NOVEL THERMALLY STABLE POLYMERS FROM A RENEWABLE RESOURCE (CASHEW NUT SHELL LIQUID): SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

A thesis submitted to the

UNIVERSITY OF PUNE

for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

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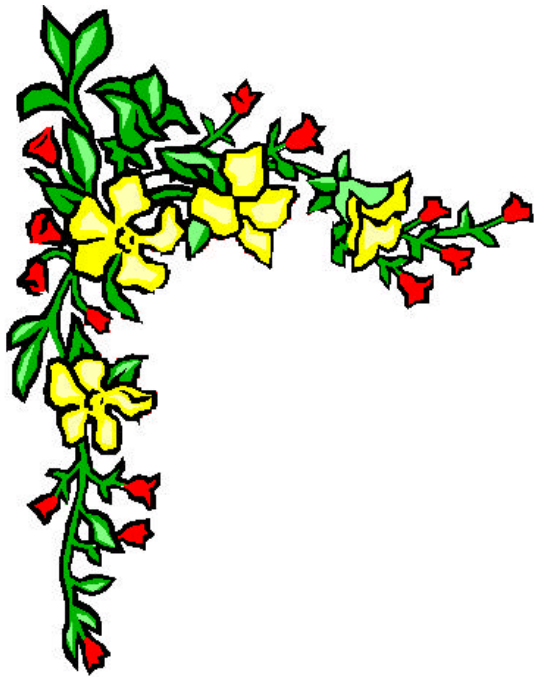*India*

July 2001

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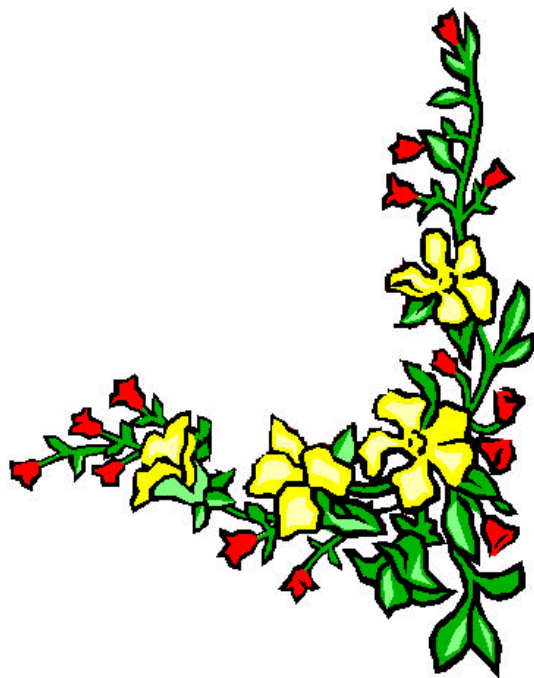
July, 2001   **Dr. S. P. Vernekar**

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Dedicated to Pappa and Mummy

ACKNOWLEDGEMENT

July 2001

Pune   **Jinu S. Mathew**

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Chapter 2   **Synthesis and Characterization of Monomers**

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<u>Abstract</u>

This work is a part of the ongoing program concerning the utilization of cashew nut shell liquid for the synthesis of polymers having specialty applications.

Cashew nut shell liquid, an agricultural byproduct abundantly available in the country, holds considerable promise as a source of unsaturated hydrocarbon phenol, an excellent monomer for polymer production. Cardanol, the major constituent of cashew nut shell liquid and a potential natural source for biomonomers, cannot even today be said to have found its niche in terms of an appropriate industrial application. The unique structural feature that makes cardanol an interesting monomer is the presence of a long alkyl group in the meta position. Alkyl groups are known to improve the solubility alignment properties, dielectric properties and gas permeability properties of polymers. Aromatic polyamides and polyimides are thermally stable polymers having a wide range of applications but are generally difficult to process due to low solubility. Therefore the main focus of this work was the synthesis of futuristic products like polyimides and polyamides with improved solubility from cardanol having specialty applications, as alignment layers for liquid crystal display devices, low dielectric materials for use in electronics industry and as gas separation membranes.

In *Chapter* 1, a detailed review on the use of cardanol, (a constituent of cashewnut shell liquid) in the production of specialty and high value polymers is presented. A detailed literature review on the synthesis of polyamides and polyimides, their structure-property relationships and applications is also presented here. The main emphasis is given on the various approaches used for the synthesis of processable polyamides and polyimides and the scope of the thesis is justified.

Chapter 2 presents a detailed study on the synthesis of three different dinitro compounds and the corresponding diamino compounds from cashewnut shell liquid, that are useful monomers in the synthesis of processable polyamides and polyimides The three diamines synthesized were (1) 4-(3-pentadecylphenoxy)benzene-1,3-diamine (2) 3-pentadecylphenyl-3,5-diaminobenzoate (3) 3,5-diamino-N-(4-(3-pentadecylphenoxy) phenyl)benzamide. The diamines were characterized using NMR, IR and elemental analysis. A silicon containing dianhydride bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and a silicon containing diacid chloride, bis(4-

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chlorocarbonylphenyl)dimethylsilane was also synthesized in good yields and purity and characterized.

    Chapter 3 presents a detailed study on the synthesis of polyamides from the substituted m-phenylene diamines mentioned in Chapter 2. New series of polyamides having pendant pentadecylphenoxy, pentadecylbenzoate and pentadecyphenoxybenzamide groups were synthesized from substituted m-phenylene diamines namely (1) 4-(3-pentadecylphenynoxy) benzene-1,3-diamine (PPDBN) (2) 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT) and (3) 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (PPPB) by low temperature interfacial polycondensation. The polyamides were characterized by IR spectroscopy, inherent viscosity, solubility tests, X-ray diffraction studies, differential scanning calorimetry and thermogravimetric analysis. Incorporation of pendant alkyl groups improved the solubility of polyamides without affecting the thermal stability significantly. The solubility was found to be dependent on the nature of pendant groups and the polyamides having pentadecylbenzoate groups exhibited the highest solubility. The polyamides based on silicon containing diacid chloride, DMSC showed higher solubility than those based on terephthaloyl and isophthaloyl chlorides. Pendant pentadecyphenoxybenzamide and pentadecylbenzoate groups did not have much effect on the $T_{g,}$, however the (T_g) was lowered by the incorporation of silicon and pentadecylphenoxy group. The incorporation of alkyl groups and silicon improved the permeability without affecting the permselectivity significantly. The silicon containing polyamides showed good permeability towards gases like N_2, O_2, H_2 and CO_2. The polyamide containing silicon and pentadecyl benzoate group showed good selectivity for the separation of gases like O_2 and N_2 and thus seemed to be a promising gas separation membrane.

