvent and the chemical shifts reported as δ, ppm.

X-Ray diffractograms of polyesters were obtained on free standing polyester films. Analysis was carried out on a Rigaku Dmax 2500 X-ray diffractometer at a tilting rate of 2^{o} / minutes. Polymer was dissolved in chloroform and the solution was filtered on a petri dish; solvent was evaporated gradually at 40^{o}C in oven, and the semidried films were further dried at 70^{o}C for 5 days under reduced pressure to obtain films for XRD studies

Thermogravimetric analysis (TGA) was performed on Perkin Elmer TGA-7 at a heating rate of 20^{o}C / min in nitrogen atmosphere.

DSC analysis was carried out on TA instruments DSC Q 10, at a heating rate of 20°C / min in nitrogen atmosphere.

Instron Universal Tester Model No. 4204 with a load cell of 1 Kilo Newton was used to measure the stress-strain behavior of samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used. Measurements were carried out at room temperature using film specimens (10 mm wide, 5 cm long, and ~ 50 micron thick); five measurements were taken for each polymer sample.

6.3 Synthesis of aromatic polyesters containing bulky pendant groups

6.3.1 Synthesis of homopolyesters containing bulky pendant groups

A representative procedure for synthesis of polyesters is described below.

In a typical polymerization reaction, 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane (DPSBP) (2.15 g, 5.0 mmol) was taken in a 100 mL two-necked round bottom flask equipped with a mechanical stirrer. A solution of sodium hydroxide (10 mL of 1M NaOH) was added to it. The mixture was stirred for 1h at 10°C. BTEAC (30 mg) was added to the reaction mixture and stirring was continued. After 30 minutes, solution of isophthaloyl chloride (1.01 g, 5 m mol) in 20 mL of dichloromethane was added to the reaction mixture and the mixture was stirred vigorously at 2000 rpm for 1h. The aqueous layer was separated and dichloromethane layer was diluted with additional dichloromethane (10 mL) and poured into excess methanol. The precipitated polymer was filtered and washed repeatedly with water and methanol and dried under reduced pressure at 80 °C for 24 h.

6.3.2 Synthesis of aromatic copolyesters

A representative procedure for synthesis of co polyesters is described below.

In a typical polymerization reaction, DPSBP (1.08 g, 2.5 mmol) and BPA (0.57 g, 2.5 mmol) were taken in a 100 mL two-necked round bottom flask equipped with a mechanical stirrer. A solution of sodium hydroxide (10 mL of 1M NaOH) was added to it. The mixture was stirred for 1h at 10°C. BTEAC (30 mg) was added to the reaction mixture and the stirring was continued. After 30 minutes, solution of terephthaloyl chloride (1.01 g, 5 mmol) in 20 mL of dichloromethane was added to the reaction mixture and the mixture was stirred vigorously at 2000 rpm for 1h. The aqueous layer was separated and dichloromethane layer was diluted with additional dichloromethane (10 mL) and poured into excess methanol. The precipitated polymer was filtered and washed repeatedly with water and then with methanol, dried under reduced pressure at 80 ^{o}C for 24 h.

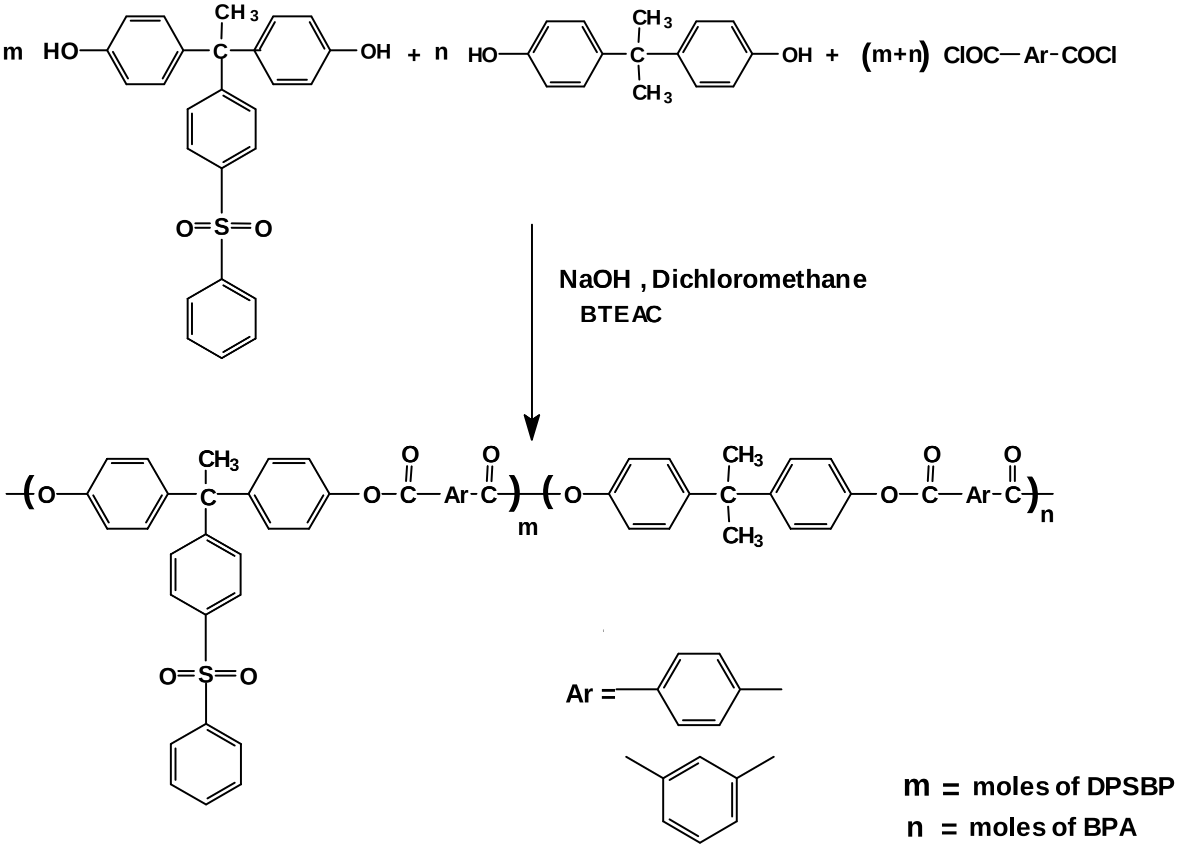
Similar procedure was followed for synthesis of other copolyesters

6.4 Results and Discussion

6.4.1 Synthesis and characterization of aromatic polyesters and copolyesters containing phenyl sulfonyl phenyl pendant groups

Aromatic polyesters are well known for their high thermal stability and mechanical properties.[1,2] However, they are difficult to process due to their insolubility in common organic solvents. Polyester derived from bisphenol-A and a mixture (50:50 mol %) of isophthaloyl chloride and terephthaloyl chloride has been commercialized.[38]. Copolymerization is one of the most useful approaches for improving solubility and, in-turn, processibility of polymers. Since bisphenol-A and TPC based polyesters are insoluble in common organic solvents such as chloroform and dichloromethane, it was of interest to study the effect of incorporation of DPSBP on the properties of polyester derived from bisphenol-A and TPC.

In the present study, copolyesters containing phenyl sulfonyl phenyl pendant groups were synthesized in order to study the effect of incorporation of bulky pendant groups on the polymer properties. **Scheme 6.1** illustrates synthesis of copolyesters from DPSBP, BPA and aromatic diacid chlorides.



Scheme 6.1: Synthesis of polyester and copolyesters from1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)] ethane, BPA and aromatic diacid chlorides.

Homopolyesters and copolyesters were synthesized by phase transfer-catalyzed interfacial polycondensation technique.[8,17,39] Homopolymers and copolymers were synthesized from combinations of DPSBP, BPA, and TPC in dichloromethane-aqueous sodium hydroxide system using BTEAC as a phase transfer catalyst. Homopolymers from BPA-TPC and BPA-IPC as well as copolymer from BPA with TPC: IPC (50:50 mol %) were synthesized as reference materials. The results of polymerizations are summarized in **Table 6.1.**

Inherent viscosity (η_{inh}) of polyesters was in the range 0.56-1.57 dL/g indicating formation of medium to high molecular weight polymers. This is also reflected in the results of measurement of molecular weights of the polyesters by GPC **(Table 6.1).** Number average molecular weights (Mn) of polyesters with phenyl sulfonyl phenyl pendant groups were in the range 28,650 to 80,230 with polydispersity index in the range 2.0 -3.1. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards. Tough transparent and flexible films of polyesters containing phenyl sulfonyl phenyl pendant group could be cast from their solutions in chloroform.

Table 6.1 Synthesis of aromatic polyesters containing phenyl sulfonyl phenyl pendant groups

Polymer	Composition of diols (mol %)		Diacid chloride	η_{inh} [a] (dL/g)	Molecular weight [c]		
	DPSBP	BPA			Mn	Mw	Mw/Mn
PES-I	100	0	TPC	1.04	62080	155700	2.5
PES-II	100	0	IPC	0.56	43490	86800	2.0
PES-III	100	0	TPC: IPC (50:50)	0.75	28650	88800	3.1
PES-IV	75	25	TPC	1.13	63210	177000	2.8
PES-V	50	50	TPC	1.16	74670	159000	2.1
PES-VI	25	75	TPC	1.57	80230	195700	2.4
PES-VII	0	100	TPC	1.23[b]	-	-	-
PES-VIII	0	100	IPC	0.90[b]	-	-	-
PES-IX	0	100	IPC/ TPC (50:50)	1.46	1,33,180	217490	1.7

a: η_{inh} of polyester was measured with 0.5% (w/v) solution of polyester in chloroform 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

c: measured by GPC in chloroform; polystyrene was used as the calibration standard.

6.4.1.1 Structural characterization

The formation of polyesters was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of polyester derived from 1,1-bis-[4-hydroxyphenyl-1-(4-phenylsulfonylphenyl)]ethane and terephthaloyl chloride is reproduced in **Figure 6.1**. Ester carbonyl band of polyesters was observed at 1736 cm^{-1}. The asymmetric and symmetric stretching of sulfonyl group give rise to the bands at 1320 and 1165 cm^{-1}, respectively.

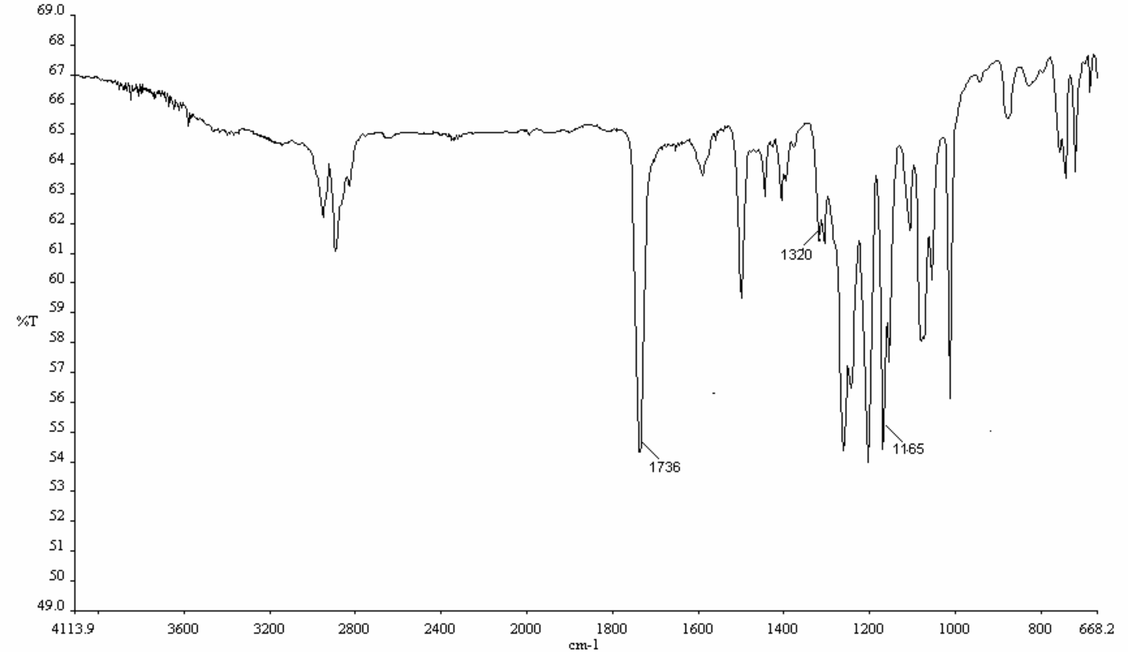


Figure 6.1: FTIR spectrum of polyester derived from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane and TPC.