    Chapter 4 presents a detailed study on the synthesis of polyimides from the substituted m-phenylene diamines and different dianhydrides like PMDA, BPDA, BTDA, ODPA, 6-FDA and SiDA. The effect of variation of dianhydrides on the different properties like crystallinity, solubility, glass transition temperature, thermal stability and optical transparency was investigated. Several copolyimides were also synthesized by incorporating different ratios of PPDBN in some commercially important ODA containing polyimides, to find out the effect of varying ratios of alkyl group on the

properties of these ODA containing polyimides. Some copolyimides containing 50% SiDA and 50 % other dianhydrides with diamine PPDBN were also synthesized to study the effect of incorporation of silicon on the solubility. The possible application of these homo and copolyimides as gas separation membranes, alignment layers for liquid crystal display devices, as interlayer dielectrics with low dielectric constant and as coating materials for TEM grids was also explored.

It was observed that the incorporation of alkyl group improved the solubility of homo and copolyimides without affecting the thermal stability significantly. Polyimides synthesized from flexible dianhydrides like ODPA, 6-FDA and SiDA and the diamines containing bulky pendant groups show higher solubility than those synthesized from rigid dianhydrides like PMDA, BPDA and BTDA indicating that bulky pendant groups do not improve the solubility of polyimides synthesized from rigid dianhydrides and rigid diamines significantly. The thermal stability and glass transition temperatures were dependent on both the monomers. The introduction of alkyl groups decreased the glass transition temperatures to some extent. Homo and copolyimides based on these silicon containing monomers showed improved solubility, whereas the thermal stability and T_g decreased to some extent. All homo and copolyimides incorporating pendant bulky groups and silicon showed good optical transparency. The pretilt angle of the polyimides was found to be dependent on the electronic and steric interactions between the polymer chain and liquid crystals. The polyimide PI-1d having high solubility, good adhesion, good pretilt angle and high optical transparency seemed to be a potential alignment layer for liquid crystal display devices. Incorporation of pendent bulky groups and silicon improved the gas permeability properties of these homo and copolyimides. These polyimides had low dielectric constant and were found to have potential application as coating materials for transmission electron microscopy grids.

Glossary

BPDA	3,3',4,4'-bipenyl tetracarboxylicacid dianhydride
BTDA	3,3',4,4'-benzophenonetetracarboxylicacid dianhydride
DMAc	N,N-dimethyl acetamide
DMF	N,N-dimethyl formamide
DMSC	bis(4-chlorocarbonylphenyl)dimethylsilane
DMSO	Dimethyl sulphoxide
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transform Infra Red
6-FDA	4,4'-bis(hexafluoroisopropylidenebis(phthalic anhydride)
IDT	Initial Decomposition Temperature
IPCl	Isophthaloyl chloride
NMP	N-methyl pyrrolidone
NMR	Nuclear Magnetic Resonance
ODA	4,4'-oxydianiline
ODPA	3,3',4,4'-oxydiphthalicdianhydride
PPDBN	4-(3-pentadecylphenoxy)benzene-1,3-diamine
PPDBT	3-pentadecylphenyl-3,5-diaminobenzoate
PPPB	3,5-diamino-N-(4-(3-pentadecylphenoxy) phenyl) benzamide
PMDA	Pyromellitic dianhydride
SiDA	bis(3,4–dicarboxyphenyl)dimethylsilane dianhydride
T_{10}	Decomposition temperature at 10% weight loss
T_{max}	Maximum Decomposition Temperature
T_g	Glass Transition Temperature
TGA	Thermo Gravimetric Analysis
THF	Tetrahydrofuran,
TPCl	Terephthaloyl chloride
UV	Ultra Violet
WAXD	Wide angle X-ray Diffraction
η_{inh}	Inherent viscosity

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Chapter-1

Introduction and Literature Survey

1.1 Introduction

Much of the humanity's progress has been marked by dramatic improvements in the materials that chemists have developed, from the 'Stone Age' to the 'Iron Age' to the 'Bronze Age' and now to the "Polymer Age". The development of polymers is perhaps the biggest achievement chemistry has made and it has a significant effect on every day life. "Polymer" is not a household word. Polymers are big molecules, the materials that constitute most of our natural and synthetic environment. The world would have appeared totally different without artificial fibers, plastics, elastomers, etc., and as cheaper, better and stronger synthetic materials are developed, their use will undoubtedly increase further. Polymeric materials, as they are constantly being modified, improved and fine-tuned for current and additional needs, and more readily accepted by the public, will have an ever-expanding influence on everyday life. Today polymers are used as replacements for woods, glass and metals and for a wide variety of applications in industries such as packaging, automobiles, building and construction, electronics, aerospace, electric equipments etc. In the high technology microelectronics area, many opportunities exist for polymers to serve as improved dielectrics, improved plasma etch resistance barriers, improved lithographic resists etc. Polymers for biomedical applications, likewise, provide a rich opportunity for synthetic innovation. Polymers are materials for the future and are versatile substances that can be tailored in an almost infinite number of ways to meet evolving needs. It is not surprising then that much of the high technology in future, from biotechnology to microelectronics, will depend on our ability to synthesize and manipulate polymers.

Synthesis of new monomers with special functionalities are greatly needed to fine-tune existing polymers for specific tasks. The raw materials cost, market size, energy needs, and health and environmental concerns have been the important factors especially for discovery and introduction of new monomers. There have been always a constant search for new cost-effective monomers that can be used in the synthesis of polymers for specialty applications. In this respect, the synthesis of polymers from renewable resources has attracted considerable attention of research workers throughout the world. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer

industry. In this regard cashew nut shell liquid (CNSL), an agricultural byproduct abundantly available in the country, is one of the few major and economic sources of naturally occurring phenols and can be regarded as a versatile and valuable raw material for polymer production.[1] Cardanol, a natural alkylphenol from cashew nut shell liquid (Anacardium occidentale), a potential natural source for biomonomers, cannot even today be said to have found its niche in terms of an appropriate industrial application. Considerable research work have been done by scientists all over the world to find out the multifarious uses of CNSL and recent investigations have revealed that the constituents of CNSL possess special structural features, which can be chemically transformed into specialty and high value products/ polymers.

Cashew nut shell liquid occurs as a reddish brown viscous fluid in the soft honeycomb structure of the shell of cashew nut, a plantation product obtained from the cashew tree. Many researchers have investigated its extraction,[2] chemistry and composition.[3] The components of cashew nut shell liquid are shown in Figure 1. Cardanol is formed when anacardic acid is heated and can be isolated from the raw oil by double vacuum distillation. (245^oC at 6 mm Hg).[2d,4]
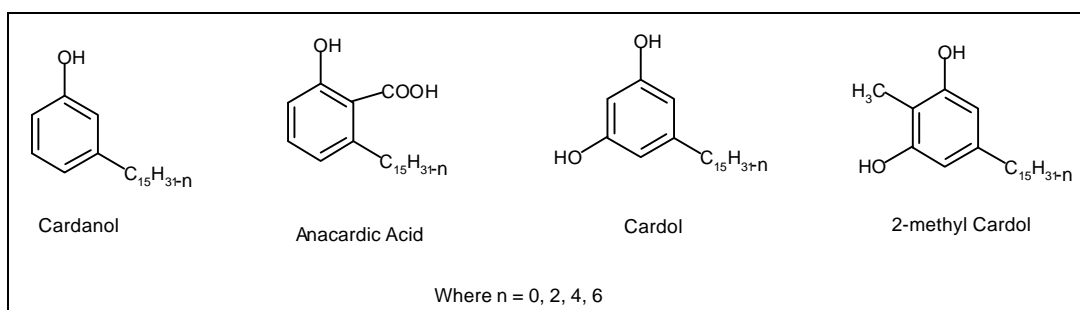
Figure 1.1. Constituents of Cashew Nut Shell Liquid

The literature on cardanol is replete with innumerable patents[5] and reports[2c] and many reports deal with the synthesis of several futuristic products from CNSL namely melt processable liquid crystal polymers, melt/solution processable polyaniline, polyurethanes, cardanol grafted cellulose, multi-functional additives for natural rubber, azobenzene based cross linked network structures for liquid crystal phase stabilization, etc.

By far the greatest amount of work on polymeric materials derived from CNSL have been concerned with its use in the manufacture or modification of phenolic resins.[6] The

phenolic nature of the material makes it possible to react under a variety of conditions to form both resols (condensation in presence of alkaline catalysts) and novalcs (condensation in presence of acid catalysts). Lima et al.[7] condensed the phenolic monomers, cardol, cardanol and anacardic acid present in CNSL with formaldehyde, in presence of NaOH catalyst to obtain liquid resols. Cardol showed higher reactivity in the reaction, compared to cardanol and anacardic acid and the resins obtained were found to be insoluble in common organic solvents, and melted at about $350^{o}C$. Studies have shown that the phenolic resins made from a mixture of cardanol, phenol and formaldehyde have improved chemical resistance and mechanical properties such as tensile, flexural, and Izod impact strengths than those of pure phenol-formaldehyde resins.[8] The cardanol-formaldehyde resins have been studied for producing protective varnishes with improved properties in food industry.[9] Cardanol have been used for the manufacture of special phenolic resins for coatings, laminates and friction materials.[10] The phenolic resins made from cardanol can also be used for breaking crude oil emulsions[11] and as selective ion exchangers for certain metal ions.[12] Hydroxyalkylated cardanol-formaldehyde resins have been used for the synthesis of polyurethanes with good thermal and mechanical properties.[13] Certain base catalyzed oxalkylated-cardanol-alkylphenol-aldehyde resins have been utilized in refinery demulsification operations.[14] These materials find particular utility in breaking water-in-oil emulsions resulting from the water wash of crude oils. The materials have also been employed to break other water-in-oil refinery emulsions. Poly(vinyl formal) (PVF) was modified by phenol-cardanol-formaldehyde resins (PCF) to improve properties of the insulating enamel varnish for copper wires.[15] The varnish films prepared from modified PVF showed better physico-mechanical properties, heat resistance and electrical properties.

CNSL can be used to manufacture epoxy resins by reacting with glycidyl ethers and phenol (followed by epoxidation). Tan et al.[16] reported the synthesis of cardanol-lignin based epoxy resins. A study of their mechanical properties indicated that an increase of the cardanol content increases the tensile strength and Young's modulus of the film products. Cardanol was treated with phenol using boron trifluoride as catalyst to give 1,8-bis(hydroxyphenyl)pentadecane, which was polymerized with epichlorohydrin to give epoxy resins useful for the preparation of baking coatings having comparable corrosion and

chemical resistance and better flexibility to conventional epoxy resins prepared from bisphenol A.[17] The cardanol epoxy resin could be further modified with vinyl monomers to give air drying components which were cheaper than the conventional epoxy coatings. Cardanol based epoxy resins are also used as binders for cathodic electrodepositions[18] and in automated bonding processes in electronics industry.[19] Phosphate ester-terminated epoxy novolak/phenolic resins having higher thermal stability than the conventional epoxy resins were also synthesized from cardanol and used in interpenetrating network coatings.[31c] There are several other reports on the use of cardanol for the synthesis of modified epoxy resins.[20]

Cardanol functionalized with methacrylate was found to have application in the synthesis of several heat-resistant resins.[21] Copolymers of MMA and cardanyl acrylate having a small fraction of cardinyl acrylate showed better thermal stability than the PMMA homopolymer.[22]

Cardanol was also used in the synthesis of thermoplastic polyurethanes.[23] Bhunia et al.[24] investigated the synthesis of novel polyurethanes by solution polycondensation reaction of 1,6-diisocyanatohexane with 4-[(4-hydroxy-2-pentadecenylphenyl)azo]phenol (HPPDP) and 1,4-butanediol.

Liquid crystal (LC) polymers with cross-linked network structures containing azobenzene mesogens were synthesized from cardanol, the unsaturated C_{15} hydrocarbon side chain of which was utilized for crosslinking reactions.[25] 8-(3-hydroxyphenyl)octanoic acid obtained by the side chain oxidation of cardanol was used in the synthesis of thermotropic liquid-crystalline copolyesters and these polyesters were found to be anisotropic under crossed polarized light at 200-409°C.[26]

The fuel blends of norbornadiene and carene (50:50 by wt.) and norbornadiene, carene and cardanol (40:40:20 by wt.) exhibited good ignition with red fuming nitric acid (RFNA) as oxidizer. The fuel blends with their low cost and toxicity and relatively high density can replace G-fuel, used in several Indian missiles, without impairing the performance.[27]

A number of semi-interpenetrating polymer networks (semi-IPNs) have been synthesized using polyurethane and cardanol derivatives like acetylated cardanol and phosphorylated cardanol.[28] Mohapatra et al.[29] synthesized some semi-interpenetrating networks by condensing cardanol-formaldehyde-p-hydroxyacetophenone or furfural novalc resins with

polyurethanes prepared from castor oil and diisocyanates. The thermal characteristics of poly(methylmethacrylate) (PMMA) interpenetrated with cardanol-formaldehyde resin was studied by Manjula et al.[30] The interpenetrating networks showed only 15% weight loss at 350^0C whereas PMMA showed around 50% weight loss at this temperature. There are several other reports on the synthesis of semi-interpenetrating polymer networks from cardanol.[31]

Synthesis of new polyphenols with attractive properties from natural phenolic compounds such as cardanol by oxidative polymerization using enzymes have been reviewed by Uyama et al.[32] Enzymic homo and copolymerization of alkylphenols derived from cashew nut shell gave homopolymers that are soluble in organic solvents, but the copolymers were crosslinked, with negligible solubility.[33] The enzymic polymerization was found to be dependant on the solvent mixture used. Polymerization in a dioxane-water solvent mixture resulted in spherical particles in the case of homopolymerization while structures without distinctive morphologies were obtained in the case of copolymerization. There are many reports on the synthesis of polyethers from cardanol.[34] A novel polyether was synthesized by cationic polymerization of glycidyl 3-pentadecenylphenyl ether (GPPE) in the presence of a latent thermal initiator, N-(benzyl)N,N-di-Me anilinium hexafluoroantimonate (BDAHA). Nguyen et al.[35] reported the modification of unsaturated polyester with maleated cardanol-epoxy resin.