^{1}H-NMR spectrum of polyester derived from DPSBP and TPC along with assignments is shown in **Figure 6.2**. A singlet for four protons of TPC appeared down field at 8.32 δ, ppm. Protons 3, 9 and 4, 8 of bisphenol DPSBP appeared as separate doublets at 7.87 and 7.97 δ, ppm, and the protons 10, 2, 11 appeared as multiplet centered at 7.17 δ, ppm. Protons 5,6,7 appeared as multiplet centered at 7.54 δ, ppm. Protons 12 appeared as doublet at 7.31 δ, ppm. The methyl protons 1 attached to the quaternary carbon of DPSBP segment appeared as a singlet at 2.22 δ, ppm.

Figure 6.3 presents ^{1}H-NMR spectrum of polyester derived from DPSBP and IPC alongwith assignments. Proton 13, which is flanked by two carbonyl groups, appeared down field at 8.99 δ, ppm. Protons 14 and 15 appeared as doublet at 8.44 δ, ppm and as multiplet centered at 7.54 δ, ppm respectively. Protons 3, 9 and 4, 8 appeared as doublets at 7.58 and 7.86 δ ppm, and the protons 10, 2, 11 appeared as multiplet centered at 7.19 δ, ppm. Protons 12 appeared as doublet at 7.32 δ, ppm. The methyl protons 1 attached to the quaternary carbon of DPSBP segment appeared as a singlet at 2.21 δ, ppm.

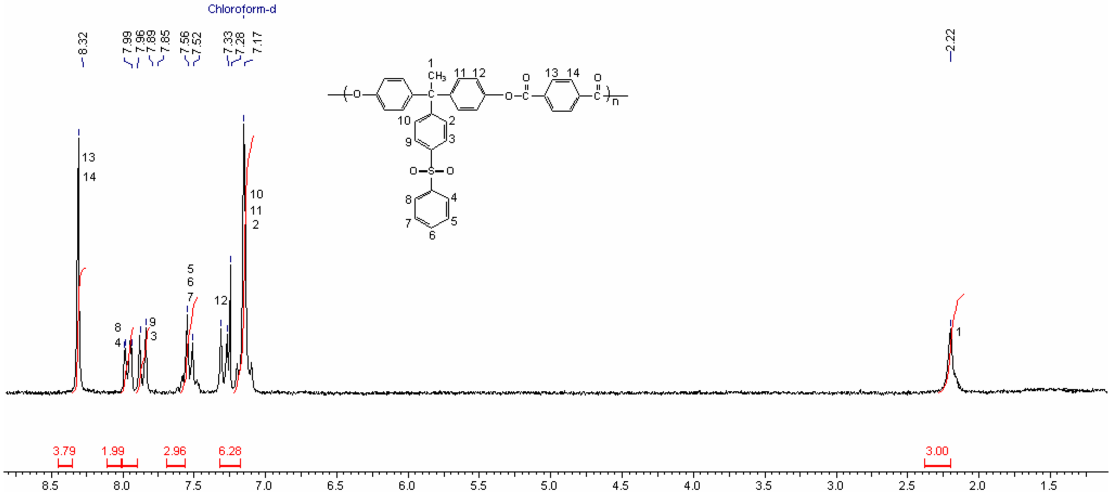


Figure 6.2: ^{1}**H-NMR (CDCl$_3$) spectrum of polyester derived from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane and TPC.**

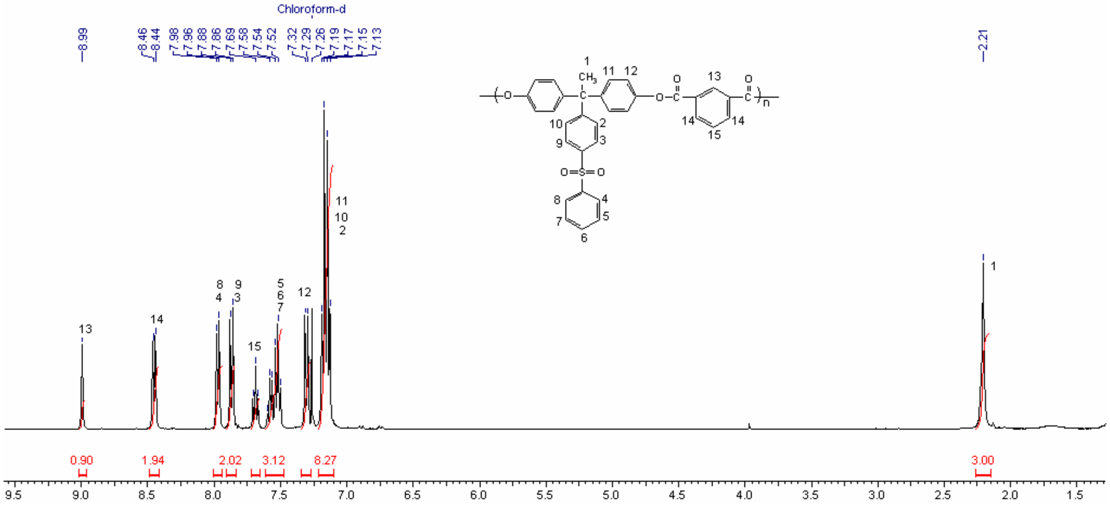


Figure 6.3: ^{1}**H-NMR(CDCl$_3$) spectrum of polyester derived from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane and IPC.**

The composition of copolyesters was determined by ^{1}H-NMR spectroscopy. In the ^{1}H-NMR spectra of copolyester PES-V **(Figure 6.4)**, there are two different characteristic singlets in the aliphatic region: 2.20 δ, ppm and 1.73 δ, ppm which were assigned to the protons 1 of methyl group bonded to a quaternary carbon bearing the phenyl sulfonyl phenyl group and the methyl protons 19 of isopropylidene linkage of BPA, respectively. The ratio of integration of peak at 2.20 δ, ppm and peak at 1.73 δ, ppm was used to determine the ratio of the co-monomers namely DPSBP and BPA. There was a reasonably good agreement between the observed incorporation of DPSBP and the feed composition.**(Table 6.2).**

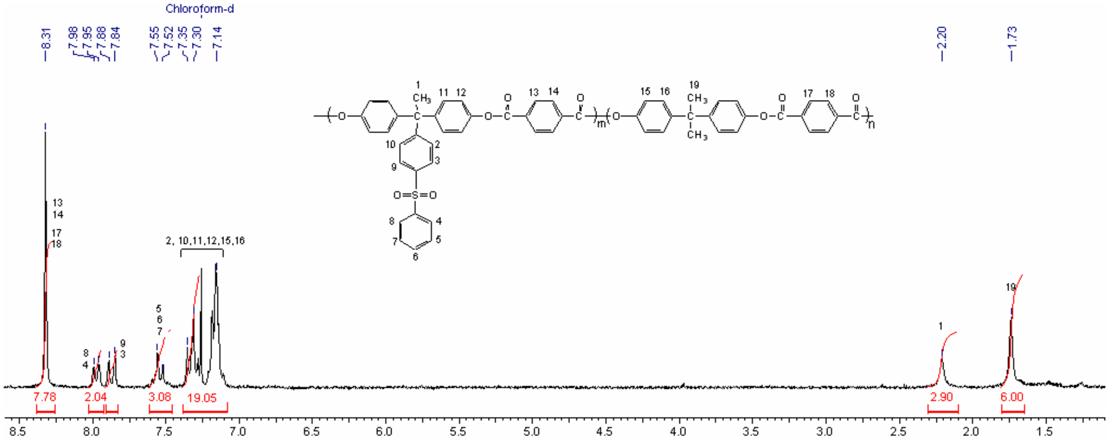


Figure 6.4: ^{1}H-NMR (CDCl$_3$) spectrum of copolyester obtained from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane (50%) and BPA (50%) and TPC.

Table 6.2: Copolyester composition determined from ^{1}H-NMR spectra.

Copolyester	Observed DPSBP, mol %	Feed DPSBP, mol %
PES-IV	74	75
PES-V	48	50
PES-VI	21	25

^{13}C-NMR spectra of polyesters obtained from DPSBP and terephthaloyl chloride (**Figure 6.5**) and DPSBP and isophthaloyl chloride (**Figure 6.6**) are produced along with the assignment of the carbon atoms.

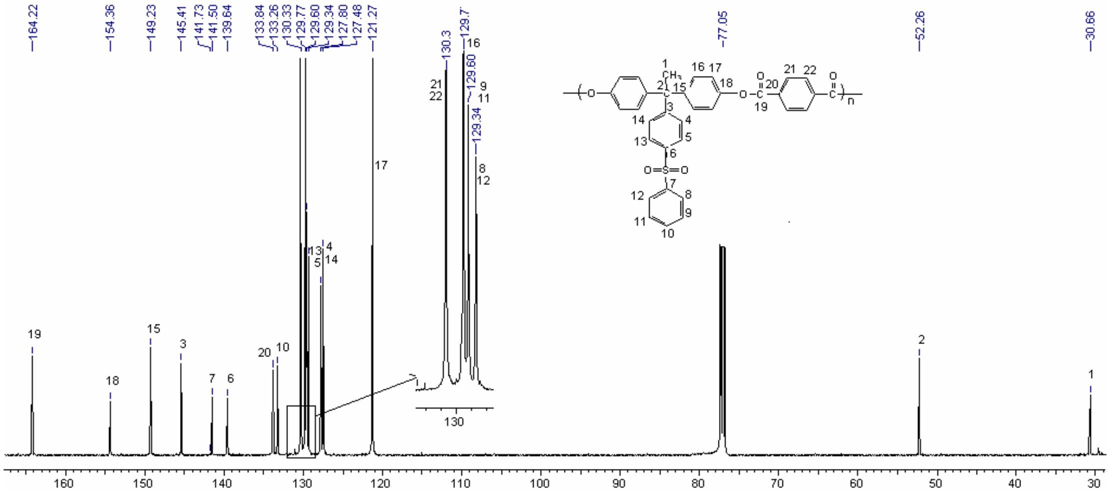


Figure 6.5: ^{13}C-NMR ($CDCl_3$) spectrum of polyester obtained from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane and TPC.

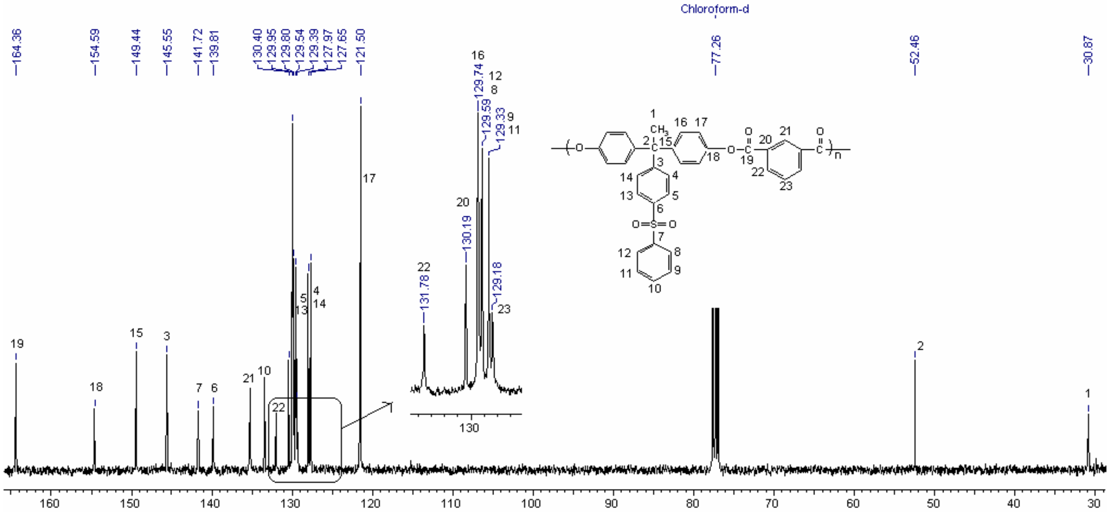


Figure 6.6: ^{13}C-NMR ($CDCl_3$) spectrum of polyester obtained from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane and IPC.

6.4.2 Properties of polyesters

6.4.2.1 Solubility of polyesters

The solubility data of copolyesters in different organic solvents at 3 % (w/v) is shown in **Table 6.3.**

Homopolyesters derived from DPSBP with TPC (PES-I) and IPC (PES-II) were soluble in common organic solvents such as DCM, chloroform, tetrahydrofuran and aprotic polar solvents such as NMP, DMAc and were found to be insoluble in DMSO.

Copolyesters PES-III, PES-IV, PES-V and PES-VI were also soluble in common organic solvents such as DCM, chloroform, tetrahydrofuran and aprotic polar solvents such as NMP, DMAc and were insoluble in DMSO. Homopolyesters derived from BPA with IPC (PES-VII) and TPC (PES-VIII) were insoluble in all the solvents tested. These results indicate that the incorporation of phenyl sulfonyl phenyl pendant groups enhanced the solubility of the homopolyesters and copolyesters. This is due to the disturbance caused by the pendant phenyl sulfonyl phenyl units in dense chain packing of the polymer chains, which in turn, facilitates the penetration of solvent molecules resulting in improved solubility.

Table 6.3: Solubility data of aromatic polyesters containing phenyl sulfonyl phenyl pendant group[a] and reference polyesters based on bisphenol-A.

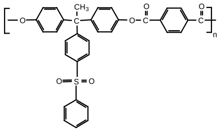
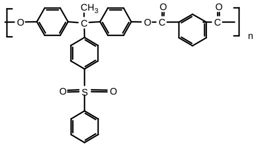
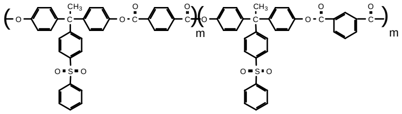
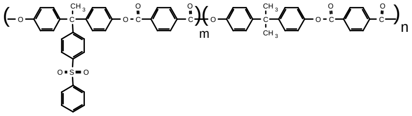
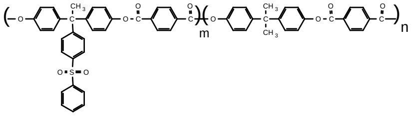
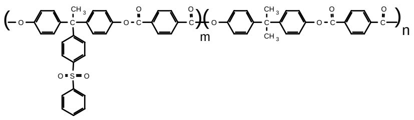
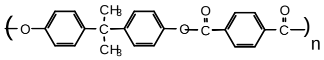
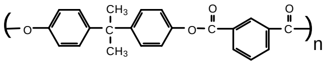
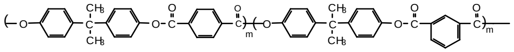
Polyester	$CHCl_3$	DCM	NMP	DMSO	DMAc	Pyridine	m-Cresol	THF
 PES-I (DPSBP : TPC)	++	++	++	-	++	++	++	++
 PES-II (DPSBP : IPC)	++	++	++	-	++	++	++	++
 PES-III (DPSBP and IPC:TPC:: 50:50 mol %)	++	++	++	-	++	++	++	++
 PES-IV (DPSBP : BPA :: 75:25 mol %)	++	++	++	-	++	++	++	++
 PES-V (DPSBP: BPA:: 50:50 mol %)	++	++	++	-	++	++	++	++

Table 6.3: Solubility data of aromatic polyesters containing phenyl sulfonyl phenyl pendant group [a] continued…

Polyester	$CHCl_3$	DCM	NMP	DMSO	DMAc	Pyridine	*m*-Cresol	THF
 PES-VI (DPSBP: BPA :: 25:75 mol %)	++	++	++	-	++	++	++	++
 PES-VII (BPA :TPC)	-	-	-	-	-	-	-	-
 PES-VIII (BPA :IPC)	-	-	-	-	-	-	-	-
 PES-IX (BPA and IPC:TPC:: 50:50 mol %)	++	++	++	-	++	++	++	++

[a] Solubility : ++ soluble at room temperature, - insoluble

6.4.2.2 X-Ray diffraction studies

Wide-angle X-ray diffraction (WAXD) patterns of polyesters showed amorphous halo over 2θ range of 2-40° (Figure 6.7). Introduction of phenyl sulfonyl phenyl pendant group into the polymer backbone hindered the chain packing resulting in amorphous nature of these polyesters, which is also reflected from their enhanced solubility

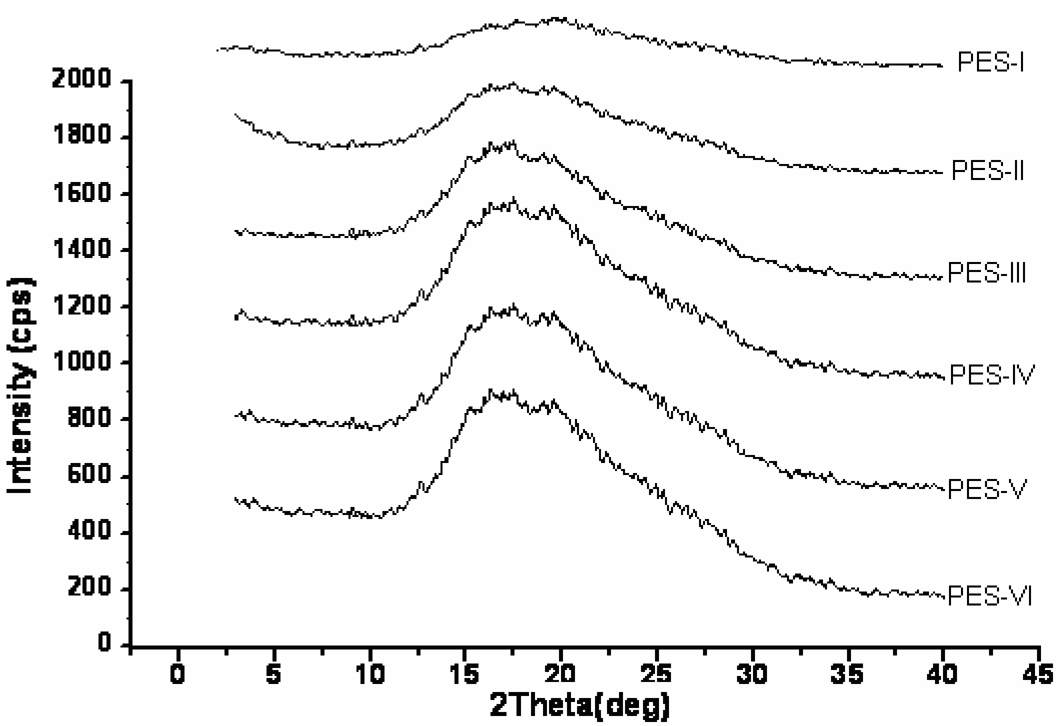


Figure 6.7: X-Ray diffractograms of aromatic polyesters containing phenyl sulfonyl phenyl pendant group.

6.4.2.3 Thermal behavior of polyesters

Thermal stability of polyesters was studied by thermogravimetric analysis (TGA) in nitrogen atmosphere at a heating rate of 20°C/min (Figure 6.8). The initial decomposition temperature (IDT) and the decomposition temperature at 10% weight loss (T_{10}) were calculated from the TG curves and the values are given in **Table 6.4.**

For homopolyesters obtained from terephthaloyl chloride and DPSBP and isophthaloyl chloride and DPSBP, initial decomposition temperature was 475°C and 470°C respectively. Temperature at 10% weight loss (T_{10}) was 484 °C and 477 °C. In case of co-polyesters of DPSBP, BPA and TPC the initial decomposition temperature (IDT) is in the range 468-472°C and temperature at 10% weight loss (T_{10}) is in the range 477- 479 °C indicating their good thermal stability.

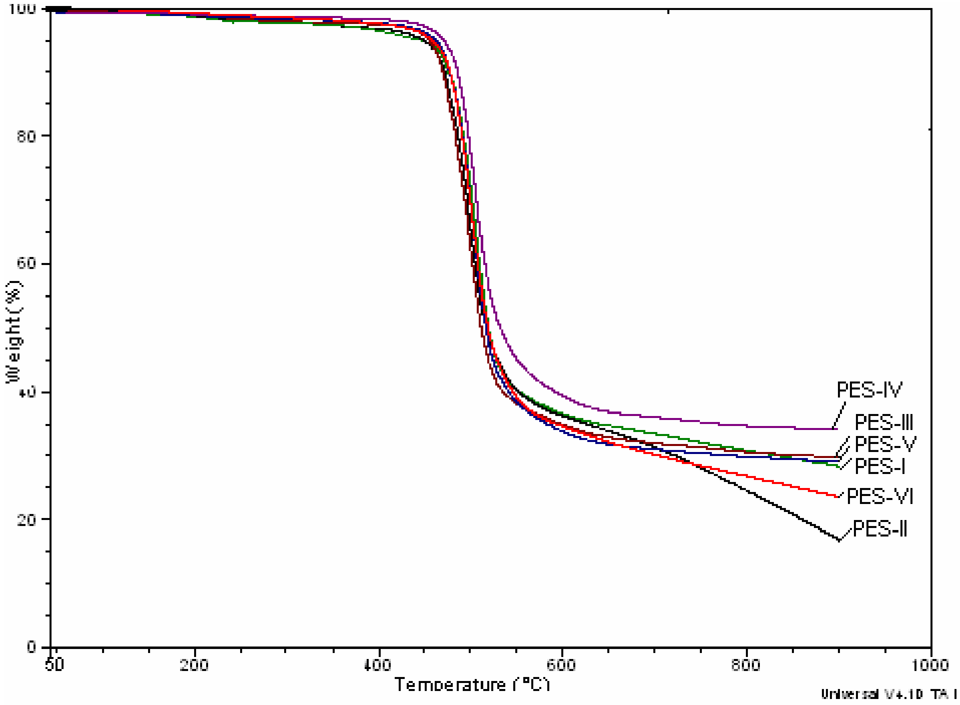
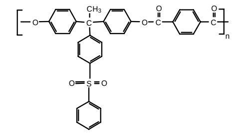
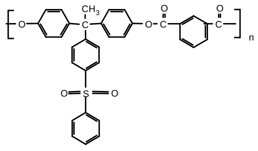
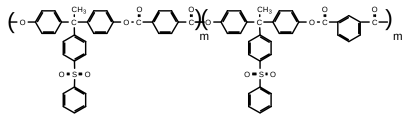
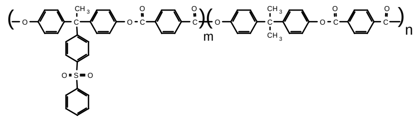
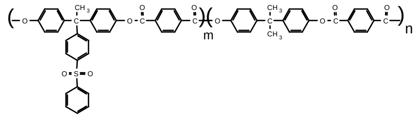
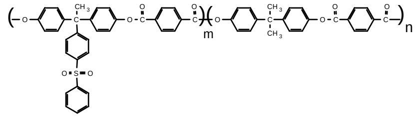
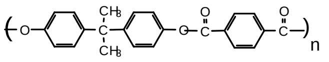
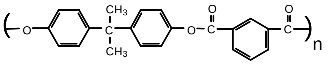
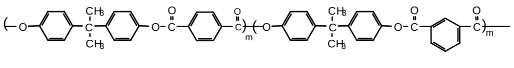


Figure 6.8: TG curves of polyesters and copolyesters containing phenyl sulfonyl phenyl pendant groups

Table 6.4: Thermal properties of aromatic polyesters containing phenyl sulfonyl phenyl pendant group

No.	Polyester	Tg (°C)[a]	IDT (°C)[b]	T_{10} (°C)
1	 PES-I (DPSBP : TPC)	260	475	484
2	 PES-II(DPSBP : IPC)	223	470	477
3	 PES-III (DPSBP and IPC:TPC:: 50:50 mol %)	245	462	469
4	 PES-IV (DPSBP : BPA :: 75:25 mol %)	257	472	477
5	 PES-V (DPSBP: BPA:: 50:50 mol %)	252	471	477
6	 PES-VI (DPSBP: BPA :: 25:75 mol %)	246	468	479
7	 PES-VII (BPA :TPC)	210	487	495
8	 PES-VIII (BPA :IPC)	181	475	490
9	 PES-IX (BPA and IPC:TPC:: 50:50 mol %)	197	491	501

a : Measured on DSC at a heating rate of 20 °C/min.
b : Measured by TGA at a heating rate of 20 °C/min in nitrogen.