The suitability of a flame retardant, 3-(tetrabromopentadecyl)-2,4,6-tribromophenol (TBPTP) developed from cardanol was evaluated by Pillai et al.[36] for use in cable insulating and jacketting materials based on low density polyethylene (LDPE) and ethylene vinyl acetate copolymer (EVA). Simple chemical modifications of cardanol such as introducing phosphorus and/or bromine gave a series of multi-purpose resins that can be used as flame retardants (FRs), adhesives, matrix resins for brake linings and composites.[37] Asbestos short fiber-filled phosphorylated cashew nut shell liquid (PCNSL) polymers are used for automobile brake lining applications.[38] PCNSL polymer-based brake linings gave a coefficient of friction within the recommended value for medium-range brake linings. Phosphorylated cardanol was also used as a dopant for conducting polyaniline.[39] The resulting complexes induced solubility of polyaniline in commonly used weakly polar or non-polar organic solvents such as xylene, THF, chloroform, etc.

Hydrophobe-modified hydroxyethyl cellulose polymers for use as rheology modifiers in

latex paints were prepared by using cashew nutshell liquid as a source of the hydrophobe.[40] Cardanol was grafted onto cellulose (filter paper) using $BF_3.Et_2O$ as carbocationic initiator and the resulting filter paper showed extensive water repellency.[41]

Novel blends were prepared from elastomeric materials and thermosetting resins, for example natural rubber and cardanol-formaldehyde resins, in order to improve mechanical properties (such as toughness) and thermal properties (such as high-temp. resistance).[42] Cardanol-formaldehyde resin (CF) and cardanol glycidyl ether (CGE) were synthesized for reinforcing natural rubber (NR), blend of NR and styrene-butadiene rubber (SBR), and nitrile-butadiene rubber (NBR).[43] The novolac CF resin reinforced NR, SBR, and NBR and the resol CF was found to be a hardener for NBR. The CGE could be used as a reinforcing agent for NR and for crosslinking maleated NR.

Even though the application of cardanol in the synthesis of a variety of polymers have been extensively reviewed,[44] reports on its application for the synthesis of polyamides and polyimides are limited. Maldar[45] reported the synthesis of some polyimides from substituted p-phenylene diamines based on cardanol. Vernekar et al.[46,47] reported the synthesis of novel polyimides and polyamides from a cardanol based diamine 4,4'-[sulfonylbis(p-phenyleneoxy)]-3-pentadecylbis(benzeneamine). Most of the polyimides were soluble in aprotic polar solvents like N-methyl-2-pyrrolidone (NMP), N,N'-dimethylacetamide (DMAC), dimethylsulfoxide (DMSO) and m-cresol and some were soluble in common organic solvents like chloroform. These polyimides had glass transition temperatures between 114 -125°C and their 10 % wt. loss temperatures were recorded in the range of 441 - 526°C in nitrogen atmosphere. The polyamides were also soluble in a variety of solvents and they were stable up to 422°C in nitrogen atmosphere.

An analysis of literature on cardanol shows that the important structural factor that makes cardanol suitable for a variety of applications is its pendant long alkyl group. Pendant alkyl groups and alkoxy groups are known to improve the solubility and processability of polyamides and polyimides. These alkyl groups can be attached directly to the main chain or can be a substituent of the side chain, which in turn is connected to the main chain through some flexible connecting groups. In both these cases literature reports are mainly based on the

incorporation of small and bulky alkyl groups like methyl and t-butyl and there are only very few reports on the incorporation of long pendant alkyl groups because of the difficulty in synthesizing monomers containing them. Phenols containing alkyl group substituents are useful starting materials for the synthesis of these monomers and the corresponding polymers. Most of the phenols containing long alkyl groups are synthesized by the Friedel Crafts reaction of phenol with alkyl halides, which usually gives ortho, and para alkylated products. The position and length of pendant alkyl group can affect the final properties of the polymers and therefore it will be interesting to study the properties and applications of polyamides and polyimides synthesized from phenols having long alkyl groups in the meta position. In this regard cashew nut shell liquid can be considered as a potential natural resource of long chain alkyl phenol like cardanol, where the substitution is at the meta position which is very difficult to obtain by any synthetic method and can be used in the synthesis of monomers and polymers having pentadecyl groups directly attached to the main chain[46,47] or as a meta substituent of the pendant phenyl group.

The most important areas of application of polyamides and polyimides include alignment layers in liquid crystal display devices, gas separation membranes and as low dielectric materials in interlayer dielectrics. Earlier reports indicate that the polymers having pendant alkyl groups are suitable candidates for these applications. In the field of liquid crystal display devices the molecular scale orientation at the surface of alignment layers plays a key role in aligning the liquid crystal molecules at the surface.[48] The changes in molecular surface structures affect the pretilt angle (angle between the liquid crystal director and the polymer alignment surface) which is a key parameter affecting the electro-optical properties of liquid crystal displays. Some researchers have shown that long alkyl and fluorinated alkyl side chains[49] generate high pretilt angles of liquid crystals due to a hydrophobic interaction[50] with the polar liquid crystal molecules and the length of the alkyl group also affect the pretilt angle.[51] In gas separation applications the pendant alkyl groups are important since they cause an increase in the free volume of the resulting polymer and thereby increase the permeability.[52] Dielectric properties of polymers are dependant on their hydrophobicity[53] and therefore polymers having pendant alkyl groups are expected to have low dielectric constant, which makes them useful as interlayer dielectrics. The synthesis of polyamides and

polyimides from cardanol opens up an easy and economic process for the introduction of a long pendant pentadecyl group into their structure and it is expected that such polyimides and polyamides will have improved properties, which make them useful for the above mentioned applications.

1.2   Polyamides

Polyamides are polymers with recurring amide groups (-CO-NH-) as an integral part of the main polymer chain and they are the largest and most important group of linear-acyclic nitrogen polymers. Hetero-chain polyamides are widely represented in nature as various proteins and numerous other substances of biological importance, which are found among the constituents of animal and plant organisms. The synthetic hetero-chain polyamides as a class include an immense number of high molecular compounds, which are of great scientific and practical importance. Polyamides occupy a prominent position among the synthetic high polymers. The first synthetic polyamide, polybenzamide was obtained by Harbordt in 1862.[54] Further development in the polyamide chemistry resulted in the synthesis of a variety of polyamides that provide a wide range of materials.[55] The extensive research in this area was due to the success of the aliphatic and later aromatic systems, which have been developed into commercial products by fiber producers like Monsanto, DuPont etc.[56] Given this impetus and the desirable properties of fully aromatic polymers, this class of materials was one of the first exploited on a large scale as thermally stable polymers. The first synthetic fibers of practical importance were obtained from polyamides and were conspicuous by their extremely high strength and occupy the first place among all synthetic fibers.