Glass transition temperature (Tg) of polyesters was determined by differential scanning calorimetry **(Figure 6.9).** DSC curves of homopolyesters based on DPSBP with TPC and IPC obtained from second heating scan at a heating rate of 20°C / minute showed Tg at 260 °C and 223°C, respectively. The Tg value observed for copolyester obtained from DPSBP with IPC/TPC (50:50 mol%) was 245°C. Copolyesters obtained from DPSBP,BPA and TPC showed Tg values in the range 246°C-257 °C.

Glass transition temperature for homopolyesters of DPSBP and IPC and DPSBP and TPC were higher than those of the corresponding polyesters based on bisphenol A. This behavior is attributed to the presence of phenyl sulfonyl phenyl pendant group in polyesters, which hinders the free rotation of the polymer chain and leads to higher Tg values. In the copolyesters synthesized utilizing different molar proportions of DPSBP and BPA with TPC, Tg values tend to increase as a function of DPSBP.

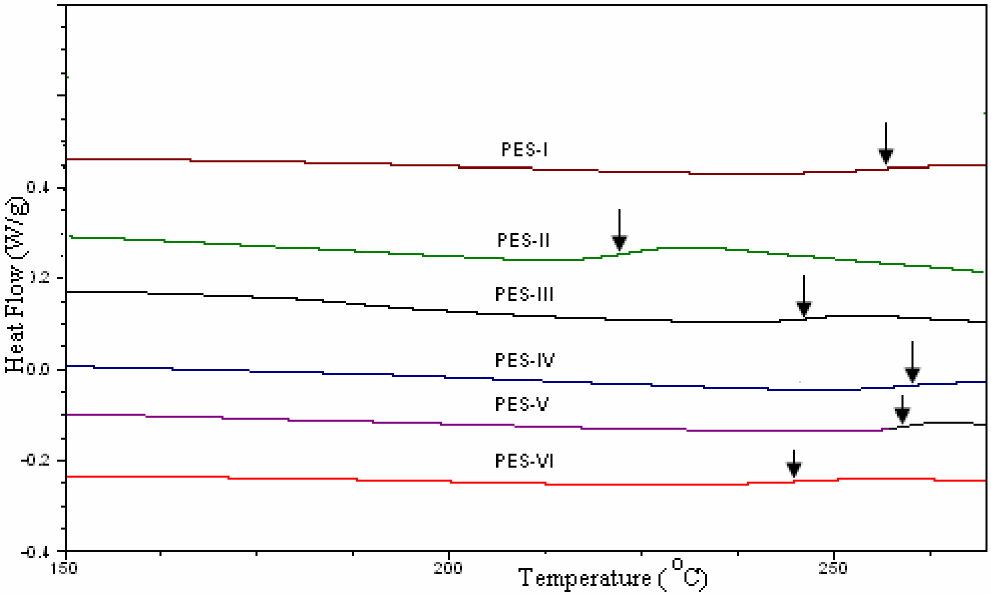


Figure 6.9: DSC curves of polyesters and copolyesters containing phenyl sulfonyl phenyl pendant groups.

6.4.2.4 Mechanical properties

Mechanical properties of polyester samples obtained from DPSBP, BPA and TPC were tested on Instron Universal Tester and the data is given in Table 6.4.

The tensile strength of polyester samples was in the range 40-50 MPa, % elongation was in the range 5-18.3 % and initial modulus was in the range 1.16-1.35 GPa indicating that they are tough and flexible materials. As the proportion of DPSBP increased, % elongations tend to decrease, this can be attributed to the structural rigidity of the monomer DPSBP.

Table 6.4 Mechanical properties of aromatic copolyesters containing phenyl sulfonyl phenyl pendant groups.

Polyester	Composition		Strength at break (MPa)[a]	Elongation at break (%)[a]	Initial Modulus (GPa)
	DPSBP (mol %)	BPA (mol %)			
PES-II	100	0	42 (0.95)	6 (1.49)	1.23
PES-IV	75	25	40 (1.34)	5 (1.22)	1.25
PES-V	50	50	49 (2.50)	13.6 (2.67)	1.35
PES-VI	25	75	50 (2.50)	18.3 (2.60)	1.16

a: Values in the brackets show the standard deviation of the measurement data obtained for five individual samples of each polymer.

6.5 Conclusions

1. Homopolyesters and copolyesters containing phenyl sulfonyl phenyl pendant groups were obtained from 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane and aromatic diacid chlorides by phase transfer catalysed interfacial polycondensation technique.
2. Medium to high molecular weight polyesters and copolyesters with improved solubility in organic solvents such as dichloromethane, chloroform, tetrahydofuran, DMF and DMAc were obtained using DPSBP.
3. Tough, transparent and flexible films could be cast from solutions of homopolyester and copolyesters in chloroform.
4. Wide-angle X-ray diffraction patterns of homopolyesters and copolyesters showed that they were amorphous in nature.
5. Aromatic polyesters derived from DPSBP exhibited glass transition temperature in the range 223^{o}C-257 ^{o}C which were higher than Tg of corresponding polyesters based on bisphenol-A.
6. The IDT and T_{10} values of aromatic polyesters were in the range 462- 491^{o}C and 469-501^{o}C, respectively indicating their good thermal stability.
7. Polyesters containing phenyl sulfonyl phenyl pendant groups showed tensile strength in the range 40-50 MPa , % elongation in the range 5-18.3 % and initial modulus was in the range 1.16-1.35 GPa indicating that they are tough and flexible materials.

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Chapter 7 Summary and Conclusions

The main objectives of the present research were: (1) To design and synthesize difunctional monomers namely bisphenols containing bulky pendant groups / cardo groups and to synthesize diamines and diacids based on these bisphenols, (2) To obtain processable /soluble high performance polymers such as polyimides, polyamides and polyesters starting from these difunctional monomers and (3) To study the gas permeability of selected polyimide films.

The following six bisphenols, four new diamines and two diacids containing bulky pendent groups / cardo groups were synthesized starting from commercially available raw materials.

Bisphenols

1) 1,1-Bis-[4-hydroxyphenyl-1-(2-naphthyl)] ethane (NABP)
2) 1,1-Bis–[4-hydroxyphenyl-(1-biphenyl)] ethane (BBHPE)
3) 1,1-Bis-[4-hydroxyphenyl-1-(4-phenylsulfonylphenyl)] ethane (DPSBP)
4) 1,1-Bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP)
5) 1,1-Bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP)
6) 1,1-Bis-[4-hydroxy-(3,5-dimethyl phenyl)]-4-perhydrocumylcyclohexane (TMPCPBP)

Diamines

1) 1,1-Bis-[4-(4-aminophenoxy) phenyl-1-(2-naphthyl)]ethane (NABPDA),
2) 1,1-Bis-[4-(4-aminophenoxy)phenyl-1-biphenyl] ethane (BBHPDA),
3) 1,1-Bis-[4-(4-aminophenoxy)3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMDA)
4) 1,1-Bis-[4-(4-aminophenoxy) phenyl]-octahydro-2(1H)-naphthalene (DCHDA),

Diacids

1) 1,1-Bis-[4-(4-carboxy phenoxy) phenyl]-4-perhydrocumyl cyclohexane (PCPDA).
2) 1,1-Bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclohexane (TMPCPDA)

All the difunctional monomers and intermediates involved in their synthesis were characterized by spectroscopic techniques. Crystallographic studies were performed in case of monomers/intermediates whose suitable crystals could be obtained.

A detailed investigation of spectral data of three bisphenols viz 1,1-bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP), 1,1-bis-[4-hydroxy-(3,5-dimethylphenyl)]-4-perhydrocumylcyclohexane (TMPCPBP) and 1,1-bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene(DCHBP) showed the presence of disteriotopic phenyl rings, which are magnetically nonequivalent. These bisphenol molecules are not symmetrical about a C2 axis between the two phenyl rings. The two phenyl rings in the molecules do not lie in the same plane, so the axial and equatorial phenyl rings can be differentiated. Crystallographic studies were performed in case of DCHBP to support this observation.

Twenty four new polyimides (PI-Ia to PI-IVf, Chapter 4) were synthesized by polycondensation of diamines containing bulky pendant groups/cardo groups, with commercially available aromatic dianhydrides. Poly (amic acid)s obtained were converted into polyimides by thermal cyclodehydration.

Inherent viscosity of polyimides was in the range 0.40-1.62 dL/g indicating formation of medium to high molecular weight polymers. Except for polyimides based on rigid dianhydrides namely PMDA and BTDA, most of the polyimides were soluble in organic solvents such as DMAc, NMP and m-cresol. Polyimides obtained from TMDA and aromatic dianhydrides showed solubility in aprotic polar solvents like NMP, DMAc as well as in common organic solvents such as chloroform and THF. The presence of perhydrocumyl cyclohexylidene cardo group, arylene ether linkages and substitution of four methyl groups along the backbone improved the solubility of polyimides significantly.

The initial decomposition temperature for polyimides containing bulky pendant groups was in the range 480^{o}C-538 ^{o}C indicating good thermal stability and the glass transition temperature was in the range 246^{o}C -316^{o}C. The initial decomposition temperature for polyimides containing cardo groups was in the range 430^{o}C -502^{o}C, and the glass transition temperature was in the range 244 ^{o}C-313 ^{o}C.

Tough, transparent and flexible films of polyimides could be cast from solutions in chloroform or DMAc. Optical properties of selected polyimide films (~30-40µ thick) were studied by UV –visible spectroscopy. Polyimides showed cutoff wavelength in the range 330-444 nm. The % transmittance was in the range 52-86 %. Diamine TMDA produced fairly transparent and almost colorless films with dianhydrides 6FDA and ODPA.

Wide angle X-ray diffraction analysis of polyimide films showed their amorphous nature.

Mechanical properties of polyimide films based on TMDA and aromatic dianhydrides were tested. Polyimide films possess tensile strength in the range 76-87 MPa, elongation at break in the range 6.02 -11.51 % and initial modulus in the range 1.64 -2.12 GPa indicating that these polyimide films were tough and flexible to be used as strong polymeric materials

Polyimide films obtained from TMDA-6FDA and TMDA-ODPA were examined for gas permeability studies. The replacement of –O- linkage in the dianhydride ODPA (PI-IVa, chapter 4) with –$C(CF_3)_2$- linkage in 6FDA (PI-IV b chapter 4) increased the permeability of various gases by 2 -3 times in magnitude. Though an increase in permeability is expected in 6FDA based polyimide the trend in selectivity is not monotonous. Only helium based selectivities have decreased while other selectivities remained practically similar or slightly increased in case of $\alpha(CO_2/ CH_4)$ (Table 3, chapter 4). Thus, comparatively high permeabilities without sacrificing much of selectivities were obtained , and hence the utility of these polyimides as membrane materials for gas separation was demonstrated.

The dielectric constant of polyimide films obtained from 6FDA and BBHPDA, DCHBPDA and TMDA were determined and were found in the range 3.5122-3.8012. Therefore, the application of these materials in microelectronics and related field are foreseen.

Twenty new polyamides (PA Ia- PA IVe, Chapter 5A) were synthesized starting from four new diamine namely NABPDA, BBHPDA, DCHBPDA and TMDA and commercially available diacids such as isophthalic acid , terephthalic acid, 4,4'-oxybisbenzoic acid, biphenyl-4,4'-dicaboxylic acid, and 4,4'-(hexafluoro isopropylidene) bis (benzoic acid) using phosphorylation polycondensation method .

Inherent viscosity of polyamides was in the range 0.50 -0.82 dL/g indicating formation of medium to high molecular weight polyamides. All polyamides exhibited good solubility in polar aprotic solvents such as DMAc, DMF and NMP. Polyamides obtained from the diamine TMDA were found to be soluble in common organic solvent such as THF at room temperature or upon heating.

The IDT of the polyamides containing bulky pendant groups was in the range 496 °C - 522°C indicating good thermal stability and glass transition temperature was in the range 248°C-278°C. The IDT of the polyamides containing cardo group was in the range 378 °C -506 °C and glass transition temperature was in the range 264°C-301°C.

Tough, transparent and flexible films of polyamides could be cast from solutions in DMAc. The mechanical properties of polyamide films based on the diamines TMDA and BBHPDA were studied. Polyamides based on BBHPDA possess tensile strength in the range 61-75 MPa, % elongations in the range 6-10 % and modulus in the range 1.70-2.17 GPa. Polyamides based on TMDA possess tensile strength in the range 52-62 MPa, % elongations in the range 5-6 % and modulus in the range 1.30-2.10 GPa. indicating their applicability as strong polymeric materials.