In 1974, the aliphatic and aromatic polyamides were given separate generic nomenclature by the 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).[57] A number of excellent review articles on aramids have been published.[58]

1.2.1 Synthetic methods for the preparation of aromatic polyamides

Aromatic polyamides have been prepared by several methods,[59] which include

- High temperature melt polycondensation of diamines and diacids
- Low temperature polycondensation (<100°C) of diacid chlorides and diamines
- High temperature solution polycondensation of dicarboxylic acids and diamines
- Polycondenstion of N-silylated diamines and diacid chlorides
- Polycondensation of diisocyanates and dicarboxylic acids
- Transition metal catalyzed polycondensation of aromatic diamines, dihalides and carbon monoxide

1.2.1.1 High temperature melt polycondensation of diamines and diacids

This method has been successfully used in the synthesis of aliphatic polyamides, especially in the fabrication of nylon.[60] But this method is not useful for the synthesis of aromatic polyamides because their melting temperatures are very high and therefore the melting is always accompanied by their decomposition. Also many dicarboxylic acids get decarboxylated and the diamines get oxidized and also have a tendency to sublime at such high temperatures.

1.2.1.2 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[61] and is advantageous over the high temperature melt polycondensation route, which results in decomposition of polymer at elevated temperatures. The high reactivity of acid chlorides has enabled the low temperature condensation polymerization with minimum side reactions. The two types of low temperature polycondensation polymerization methods are[61]

- Solution polycondensation method and
- Interfacial polycondensation method.

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1.2.1.2 (a) Solution polycondensation of diamine and diacid chloride

Solution polycondensation involves a diamine and a diacid chloride reacting in an amide solvent such as N-methylpyrrolidone (NMP), hexamethylphosphoramide (HMPA), dimethyl acetamide (DMAc) or tetramethylurea (TMU) (Scheme 1.1).

Scheme 1.1. Solution polycondensation of diamine and 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 key factors required in polycondensation for obtaining high molecular weight polymers are

- Stoichiometry of the monomers
- Purity and concentration of monomers
- Temperature of the reaction medium and reaction time
- Nature of solvents and addition of salts
- Solubility of the polymer
- Speed of stirring

While the importance of purity and stoichiometry of monomers seem to be obvious, the concentration of monomers also influences the molecular weight of the final polymer to a certain extent. High concentration leads to a highly viscous reaction medium and the mobility of the macromolecular chains will be restricted. Also at high concentration, heat generation favors side reactions. At low concentration, competitive side reactions[62] such as reaction of diacid chloride with the solvent becomes significant because of the lower rate of condensation reaction. The temperature should be adjusted to ensure that the condensation reaction is much faster than the side reactions. In general, low temperatures are favored in this method. The solvent should allow maximum solubility (swellablity) 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$_2$.[63]

1.2.1.2 (b) 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 1.2)

$$n \; H_2N\text{—}Ar\text{−}NH_2 \Big/ _{H_2O \,+\, base} \;+\; n \; ClOC\text{-}Ar'\text{-}COCl \Big/ _{organic\ solvent} \longrightarrow \left[\text{N-Ar-N-C-Ar'-C} \right]_n$$
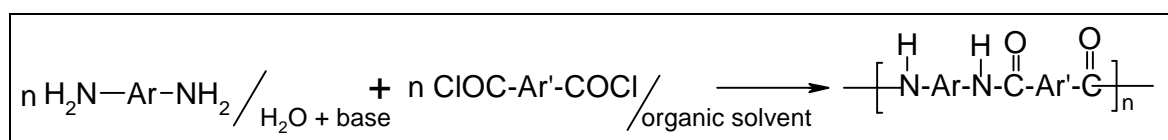
Scheme 1.2. Interfacial polycondensation of diamine and diacid chloride

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.[64,65] In this method where two phases are involved, the nature of the organic solvent influences the partition of monomers between the bulk solvent and the interface. In addition, a good solvent for the diamine would cause diffusion of this monomer into the organic phase, hence disturbing the balance of the two monomers leading to low molecular weight product. Generally, an organic solvent, which precipitates the high molecular weight polymer, but not the low molecular weight polymer, is preferred. The volume ratio of the two phases and concentration of reactants influence the reaction rate of the polycondensation and also the side reactions such as hydrolysis. Usually hydrolysis is reduced by the use of a weakly alkaline acid acceptor, such as sodium carbonate. At high concentration of the inorganic acid acceptor, the acid chloride may undergo hydrolysis to acid, which in turn will affect the polymerization rate.[66] Effective mixing can create a high interfacial surface area and hence increase the polycondensation rate. Since the temperatures needed are low, the side reactions

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

1.2.1.3 High temperature solution polycondensation of dicarboxylic acids and diamines

The direct polycondensation of dicarboxylic acids and diamines proceeds at very high temperature and the rate of polycondensation is normally very slow and is accompanied by a number of side reactions which lead to the decomposition of functional groups and the back bone structure. However, moderately high molecular weight polymer can be obtained by carrying out the reaction in the presence of a condensing agent such as aryl phosphite and an organic base. In the beginning of 1970's two Japanese groups Ogata and co-workers[67,68] and Yamazaki and Higashi[69, 70] 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 1.3).

$$R^1COOH + P(OPh)_3 + \text{(pyridine)} \longrightarrow \left[\begin{array}{c} \text{(pyridine)} \\ N \\ H\text{-}P\text{-}OCOR^1 \\ PhO \quad OPh \end{array} \right]^+ \quad {}^-OPh$$

$$\downarrow R^2NH_2$$

$$R^1CONHR^2 + H\overset{O}{\underset{||}{P}}(OPh)_2 + PhOH$$
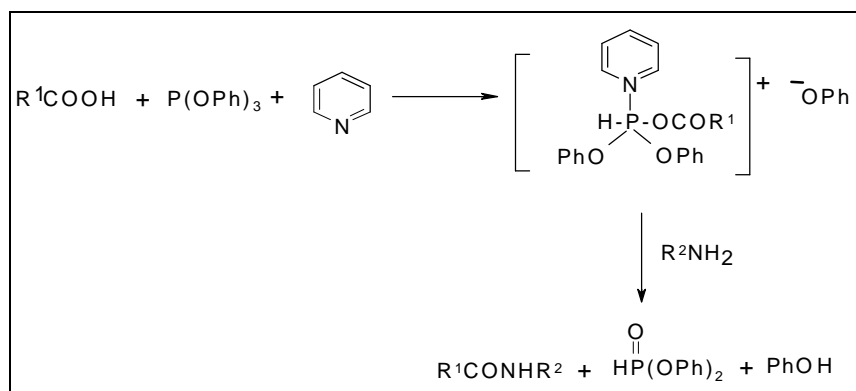
Scheme 1.3. Condensation reaction involving diacid and diamine in the presence of triphenylphosphite

$CaCl_2$ and LiCl were used along with NMP to improve the molecular weight of polymers. In this synthetic method involving phosphorylation, the key factors that can considerably influence the molecular weight of the final polymer are

- Concentration of monomers
- Ratio of triphenylphosphite to monomer

- Reaction temperature and time
- Concentration of LiCl and CaCl$_2$
- Solvent and amount of pyridine relative to the metal salt.