1,1-Bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane (PCPDA) was polycondensed with commercially available diamines such as *p*- phenylene diamine, *m*-phenylenediamine and benzidine to obtain three new polyamides with inherent viscosity in the range 0.51-0.55 dL/g. These polyamides were soluble in aprotic polar solvents such as DMAc, DMF and NMP.

Wide angle X-ray diffraction analysis of polyamide films showed their amorphous nature.

Tough and flexible films of these polyamides could be cast using DMAc as solvent. The IDT of polyamides obtained from PCPDA and aromatic diamines was in the range 382°C- 480 °C and the glass transition temperature (Tg) was in range 227-305 °C. Polyamide obtained from the rigid diamine benzidine showed the highest IDT of 480 °C and Tg of 305 °C.

A series of new aromatic polyesters was synthesized from bisphenol 1,1-bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane (DPSBP) and isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) by phase transfer catalysed interfacial polycondensation technique. Since the polyester obtained from bisphenol A (BPA) and TPC is insoluble in common organic solvents, efforts were made to obtain soluble copolyesters by incorporating DPSBP as co-monomer. Copolyesters were synthesized by interfacial polycondensation of BPA with TPC incorporating DPSBP as co-monomer in different proportions. Inherent viscosity of polyesters was in the range

0.56-1.57dL/g indicating formation of medium to high molecular weight polymers. Homo-polyesters and co-polyesters obtained from DPSBP exhibited good solubility in common organic solvents such as DCM, chloroform, THF and in aprotic polar solvents such as DMAc and NMP owing to the presence of bulky phenyl sulfonyl phenyl pendant group.

The IDT of the polyesters and co-polyesters obtained was in the range 462-475^{o}C, and glass transition temperature was in the range 223-260^{o}C.

Tough, transparent and flexible films of these polyesters could be cast using chloroform as solvent. The tensile strength of polyester films was in the range 40-50 MPa, % elongation was in the range 5-18.3 % and initial modulus was in the range 1.16-1.35 GPa indicating their applicability as tough and flexible materials.

Overall, the solubility of polyimides and polyamides in polar organic solvents was obtained by introduction of bulky pendent groups / cardo groups and flexible ether linkages. The incorporation of bulky phenyl sulfonyl phenyl pendant groups, resulted into polyesters and co-polyesters soluble in common organic solvent such as chloroform and dichloromethane. Thus improved solubility without sacrificing the inherent high temperature properties of these polymers make them attractive high performance polymeric materials.

Perspectives

The present work on synthesis of new difunctional monomers starting from commercially available raw materials has expanded the range of condensation monomers available for preparation of a host of high performance polymers, viz. polyethersulfones, polyetherketones, polyamides, polyazomethines, polyhydrazides, polyoxadiazoles, polybenzoxazoles, etc.

Diamines and diacids synthesized in the present work could easily be converted into diisocyanates which by themselves represent valuable monomers for synthesis of polyurethanes, polyureas, etc.

In view of their unique properties, polyimides have found a wide range of applications in advanced technologies. In the last fifty years, hundreds of polyimides of different structures have been studied, but there are still problems to be solved, such as the balance between higher service temperatures and processability and poor solubility of wholly aromatic polyimides. In the past two to three decades a number of fluorine-containing diamines and dianhydrides have been introduced for the preparation of fluorinated polyimides with low water uptake, low refractive indices, and low dielectric constants with many of the advantages of polyimides retained. It would be interesting to synthesize a new series of diamines based on prepared bisphenols by reaction with 2-chloro-5-nitro benzotrifluoride followed by reduction of dinitro intermediates. The ether-bridged aromatic diamines containing bulky pendant /cardo groups and trifluoromethyl groups would represent valuable monomers for synthesis of organo-soluble and light–colored polyimides having lower dielectric constant.

Appendix 1a. Bond distances of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP) in angstrom

Atom 1 Atom2	Distance	Atom 1 Atom 2	Distance
O(1)-C(14)	1.346(11)	C(12)-H(9)	1.02(9)
O(1)-H(1)	1.02(10)	C(2)-C(3)	1.530(13)
C(1)-C(11')	1.524(14)	C(2)-H(2A)	0.9700
C(1)-C(11)	1.543(13)	C(2)-H(2B)	0.9700
C(1)-C(2)	1.547(13)	C(16)-H(7)	0.94(9)
C(1)-C(6)	1.551(13)	C(14')-C(13')	1.380(15)
C(11')-C(12')	1.377(15)	C(14')-C(15')	1.389(15)
C(11')-C(16')	1.384(14)	C(3)-H(3A)	0.9700
C(14)-C(15)	1.348(13)	C(3)-H(3B)	0.9700
C(14)-C(13)	1.427(15)	C(15')-H(15')	0.9300
C(11)-C(12)	1.382(13)	C(13')-C(12')	1.369(14)
C(11)-C(16)	1.408(14)	C(13')-H(13')	0.9300
O(1')-C(14')	1.386(12)	C(10)-C(9)	1.514(17)
O(1')-H(1')	0.8200	C(10)-H(10A)	0.9700
C(15)-C(16)	1.348(13)	C(10)-H(10B)	0.9700
C(15)-H(15)	0.9300	C(6)-H(6A)	0.9700
C(4)-C(5)	1.500(16)	C(6)-H(6B)	0.9700
C(4)-C(3)	1.545(15)	C(7)-C(8)	1.542(16)
C(4)-C(10)	1.545(16)	C(7)-H(7A)	0.9700
C(4)-H(4)	0.90(10)	C(7)-H(7B)	0.9700
C(13)-C(12)	1.372(14)	C(12')-H(12')	0.9300
C(13)-H(3)	0.99(8)	C(9)-C(8)	1.519(17)
C(5)-C(6)	1.533(14)	C(9)-H(9A)	0.9700
C(5)-C(7)	1.538(15)	C(9)-H(9B)	0.9700
C(5)-H(5)	1.00(11)	C(8)-H(8A)	0.9700
C(16')-C(15')	1.373(14)	C(8)-H(8B)	0.9700
C(16')-H(16')	0.9300		

Appendix 1b. **Bond angles of 1,1- bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP) in degree.**

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(14)-O(1)-H(1)	143(6)	C(13)-C(12)-H(9)	118(4)
C(11')-C(1)-C(11)	109.0(8)	C(11)-C(12)-H(9)	118(4)
C(11')-C(1)-C(2)	111.2(8)	C(3)-C(2)-C(1)	113.0(8)
C(11)-C(1)-C(2)	109.4(8)	C(3)-C(2)-H(2A)	109.0
C(11')-C(1)-C(6)	111.9(8)	C(1)-C(2)-H(2A)	109.0
C(11)-C(1)-C(6)	108.5(8)	C(3)-C(2)-H(2B)	109.0
C(2)-C(1)-C(6)	106.8(8)	C(1)-C(2)-H(2B)	109.0
C(12')-C(11')-C(16')	115.0(9)	H(2A)-C(2)-H(2B)	107.8
C(12')-C(11')-C(1)	123.5(9)	C(15)-C(16)-C(11)	120.6(10)
C(16')-C(11')-C(1)	121.4(9)	C(15)-C(16)-H(7)	119(5)
O(1)-C(14)-C(15)	123.9(10)	C(11)-C(16)-H(7)	121(5)
O(1)-C(14)-C(13)	119.9(9)	C(13')-C(14')-O(1')	122.8(10)
C(15)-C(14)-C(13)	116.2(9)	C(13')-C(14')-C(15')	119.3(10)
C(12)-C(11)-C(16)	116.1(9)	O(1')-C(14')-C(15')	117.9(9)
C(12)-C(11)-C(1)	124.1(9)	C(2)-C(3)-C(4)	113.2(9)
C(16)-C(11)-C(1)	119.8(9)	C(2)-C(3)-H(3A)	108.9
C(14')-O(1')-H(1')	109.5	C(4)-C(3)-H(3A)	108.9
C(14)-C(15)-C(16)	124.5(10)	C(2)-C(3)-H(3B)	108.9
C(14)-C(15)-H(15)	117.7	C(4)-C(3)-H(3B)	108.9
C(16)-C(15)-H(15)	117.7	H(3A)-C(3)-H(3B)	107.8
C(5)-C(4)-C(3)	110.7(9)	C(16')-C(15')-C(14')	118.0(10)
C(5)-C(4)-C(10)	112.6(10)	C(16')-C(15')-H(15')	121.0
C(3)-C(4)-C(10)	111.5(9)	C(14')-C(15')-H(15')	121.0
C(5)-C(4)-H(4)	120(7)	C(12')-C(13')-C(14')	120.1(10)
C(3)-C(4)-H(4)	100(7)	C(12')-C(13')-H(13')	120.0
C(10)-C(4)-H(4)	101(7)	C(14')-C(13')-H(13')	120.0
C(12)-C(13)-C(14)	119.7(10)	C(9)-C(10)-C(4)	112.1(10)
C(12)-C(13)-H(3)	123(5)	C(9)-C(10)-H(10A)	109.2
C(14)-C(13)-H(3)	117(5)	C(4)-C(10)-H(10A)	109.2
C(4)-C(5)-C(6)	112.8(9)	C(9)-C(10)-H(10B)	109.2
C(4)-C(5)-C(7)	111.4(10)	C(4)-C(10)-H(10B)	109.2
C(6)-C(5)-C(7)	112.0(9)	H(10A)-C(10)-H(10B)	107.9
C(4)-C(5)-H(5)	105(6)	C(5)-C(6)-C(1)	114.6(8)
C(6)-C(5)-H(5)	109(5)	C(5)-C(6)-H(6A)	108.6
C(7)-C(5)-H(5)	106(6)	C(1)-C(6)-H(6A)	108.6
C(15')-C(16')-C(11')	124.6(10)	C(5)-C(6)-H(6B)	108.6
C(15')-C(16')-H(16')	117.7	C(1)-C(6)-H(6B)	108.6
C(11')-C(16')-H(16')	117.7	H(6A)-C(6)-H(6B)	107.6

Appendix 1b. Continued……..

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(13)-C(12)-C(11)	122.9(10)	C(5)-C(7)-C(8)	111.4(10)
C(5)-C(7)-H(7A)	109.3	C(8)-C(9)-H(9A)	109.5
C(8)-C(7)-H(7A)	109.3	C(10)-C(9)-H(9B)	109.5
C(5)-C(7)-H(7B)	109.3	C(8)-C(9)-H(9B)	109.5
C(8)-C(7)-H(7B)	109.3	H(9A)-C(9)-H(9B)	108.1
H(7A)-C(7)-H(7B)	108.0	C(9)-C(8)-C(7)	111.1(11)
C(13')-C(12')-C(11')	123.0(10)	C(9)-C(8)-H(8A)	109.4
C(13')-C(12')-H(12')	118.5	C(7)-C(8)-H(8A)	109.4
C(11')-C(12')-H(12')	118.5	C(9)-C(8)-H(8B)	109.4
C(10)-C(9)-C(8)	110.6(10)	C(7)-C(8)-H(8B)	109.4
C(10)-C(9)-H(9A)	109.5	H(8A)-C(8)-H(8B)	108.0

Appendix 2a. Bond distances of 1,1-bis[4-(4-cyanophenoxy)phenyl)]-4-per-hydrocumyl cyclo- hexane (DCNPCPBP) in angstrom