The role of CaCl$_2$ and LiCl is quite complicated. They can form complexes with pyridine and 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 phosphorus containing activating agents like triphenylphosphine dichloride,[71] (1,2-benziloxazol-3-yl) diphenylphosphate (**1**),[72] phenylbis (2,3-dihydro-2-oxobenzothiazol-3-yl)-phosphinate (**2**),[73] diphenyl (2,3-dihydro-2-oxo-3-benzothiazolyl)-phosphonate (**3**)[74] and diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)-phosphonate (**4**)[75] etc. were reported.

1.2.1.4 Polycondensation of N-silylated diamine 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 an aromatic diacid chloride.[76] 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 1.4).
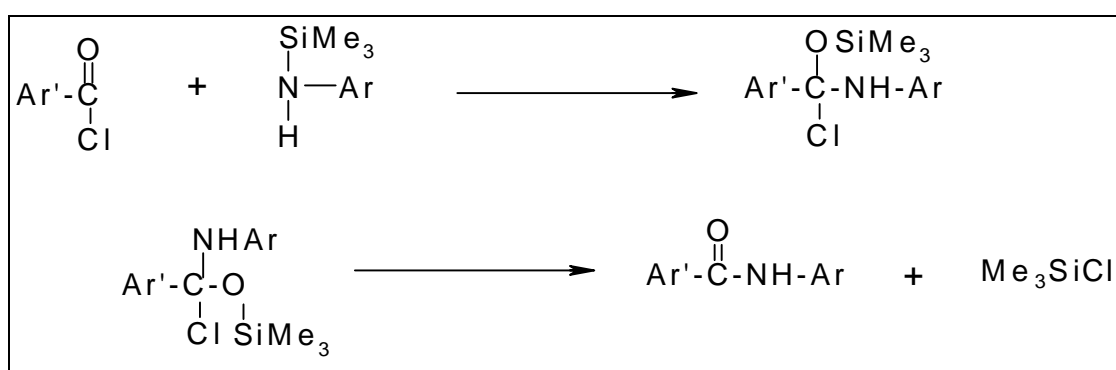
Scheme 1.4. Condensation reaction of N-silylated diamine and diacid chloride

This method is especially useful for the preparation of polyamides from aromatic diamines having low reactivity and has several advantages.

- High purity N-silylated diamines can be obtained by simple distillation
- Silylated diamines show excellent solubility in various organic solvents offering the flexibility in the polycondensation process.
- The condensation proceeds under neutral conditions with elimination of trimethylsilyl chloride

1.2.1.5 Polycondensation of diisocyanates and dicarboxylic acids

Another promising route for the preparation of aromatic-aliphatic copolyamides has been developed by Simioneseu et. al.[77] and Onder et al.[78] 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.[79] A commercial scale preparation of aromatic polyamides from 1,3-phenylene diisocyanate and isophthalic acid in presence of a catalyst has been reported.[80] Polyamides have also been prepared by the reaction of aromatic diisocyanate with aromatic hydrocarbons in the presence of Friedel-Crafts catalyst.[81]

1.2.1.6 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 1.5).[82]
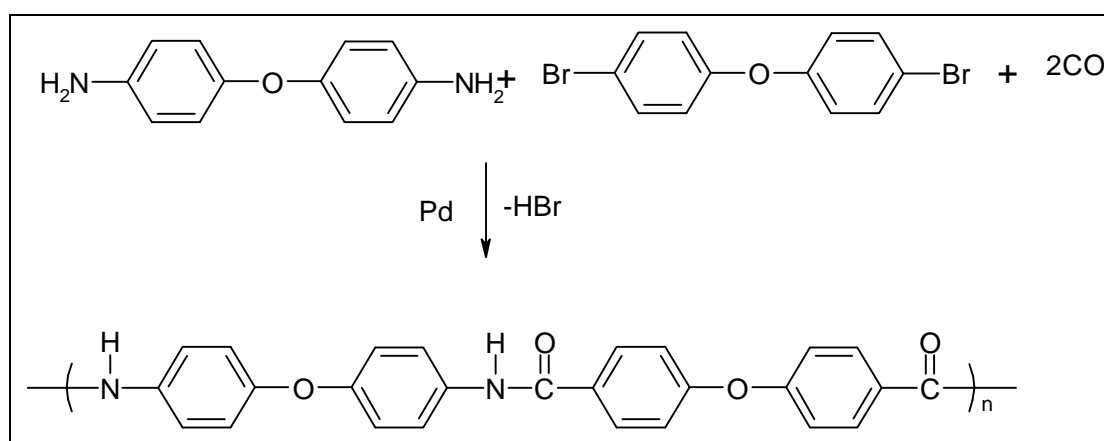
Scheme 1.5. Transition metal catalyzed carbonylative coupling of aromatic diamines and dihalides

1.2.2 Structure property relationship of aromatic polyamides
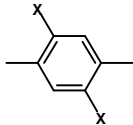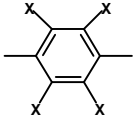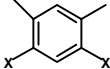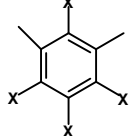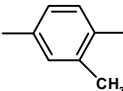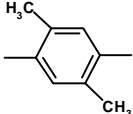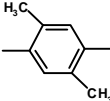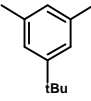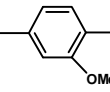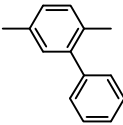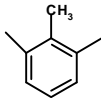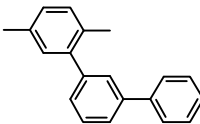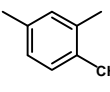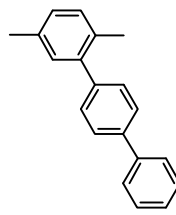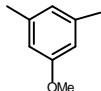
Aromatic polyamides are high performance polymers having high thermo-oxidative stability, excellent mechanical properties, good flame resistance and electrical properties and good chemical resistance. The high thermal stability and excellent mechanical properties of aromatic polyamides (aramids) such as poly (p-phenyleneterephthalamide (Kevlar)) and poly (m-phenyleneterephthalamide) have been recognized for a long time. But in aramids an inverse relationship exists between thermal stability and processability. The fabrication of most of the unsubstituted aromatic polyamides is difficult as a result of their high softening temperatures and their insolubility in common organic solvents. Recently, there has been an increasing requirement for new processable engineering plastics having a moderately high softening temperature and solubility in organic solvents. To alleviate this problem a number of strategies[83,107b] were adopted to synthesize soluble/processable polyamides without significantly affecting the thermo-mechanical properties as listed below.
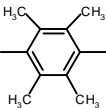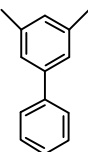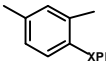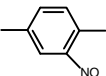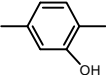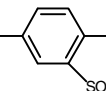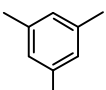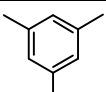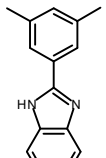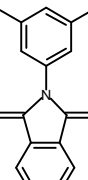
- Introduction of flexible or semiflexible spacers in the polymer backbone.
- N-alkylation or N-arylation of the amide groups to reduce inter chain hydrogen bonding
- Random copolymerization with small amounts of ortho or meta substituted benzene rings to disrupt extended chain conformation
- Use of heterocyclic monomers
- Introduction of bulky pendant groups into the diamine or the diacid monomer units and the use of non-coplanar structures

1.2.2.1 Phenylene monomers with bulky substituents
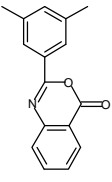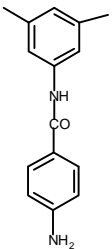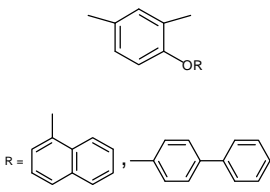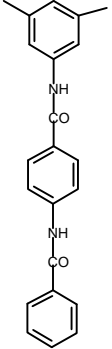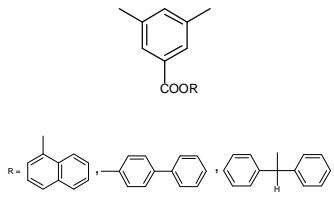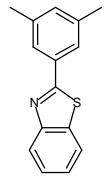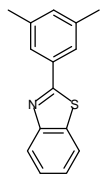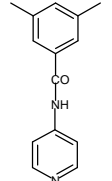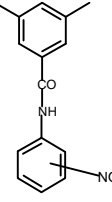
Synthesis of substituted phenylene monomers has been a very popular route to modify the properties of polyamides and is based on the direct derivatisation of the precursor aromatic monomer, both the diamine (phenylene diamine) as well as the diacid (terephthalic and isophthalic acids). Structures of various substituted phenylene diamines and diacids, which have been used for the synthesis of polyamides, are given in Table 1.1. Halogenated phenylene diamines[84] and diacids[85] have been used for the synthesis of thermostable, soluble and flame retardant polyamides.
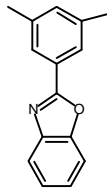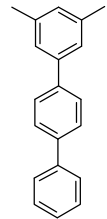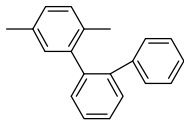
Table 1. 1. Substituted phenylene monomers

Diamines	Refs	Diacids	Refs
X = F, Br, Cl	84b,c	X = F, Br, Cl	85a, b, c
X = F, Br, Cl	84e, 85c	X = F, Br, Cl	85b
	84a, 105a		105b
	105a		106
	84a		107, 109b
	84a, 105a		109b
	84a, 105a		109b
	84a		110

Structure	Label	Structure	Label
(hexamethylbenzene)	84a	(3,5-dimethylbiphenyl)	109a, 114
X = O, S	86	OCOPH	87
NO₂	84a	NHCOPh	91, 88
OH	84a	NO₂	89
SO₃H	84a	R = H, C₄H₉, C₈F₁₇	90
CONHPh	91	SO₂PH	92
COOH	84a	COPh	93
(benzimidazole)	94	(phthalimide)	95

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	94		96
	97		96
	98		99
	100		101
			102

		103
		104
		104

The thermal stability of the halogen substituted polyamides decreases in the order H>F>Cl>Br. Thermal stability of para substituted polyamides was higher than that of meta substituted ones. Increase of halogen content in a polyamide generally leads to a decrease in the decomposition temperature and an increase in the solubility.

Methyl substitution have been used to improve the solubility of polyamides by disrupting the regularity of packing along the main chain in several substituted phenylene diamines and diacids. The study of Takatsuka et al.[105] and Chaudhuri et al.[84a] showed that for methyl substituted polyamides the solubility increases by methylation and also polyamides with unsymmetrical methyl substitution shows higher solubility [84a, 105] e.g. the polymer from 2-methyl-1,4-diamine is more soluble than the one from 2,5-dimethyl-1, 4-diamine and the polymer from 6-methyl-1, 3-diamine has a higher solubility than the one from 2-methyl-1, 3-diamine. Yang et al.[106] recently reported the use of a bulky tertiary butyl group which is more thermally stable than the methyl group to improve the solubility of polyamides. Methoxy substituted polyamides generally have lower stability than their methylated analogues.[84a]

Some studies have also been carried out using aromatic substituted monomers like phenyl,[107] phenoxy and thiophenoxy,[108] substituted diamines and phenyl,[107a,109] biphenyl[109b] and phenoxy[110] substituted diacids. Direct phenyl substitution increases glass transition

temperature (T_g) of a polyamide whereas substitution *via* ether or thioether bond decreases the glass transition temperature of the polymer. The thermal stability of substituted polyamides is decreased by phenoxy and thiophenoxy substituents but not by phenyl substitution. Generally aromatic side groups hinder free segmental motion of the polymer chain thereby increasing the Tg of polymer. But in the case of phenoxy and thiophenoxy substituents, chain separation is more, which in turn lowers the Tg. These polyamides with lower Tg and thermal stability are interesting candidates for melt processable high performance plastics. The substituents like phenoxy and thiophenoxy also enhance the solubility of these polyamides.

Several polar substituents have been introduced into the polymer backbone to improve the solubility. Chaudhuri et al.[84a] in their study of the thermal stability of wholly aromatic polyamides, introduced polar groups like NO, COOH, OH, SO$_3$, etc. in the polymer back bone. Compared to methylated or chlorinated polyamides those having polar substituents showed lower thermal stability. The thermal stability of these polyamides were in the order NO$_2$> COOH> OH> SO$_3$H. The low stability of the SO$_3$H substituted polyamide is attributed to the presence of the acid group, which can catalyze the thermal degradation of polymer.