Atom 1 Atom2	Distance	Atom 1 Atom 2	Distance
O(1)-C(28)	1.371(2)	C(17)-C(18)	1.388(3)
O(1)-C(10)	1.406(2)	C(17)-H(17)	0.9300
O(2)-C(35)	1.371(2)	C(18)-H(18)	0.9300
O(2)-C(16)	1.400(2)	C(19)-C(21)	1.537(3)
N(1)-C(34)	1.143(3)	C(19)-C(20)	1.538(3)
N(2)-C(41)	1.130(3)	C(19)-C(22)	1.563(3)
C(1)-C(13)	1.540(3)	C(20)-H(20A)	0.9600
C(1)-C(7)	1.543(2)	C(20)-H(20B)	0.9600
C(1)-C(6)	1.545(3)	C(20)-H(20C)	0.9600
C(1)-C(2)	1.546(2)	C(21)-H(21A)	0.9600
C(2)-C(3)	1.529(2)	C(21)-H(21B)	0.9600
C(2)-H(2A)	0.9700	C(21)-H(21C)	0.9600
C(2)-H(2B)	0.9700	C(22)-C(27)	1.523(3)
C(3)-C(4)	1.530(3)	C(22)-C(23)	1.536(3)
C(3)-H(3A)	0.9700	C(22)-H(22)	0.9800
C(3)-H(3B)	0.9700	C(23)-C(24)	1.522(3)
C(4)-C(5)	1.539(2)	C(23)-H(23A)	0.9700
C(4)-C(19)	1.570(2)	C(23)-H(23B)	0.9700
C(4)-H(4)	0.9800	C(24)-H(24A)	0.9700
C(5)-C(6)	1.525(2)	C(24)-H(24B)	0.9700
C(5)-H(5A)	0.9700	C(25)-C(26)	1.505(3)
C(5)-H(5B)	0.9700	C(25)-H(25A)	0.9700
C(6)-H(6A)	0.9700	C(25)-H(25B)	0.9700
C(6)-H(6B)	0.9700	C(26)-C(27)	1.520(3)
C(7)-C(8)	1.386(3)	C(26)-H(26A)	0.9700
C(7)-C(12)	1.385(3)	C(26)-H(26B)	0.9700
C(8)-C(9)	1.387(3)	C(27)-H(27A)	0.9700
C(8)-H(8)	0.9300	C(27)-H(27B)	0.9700
C(9)-C(10)	1.365(3)	C(28)-C(33)	1.372(3)
C(9)-H(9)	0.9300	C(28)-C(29)	1.383(3)
C(10)-C(11)	1.361(3)	C(29)-C(30)	1.372(3)
C(11)-C(12)	1.385(3)	C(29)-H(29)	0.9300
C(11)-H(11)	0.9300	C(30)-C(31)	1.383(3)
C(12)-H(12)	0.9300	C(30)-H(30)	0.9300
C(13)-C(18)	1.385(3)	C(31)-C(32)	1.386(3)
C(13)-C(14)	1.389(3)	C(31)-C(34)	1.437(3)
C(14)-C(15)	1.383(3)	C(32)-C(33)	1.379(3)

Appendix 2a Continued….

Atom 1 Atom2	Distance	Atom 1 Atom 2	Distance
C(14)-H(14)	0.9300	C(32)-H(32)	0.9300
C(15)-C(16)	1.370(3)	C(33)-H(33)	0.9300
C(15)-H(15)	0.9300	C(35)-C(40)	1.379(3)
C(16)-C(17)	1.368(3)	C(35)-C(36)	1.381(3)
C(36)-C(37)	1.368(3)	C(38)-C(41)	1.440(3)
C(36)-H(36)	0.9300	C(39)-C(40)	1.382(3)
C(37)-C(38)	1.383(3)	C(39)-H(39)	0.9300
C(37)-H(37)	0.9300	C(40)-H(40)	0.9300
C(38)-C(39)	1.375(3)		

Appendix 2b. **Bond angles of 1,1-bis[4-(4-cyanophenoxy)phenyl)]-4-per-hydrocumyl cyclohexane (DCNPCPBP) in degree.**

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(28)-O(1)-C(10)	119.54(15)	C(8)-C(7)-C(12)	116.11(17)
C(35)-O(2)-C(16)	119.64(15)	C(8)-C(7)-C(1)	121.16(17)
C(13)-C(1)-C(7)	109.93(14)	C(12)-C(7)-C(1)	122.71(17)
C(13)-C(1)-C(6)	110.64(15)	C(9)-C(8)-C(7)	122.8(2)
C(7)-C(1)-C(6)	110.80(14)	C(9)-C(8)-H(8)	118.6
C(13)-C(1)-C(2)	111.40(14)	C(7)-C(8)-H(8)	118.6
C(7)-C(1)-C(2)	109.09(15)	C(10)-C(9)-C(8)	118.8(2)
C(6)-C(1)-C(2)	104.88(15)	C(10)-C(9)-H(9)	120.6
C(3)-C(2)-C(1)	112.98(15)	C(8)-C(9)-H(9)	120.6
C(3)-C(2)-H(2A)	109.0	C(11)-C(10)-C(9)	120.63(18)
C(1)-C(2)-H(2A)	109.0	C(11)-C(10)-O(1)	120.4(2)
C(3)-C(2)-H(2B)	109.0	C(9)-C(10)-O(1)	118.80(19)
C(1)-C(2)-H(2B)	109.0	C(10)-C(11)-C(12)	119.9(2)
H(2A)-C(2)-H(2B)	107.8	C(10)-C(11)-H(11)	120.0
C(2)-C(3)-C(4)	113.56(15)	C(12)-C(11)-H(11)	120.0
C(2)-C(3)-H(3A)	108.9	C(11)-C(12)-C(7)	121.8(2)
C(4)-C(3)-H(3A)	108.9	C(11)-C(12)-H(12)	119.1
C(2)-C(3)-H(3B)	108.9	C(7)-C(12)-H(12)	119.1
C(4)-C(3)-H(3B)	108.9	C(18)-C(13)-C(14)	116.53(18)
H(3A)-C(3)-H(3B)	107.7	C(18)-C(13)-C(1)	121.90(17)
C(3)-C(4)-C(5)	110.08(15)	C(14)-C(13)-C(1)	121.54(16)
C(3)-C(4)-C(19)	113.39(15)	C(15)-C(14)-C(13)	122.36(18)
C(5)-C(4)-C(19)	113.36(15)	C(15)-C(14)-H(14)	118.8
C(3)-C(4)-H(4)	106.5	C(13)-C(14)-H(14)	118.8
C(5)-C(4)-H(4)	106.5	C(16)-C(15)-C(14)	119.13(19)
C(19)-C(4)-H(4)	106.5	C(16)-C(15)-H(15)	120.4
C(6)-C(5)-C(4)	112.32(15)	C(14)-C(15)-H(15)	120.4
C(6)-C(5)-H(5A)	109.1	C(17)-C(16)-C(15)	120.50(19)
C(4)-C(5)-H(5A)	109.1	C(17)-C(16)-O(2)	121.67(19)
C(6)-C(5)-H(5B)	109.1	C(15)-C(16)-O(2)	117.69(19)
C(4)-C(5)-H(5B)	109.1	C(16)-C(17)-C(18)	119.62(19)
H(5A)-C(5)-H(5B)	107.9	C(16)-C(17)-H(17)	120.2
C(5)-C(6)-C(1)	113.02(14)	C(18)-C(17)-H(17)	120.2
C(5)-C(6)-H(6A)	109.0	C(13)-C(18)-C(17)	121.82(19)
C(1)-C(6)-H(6A)	109.0	C(13)-C(18)-H(18)	119.1
C(5)-C(6)-H(6B)	109.0	C(17)-C(18)-H(18)	119.1
C(1)-C(6)-H(6B)	109.0	C(21)-C(19)-C(20)	108.78(18)

Appendix 2b. Continued…..

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(24)-C(25)-H(25B)	109.6	C(38)-C(39)-C(40)	120.6(2)
H(25A)-C(25)-H(25B)	108.1	C(38)-C(39)-H(39)	119.7
C(25)-C(26)-C(27)	112.3(2)	C(40)-C(39)-H(39)	119.7
C(25)-C(26)-H(26A)	109.1	C(35)-C(40)-C(39)	119.3(2)
C(27)-C(26)-H(26A)	109.1	C(35)-C(40)-H(40)	120.4
C(25)-C(26)-H(26B)	109.1	C(39)-C(40)-H(40)	120.4
C(27)-C(26)-H(26B)	109.1	N(2)-C(41)-C(38)	177.9(3)

Appendix 3a. Bond lengths of 1,1-bis [4-(4-cyanophenoxy)3,5dimethylphenyl)]-4-perhydrocumyl cyclohexane in angstrom.

Atom 1 Atom2	Distance	Atom 1 Atom 2	Distance
O(1)-C(28)	1.374(4)	C(15)-C(16)	1.389(5)
O(1)-C(10)	1.411(4)	C(15)-C(42)	1.509(5)
O(2)-C(35)	1.358(5)	C(16)-C(17)	1.381(5)
O(2)-C(16)	1.405(4)	C(17)-C(18)	1.380(5)
N(1)-C(34)	1.132(6)	C(17)-C(43)	1.532(5)
N(2)-C(41)	1.146(5)	C(18)-H(18)	0.9300
C(1)-C(6)	1.534(5)	C(19)-C(21)	1.534(5)
C(1)-C(7)	1.538(5)	C(19)-C(20)	1.536(5)
C(1)-C(13)	1.544(4)	C(19)-C(22)	1.555(5)
C(1)-C(2)	1.556(4)	C(20)-H(20A)	0.9600
C(2)-C(3)	1.523(5)	C(20)-H(20B)	0.9600
C(2)-H(2A)	0.9700	C(20)-H(20C)	0.9600
C(2)-H(2B)	0.9700	C(21)-H(21A)	0.9600
C(3)-C(4)	1.538(5)	C(21)-H(21B)	0.9600
C(3)-H(3A)	0.9700	C(21)-H(21C)	0.9600
C(3)-H(3B)	0.9700	C(22)-C(27)	1.517(5)
C(4)-C(5)	1.532(5)	C(22)-C(23)	1.539(5)
C(4)-C(19)	1.561(5)	C(22)-H(22)	0.9800
C(4)-H(4)	0.9800	C(23)-C(24)	1.523(6)
C(5)-C(6)	1.526(5)	C(23)-H(23A)	0.9700
C(5)-H(5A)	0.9700	C(23)-H(23B)	0.9700
C(5)-H(5B)	0.9700	C(24)-C(25)	1.497(6)
C(6)-H(6A)	0.9700	C(24)-H(24A)	0.9700
C(6)-H(6B)	0.9700	C(24)-H(24B)	0.9700
C(7)-C(8)	1.386(4)	C(25)-C(26)	1.502(6)
C(7)-C(12)	1.394(5)	C(25)-H(25A)	0.9700
C(8)-C(9)	1.393(5)	C(25)-H(25B)	0.9700
C(8)-H(8)	0.9300	C(26)-C(27)	1.524(5)
C(9)-C(10)	1.375(5)	C(26)-H(26A)	0.9700
C(9)-C(44)	1.522(5)	C(26)-H(26B)	0.9700
C(10)-C(11)	1.380(5)	C(27)-H(27A)	0.9700
C(11)-C(12)	1.385(5)	C(27)-H(27B)	0.9700
C(11)-C(45)	1.511(5)	C(28)-C(29)	1.364(5)
C(12)-H(12)	0.9300	C(28)-C(33)	1.372(5)
C(13)-C(14)	1.389(4)	C(29)-C(30)	1.386(5)
C(13)-C(18)	1.396(5)	C(29)-H(29)	0.9300
C(14)-C(15)	1.390(5)	C(30)-C(31)	1.362(6)
C(14)-H(14)	0.9300	C(30)-H(30)	0.9300

Appendix 3a. Continued…….

Atom 1 Atom2	Distance	Atom 1 Atom 2	Distance
C(31)-C(32)	1.360(6)	C(42)-H(42B)	0.9600
C(31)-C(34)	1.424(7)	C(42)-H(42C)	0.9600
C(32)-C(33)	1.391(5)	C(43)-H(43A)	0.9600
C(32)-H(32)	0.9300	C(43)-H(43B)	0.9600
C(33)-H(33)	0.9300	C(43)-H(43C)	0.9600
C(35)-C(40)	1.358(5)	C(44)-H(44A)	0.9600
C(35)-C(36)	1.379(5)	C(44)-H(44B)	0.9600
C(36)-C(37)	1.368(6)	C(44)-H(44C)	0.9600
C(36)-H(36)	0.9300	C(45)-H(45A)	0.9600
C(37)-C(38)	1.370(6)	C(45)-H(45B)	0.9600
C(37)-H(37)	0.9300	C(45)-H(45C)	0.9600
C(38)-C(39)	1.370(5)	O(3)-C(46)	1.18(4)
C(38)-C(41)	1.434(6)	O(3)-C(46)#1	1.68(5)
C(39)-C(40)	1.393(5)	C(46)-C(46)#1	1.61(9)
C(39)-H(39)	0.9300	C(46)-O(3)#1	1.68(5)
C(40)-H(40)	0.9300	O(3')-C(46')	1.20(3)
C(42)-H(42A)	0.9600	#1 -x+1,-y,-z+1	

Appendix 3b. Bond angles of 1,1-bis [4-(4-cyanophenoxy) 3,5dimethylphenyl)]-4-per-hydrocumyl cyclohexane in degree.

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(28)-O(1)-C(10)	119.2(3)	C(1)-C(6)-H(6A)	109.0
C(35)-O(2)-C(16)	119.6(3)	C(5)-C(6)-H(6B)	109.0
C(6)-C(1)-C(7)	112.5(3)	C(1)-C(6)-H(6B)	109.0
C(6)-C(1)-C(13)	110.1(3)	H(6A)-C(6)-H(6B)	107.8
C(7)-C(1)-C(13)	107.5(3)	C(8)-C(7)-C(12)	116.7(4)
C(6)-C(1)-C(2)	106.5(3)	C(8)-C(7)-C(1)	123.9(3)
C(7)-C(1)-C(2)	107.3(3)	C(12)-C(7)-C(1)	119.4(3)
C(13)-C(1)-C(2)	113.0(3)	C(7)-C(8)-C(9)	122.3(4)
C(3)-C(2)-C(1)	115.4(3)	C(7)-C(8)-H(8)	118.9
C(3)-C(2)-H(2A)	108.4	C(9)-C(8)-H(8)	118.9
C(1)-C(2)-H(2A)	108.4	C(10)-C(9)-C(8)	117.8(4)
C(3)-C(2)-H(2B)	108.4	C(10)-C(9)-C(44)	121.2(4)
C(1)-C(2)-H(2B)	108.4	C(8)-C(9)-C(44)	121.0(4)
H(2A)-C(2)-H(2B)	107.5	C(9)-C(10)-C(11)	123.1(4)
C(2)-C(3)-C(4)	112.1(3)	C(9)-C(10)-O(1)	117.9(4)
C(2)-C(3)-H(3A)	109.2	C(11)-C(10)-O(1)	118.7(4)
C(4)-C(3)-H(3A)	109.2	C(10)-C(11)-C(12)	116.8(4)
C(2)-C(3)-H(3B)	109.2	C(10)-C(11)-C(45)	121.2(4)
C(4)-C(3)-H(3B)	109.2	C(12)-C(11)-C(45)	122.0(4)
H(3A)-C(3)-H(3B)	107.9	C(11)-C(12)-C(7)	123.3(3)
C(5)-C(4)-C(3)	105.9(3)	C(11)-C(12)-H(12)	118.3
C(5)-C(4)-C(19)	116.9(3)	C(7)-C(12)-H(12)	118.3
C(3)-C(4)-C(19)	114.8(3)	C(14)-C(13)-C(18)	116.4(3)
C(5)-C(4)-H(4)	106.2	C(14)-C(13)-C(1)	123.9(3)
C(3)-C(4)-H(4)	106.2	C(18)-C(13)-C(1)	119.6(3)
C(19)-C(4)-H(4)	106.2	C(13)-C(14)-C(15)	123.2(3)
C(6)-C(5)-C(4)	110.7(3)	C(13)-C(14)-H(14)	118.4
C(6)-C(5)-H(5A)	109.5	C(15)-C(14)-H(14)	118.4
C(4)-C(5)-H(5A)	109.5	C(16)-C(15)-C(14)	117.2(3)
C(6)-C(5)-H(5B)	109.5	C(16)-C(15)-C(42)	121.1(4)
C(4)-C(5)-H(5B)	109.5	C(14)-C(15)-C(42)	121.7(4)
H(5A)-C(5)-H(5B)	108.1	C(17)-C(16)-C(15)	122.3(3)
C(5)-C(6)-C(1)	113.1(3)	C(17)-C(16)-O(2)	118.4(4)
C(5)-C(6)-H(6A)	109.0	C(15)-C(16)-O(2)	119.0(4)
C(18)-C(17)-C(16)	118.0(4)	C(24)-C(25)-H(25B)	109.6
C(18)-C(17)-C(43)	121.1(4)	C(26)-C(25)-H(25B)	109.6
C(16)-C(17)-C(43)	120.9(4)	H(25A)-C(25)-H(25B)	108.1
C(17)-C(18)-C(13)	122.9(4)	C(25)-C(26)-C(27)	111.5(4)

Appendix 3b. continued…..

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(17)-C(18)-H(18)	118.6	C(25)-C(26)-H(26A)	109.3
C(13)-C(18)-H(18)	118.6	C(27)-C(26)-H(26A)	109.3
C(21)-C(19)-C(20)	108.3(3)	C(25)-C(26)-H(26B)	109.3
C(21)-C(19)-C(22)	109.6(3)	C(27)-C(26)-H(26B)	109.3
C(20)-C(19)-C(22)	109.7(3)	H(26A)-C(26)-H(26B)	108.0
C(21)-C(19)-C(4)	110.4(3)	C(22)-C(27)-C(26)	113.3(4)
C(20)-C(19)-C(4)	108.4(3)	C(22)-C(27)-H(27A)	108.9
C(22)-C(19)-C(4)	110.5(3)	C(26)-C(27)-H(27A)	108.9
C(19)-C(20)-H(20A)	109.5	C(22)-C(27)-H(27B)	108.9
C(19)-C(20)-H(20B)	109.5	C(26)-C(27)-H(27B)	108.9
H(20A)-C(20)-H(20B)	109.5	H(27A)-C(27)-H(27B)	107.7
C(19)-C(20)-H(20C)	109.5	C(29)-C(28)-C(33)	120.4(4)
H(20A)-C(20)-H(20C)	109.5	C(29)-C(28)-O(1)	124.1(4)
H(20B)-C(20)-H(20C)	109.5	C(33)-C(28)-O(1)	115.5(4)
C(19)-C(21)-H(21A)	109.5	C(28)-C(29)-C(30)	119.3(4)
C(19)-C(21)-H(21B)	109.5	C(28)-C(29)-H(29)	120.3
H(21A)-C(21)-H(21B)	109.5	C(30)-C(29)-H(29)	120.3
C(19)-C(21)-H(21C)	109.5	C(31)-C(30)-C(29)	120.8(4)
H(21A)-C(21)-H(21C)	109.5	C(31)-C(30)-H(30)	119.6
H(21B)-C(21)-H(21C)	109.5	C(29)-C(30)-H(30)	119.6
C(27)-C(22)-C(23)	108.5(4)	C(32)-C(31)-C(30)	119.7(4)
C(27)-C(22)-C(19)	115.3(3)	C(32)-C(31)-C(34)	118.9(6)
C(23)-C(22)-C(19)	114.0(4)	C(30)-C(31)-C(34)	121.4(5)
C(27)-C(22)-H(22)	106.1	C(31)-C(32)-C(33)	120.3(5)
C(23)-C(22)-H(22)	106.1	C(31)-C(32)-H(32)	119.8
C(19)-C(22)-H(22)	106.1	C(33)-C(32)-H(32)	119.8
C(24)-C(23)-C(22)	111.7(4)	C(28)-C(33)-C(32)	119.4(4)
C(24)-C(23)-H(23A)	109.3	C(28)-C(33)-H(33)	120.3
C(22)-C(23)-H(23A)	109.3	C(32)-C(33)-H(33)	120.3
C(24)-C(23)-H(23B)	109.3	N(1)-C(34)-C(31)	178.8(7)
C(22)-C(23)-H(23B)	109.3	C(40)-C(35)-O(2)	124.6(4)
H(23A)-C(23)-H(23B)	107.9	C(40)-C(35)-C(36)	120.5(4)
C(25)-C(24)-C(23)	111.9(4)	O(2)-C(35)-C(36)	114.9(4)
C(25)-C(24)-H(24A)	109.2	C(37)-C(36)-C(35)	119.7(5)
C(23)-C(24)-H(24A)	109.2	C(37)-C(36)-H(36)	120.2
C(25)-C(24)-H(24B)	109.2	C(35)-C(36)-H(36)	120.2
C(23)-C(24)-H(24B)	109.2	C(36)-C(37)-C(38)	120.6(4)
H(24A)-C(24)-H(24B)	107.9	C(36)-C(37)-H(37)	119.7

Appendix 3b. continued…..

Atoms 1 2 3	Angle	Atoms 1 2 3	Angle
C(24)-C(25)-C(26)	110.1(4)	C(38)-C(37)-H(37)	119.7
C(24)-C(25)-H(25A)	109.6	C(39)-C(38)-C(37)	119.7(4)
C(26)-C(25)-H(25A)	109.6	C(39)-C(38)-C(41)	120.6(5)
C(37)-C(38)-C(41)	119.7(5)	H(42B)-C(42)-H(42C)	109.5
C(38)-C(39)-C(40)	119.9(5)	C(17)-C(43)-H(43A)	109.5
C(38)-C(39)-H(39)	120.0	C(17)-C(43)-H(43B)	109.5
C(40)-C(39)-H(39)	120.0	H(43A)-C(43)-H(43B)	109.5
C(35)-C(40)-C(39)	119.6(4)	C(17)-C(43)-H(43C)	109.5
C(35)-C(40)-H(40)	120.2	H(43A)-C(43)-H(43C)	109.5
C(39)-C(40)-H(40)	120.2	H(43B)-C(43)-H(43C)	109.5
N(2)-C(41)-C(38)	178.1(6)	C(9)-C(44)-H(44A)	109.5
C(15)-C(42)-H(42A)	109.5	C(9)-C(44)-H(44B)	109.5
C(15)-C(42)-H(42B)	109.5	H(44A)-C(44)-H(44B)	109.5
H(42A)-C(42)-H(42B)	109.5	C(9)-C(44)-H(44C)	109.5
C(38)-C(39)-C(40)	119.9(5)	H(44A)-C(44)-H(44C)	109.5
C(38)-C(39)-H(39)	120.0	C(11)-C(45)-H(45B)	109.5
C(40)-C(39)-H(39)	120.0	H(45A)-C(45)-H(45B)	109.5
C(35)-C(40)-C(39)	119.6(4)	C(11)-C(45)-H(45C)	109.5
C(35)-C(40)-H(40)	120.2	H(45A)-C(45)-H(45C)	109.5
C(39)-C(40)-H(40)	120.2	H(45B)-C(45)-H(45C)	109.5
N(2)-C(41)-C(38)	178.1(6)	C(46)-O(3)-C(46)#1	66(3)
C(15)-C(42)-H(42A)	109.5	O(3)-C(46)-C(46)#1	72(3)
C(15)-C(42)-H(42B)	109.5	O(3)-C(46)-O(3)#1	114(3)
H(42A)-C(42)-H(42B)	109.5	C(46)#1-C(46)-O(3)#1	42(3)
C(15)-C(42)-H(42C)	109.5	#1 -x+1-y-z+1	
H(42A)-C(42)-H(42C)	109.5		

Synopsis of the Thesis Entitled
"Processable High Performance Polymers:
Synthesis, Characterization and Application"

Introduction

Polyimides, polyamides and polyesters are important classes of high performance Polymers.[1-10] Properties of these polymers, such as, excellent thermal stability over a wide temperature range, superior mechanical strength and chemical resistance led to their uses in many applications in advanced technologies. For instance, these polymers find applications as insulating materials for microelectronics, as semipermeable membranes for gas separations, and, as high temperature adhesives and coatings, etc.

These high performance polymers possess molecular symmetry, high polarity and strong interchain interactions which results in high thermal stability thus making them suitable for above applications. On the other hand, these features also shift the glass transition temperature above the decomposition temperature, and make them virtually insoluble in common organic solvents which causes difficulties in processing. [2]

Several approaches have been suggested to improve processability / solubility of high performance polymers. These include:

1) Insertion of flexible spacer chains like - $(CH_2)_n$ - or flexible groups like - O -, - S -, - COO - to enhance the chain flexibility,
2) Introduction of 1,3-disubstituted (*m*-catenated) monomers instead of 1,4-disubstituted monomers which disrupts the molecular symmetry,
3) Incorporation of bulky pendent groups or flexible side chains into the polymer backbone.

Thus, structural modifications that disrupt the molecular symmetry inhibit close packing of the chains and increase the free volume consequently leading to improved solubility and processability. In recent years, much efforts have been focused on modified monomers, which contain flexibilizing groups, or bulky pendent groups.[11-14] Introduction of "cardo" groups (pendent loops) is also a promising approach towards the enhancement of polymer properties.[15] Cardo groups contribute to obtain a valuable combination of properties like enhanced solubility in organic solvents without sacrificing thermal stability. Cardo groups may contain aromatic[16] or alicyclic[19] rings. The cardo groups, viz., cycloalkyl, norbornyl, adamantly, etc., have been studied in the literature.[17] Cardo groups also are known to lower dielectric constant,[20] impart lighter colour, exhibit better gas barrier properties[18] as well as improve solubility.

The approach adapted in the present work was to synthesize difunctional monomers such as bisphenols, diamines and diacids containing bulky pendent groups or cardo groups.

The goal of the present investigation was to design and synthesize various difunctional monomers starting from cheap, commercially available raw materials *via* relatively inexpensive chemical routes. The difunctional monomers were to be utilized for the synthesis of polyetherimides, polyetheramides and polyesters with improved processability / solubility characteristics. Considering the above mentioned targets, the following specific work was chosen for the thesis

- Synthesis of bisphenols and diamines containing aromatic pendent groups, viz., biphenyl, naphthyl, or phenylsulfonylphenyl groups.
- Synthesis of bisphenols and diamines containing alicyclic pendent groups, viz., 4-perhydrocumylcyclohexylidene or octahydro-2(1H)- naphthylidene groups.
- Synthesis of diacids containing alicyclic pendent groups, viz., 4-perhydrocumyl cyclohexylidene group.
- Synthesis and characterization of high performance polymers such as polyetherimides, polyetheramides and polyesters containing aromatic pendent groups or alicyclic pendent (cardo) groups.
- To study the effect of bulky pendent groups or cardo groups on the solubility and thermal properties of polyetherimides, polyetheramides and polyesters.
- To evaluate selected few polymers as membrane materials for gas separation studies.

The thesis has been divided into the following seven chapters.

Chapter 1. Introduction

A brief review of literature on high performance polymers such as polyimides, polyamides, and polyesters, covering methods of synthesis, structure-property relationship and typical applications is presented.

Chapter 2. Scope and objectives

Scope and objectives of the present work are described in this chapter.

Chapter 3. Synthesis and characterization of difunctional monomers

This chapter deals with

A. Synthesis of bisphenols (Table 1: entries 1, 2 and 3) and diamines (Table 2: entries 1 and 2) containing bulky pendent groups, namely,

- 1,1-Bis-[{4-hydroxyphenyl-1-(2-naphthyl)}]ethane (NABP),
- 1,1-Bis-[(4-hydroxyphenyl)-1-(4-phenylsulfonylphenyl)]ethane (DPSBP),
- 1,1-Bis–[{4-hydroxyphenyl}-1-biphenyl] ethane (BBHPE),
- 1,1-Bis–[4-{(4-aminophenoxy)phenyl}-1-biphenyl]ethane (BBHPDA),
- 1,1-Bis-[4-{(4-aminophenoxy)phenyl}-1-(2-naphthyl)] ethane (NABPDA).

B. Synthesis of bisphenols (Table 1: entries 4, 5 and 6) and diamines (Table 2: entries 3 and 4) containing cardo groups, namely,

- 1,1-Bis-{4-hydroxy-(3,5-dimethylphenyl)}-4-perhydrocumylcyclohexane (TMPCPBP),
- 1,1–Bis-(4-hydroxyphenyl)-4-perhydrocumylcyclohexane (PCPBP),
- 1,1-Bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (DCHBP),
- 1,1-Bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydrocumylcyclo- hexane (TMDA),
- 1,1-Bis-{4-(4-aminophenoxy)phenyl}octahydro-2(1H)-naphthalene (DCHDA).

C. Synthesis of diacids (Table 3: entries 1 and 2) namely,

- 1,1-Bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane (TMPCPDA),
- 1,1–Bis-[4-(4-carboxyphenoxy)phenyl]-4-perhydrocumylcyclohexane (PCPDA).

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

Chapter 4. Synthesis and characterization of polyetherimides (PEIs)

This chapter deals with synthesis of polyetherimides based on new diamines containing aromatic pendent group, namely, BBHPDA and NABPDA and new diamines containing cardo groups, namely, TMDA and DCHDA with commercially available dianhydrides, viz., oxydiphthalic anhydride (ODA), 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), and 3,3'4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA). Selected polyetherimides were evaluated as membrane materials for gas separation studies.

Chapter 5A. Synthesis and characterization of polyetheramides (PEAs)

Synthesis and characterization of polyetheramides starting from new diamines, namely, BBHPDA, NABPDA, TMDA, DCHDA and commercially available diacids, viz., isophthalic acid, terephthalic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-(hexafluoroisopropylidene)diphthalic acid and 4,4'-oxybisbenzoic acid is described in this chapter.

Chapter 5B. Synthesis and characterization of polyetheramides based on new diacid

This chapter deals with synthesis of polyetheramides starting from new diacids, namely, TMPCPDA, and PCPDA and commercially available diamines, namely, 1,3-phenylenediamine, 1,4-phenylenediamine and benzidine.

Chapter 6. Synthesis and characterization of polyesters

This chapter describes synthesis and characterization of polyesters and co-polyesters starting from bisphenol DPSBP and aromatic diacid chlorides, viz., isophthaloyl chloride acid and terephthaloyl chloride.

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

Chapter 7. Summary and Conclusions

This chapter summarizes results and salient conclusions of investigations presented in the thesis.

Table 1: Synthesized Bisphenols

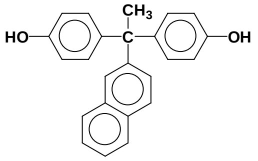
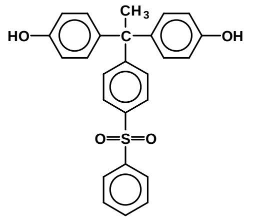
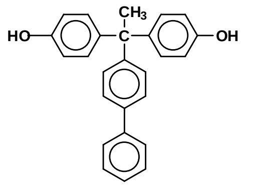
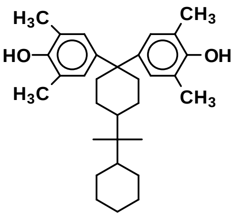
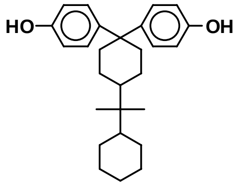
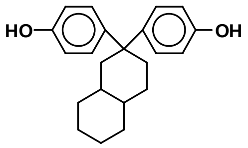
1.	1,1-Bis-[{4-hydroxyphenyl}-1-(2-naphthyl)]ethane **(NABP)**	
2.	1,1-Bis-[{(4-hydroxyphenyl)-1-4-phenylsulphonyl phenyl}]ethane (**DPSBP**)	
3.	1,1-Bis–[{4-hydroxyphenyl}-1-biphenyl]ethane (**BBHPE**)	
4.	1,1-Bis-{4-hydroxy-(3,5-dimethylphenyl)}-4-perhydrocumylcyclohexane (**TMPCPBP**)	
5.	1,1–Bis-(4-hydroxyphenyl)-4-perhydrocumyl cyclohexane (**PCPBP**)	
6.	1,1-Bis-(4-hydroxyphenyl)octahydro-2(1H)-naphthalene (**DCHBP**)	

Table 2: Synthesized Diamines

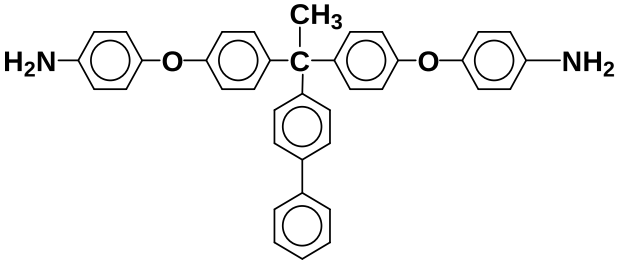
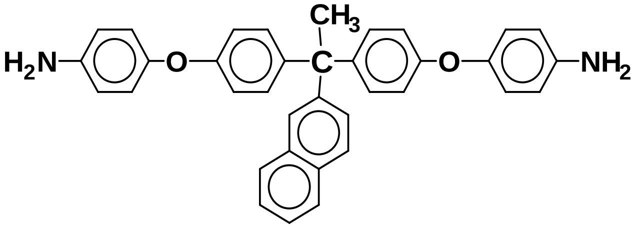
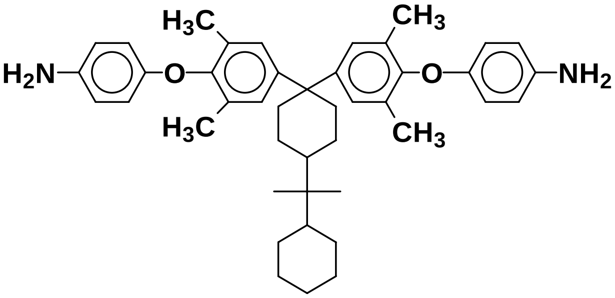
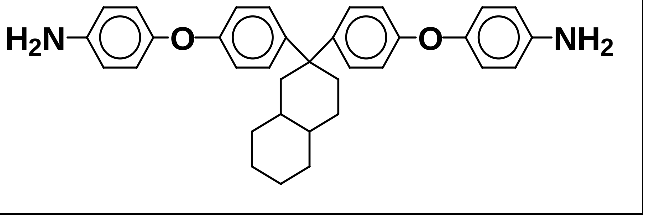
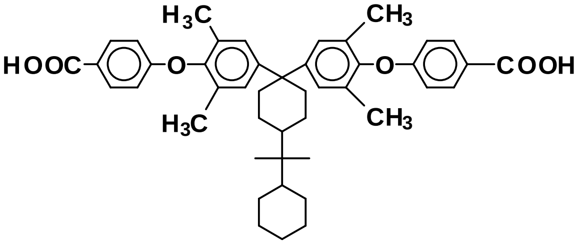
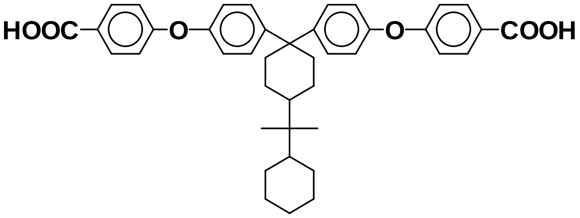
1.	1,1-Bis–[4-(4-aminophenoxy) phenyl]-1-biphenyl ethane **(BBHPDA)**	
2.	1,1-Bis-{(4-aminophenoxy) phenyl}-1-(2-naphthyl)ethane **(NABPDA)**	
3.	1,1-Bis-[4-(4-aminophenoxy)-3,5-dimethylphenyl]-4-perhydro cumylcyclohexane **(TMDA)**	
4.	1,1-Bis-[4-(4-aminophenoxy) phenyl]octahydro-2(1H)-naphthalene **(DCHDA)**	

Table 3: Synthesized Diacids

1.	1,1-Bis-[4-(4-carboxyphenoxy)-3,5-dimethylphenyl]-4-perhydrocumyl cyclohexane (**TMPCPDA**)	
2.	1,1–Bis-[4-(4-carboxyphenoxy) phenyl]-4-perhydrocumylcyclohexane **(PCPDA)**	

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Student Research Guide

List of Publications

1. Synthesis and Characterization of New Organosoluble Poly(ether-imide)s Derived from 1,1-Bis [4-{4-aminophenoxy}3,5 –dimethyl phenyl]-4-perhydrocumyl cyclohexane and Aromatic Dianhydriedes."
   Snehalata P. Bapat, Rahul D. Shingte, Prakash P. Wadgaonkar*, Oral presentation, presented at national symposium MACRO-2004 held at Trivandrum (Kerala)

2. Synthesis and Characterization of New Organosoluble Poly (ether-amide)s Derived from 1,1-Bis [4-{4-carboxy phenoxy}3,5–dimethyl phenyl]-4-perhydrocumyl cyclohexane and Aromatic Diamines."
   Snehalata P. Bapat and Prakash P. Wadgaonkar
   Poster presented at national symposium MACRO-2006 held at NCL, Pune (Maharashtra)

3. "Synthesis and Characterization of New Organosoluble Poly(etherimide)s Derived from 1,1-Bis [4-{4-aminophenoxy}3,5 –dimethyl phenyl]-4-perhydrocumyl cyclohexane and Aromatic Dianhydriedes."
   Snehalata P. Bapat, Rahul D. Shingte, Prakash P. Wadgaonkar* communicated.