Other substituents like ester and amide groups have also been introduced into the polymer backbone.[111] Polyamides containing these groups were soluble in highly polar solvents and some are soluble or swellable in m-cresol. The oxybenzoyl substitution does not change the T_g of a polymer but the T_g is decreased by 50°C by an amide substitution in the amine part and is increased by 20°C by the introduction of an amide group in the diacid part. The polyamides substituted with amide groups have higher thermal stability than those substituted with oxybenzoyl groups.
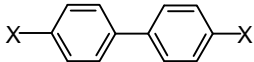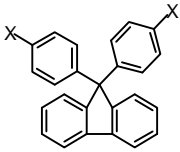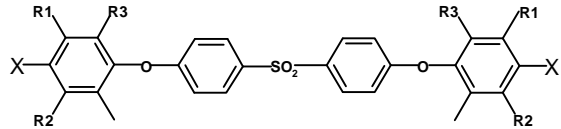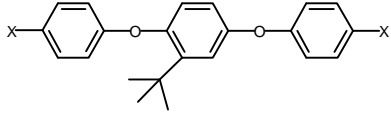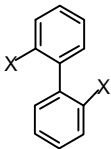
Some heterocyclic groups like 5-(2-benzimidazolyl),[94] 5-(4-oxo-3,1-benzoxazin-2-yl),[94] imide,[95] benzoxazole,[103] benzothiazole[99,100] etc. have also been introduced into the polymer backbone to improve the properties of the resulting polyamides. These polyamides were found to have better solubility in polar aprotic solvents and showed enhanced hydrophilicity, low glass transition temperatures and thermal stability than those without these substitutions.
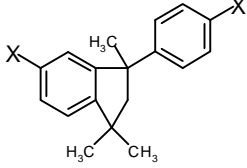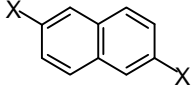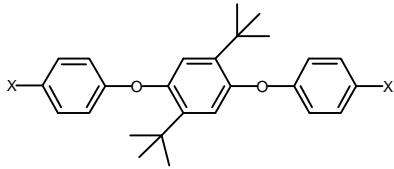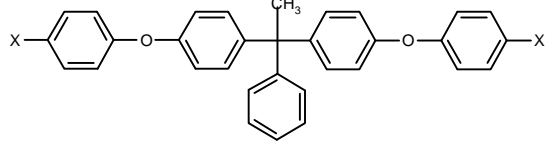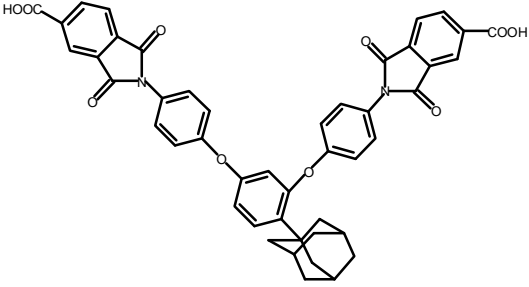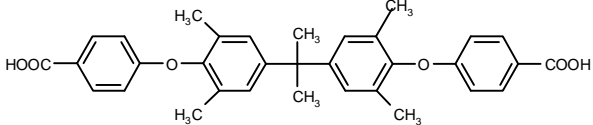
1.2.2.2 Monomers containing several benzene rings
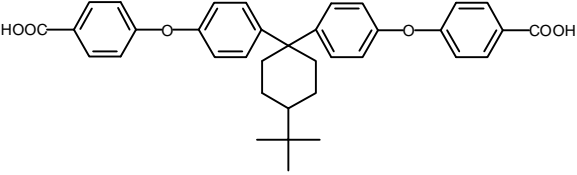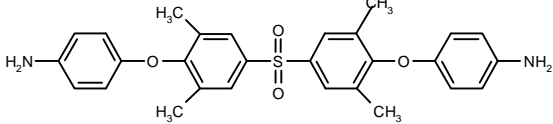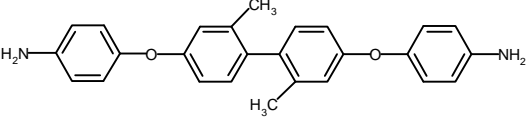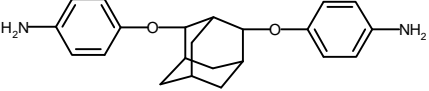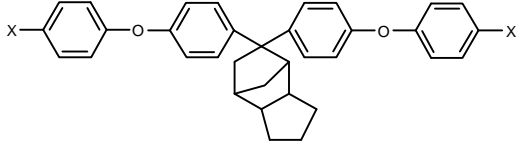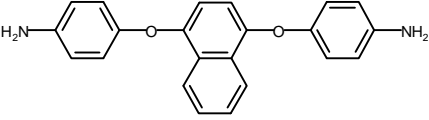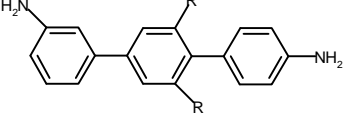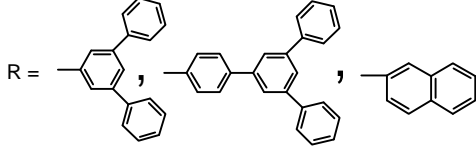
Numerous monomers containing several aromatic rings and flexible groups like –CH$_2$–,[106,112,111b,117a,84e] –C(CF$_3$)$_2$–,[112,117b,115,106,136] –C(CH$_3$)$_2$–,[111b] –O–,[106,112,117a,113] –NPh–,[117b] –S–
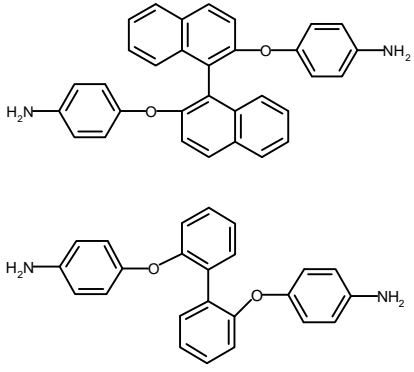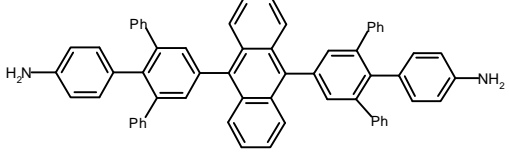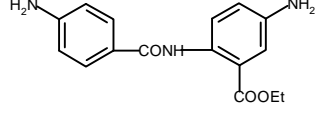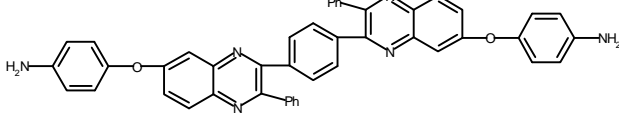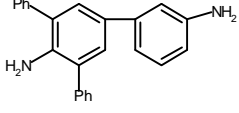
,[112] –SO$_2$–,[114,106,112,117a,b,84 e] –CO–,[106,112,113,117a] –SiR$_2$–[115,136,116] have also been employed in the synthesis of soluble polyamides. Some of these multiring aromatic monomers having flexible groups and bulky side substituents are shown in Table1.2.

Table 1.2. Diamines/Diacids based on multiring aromatics

Diamines/Diacids	Refs
X = NH$_2$/ COOH	117
X = NH$_2$/ COOH	112
X = NH$_2$/ COOH R$_1$ = CH$_3$, R$_2$ = R$_3$ = H R$_1$ = H, R$_2$ = R$_3$ = CH$_3$ R$_1$ = R$_2$ = CH$_3$, R$_3$ = H	118, 117a
X = NH$_2$/ COOH	119
X = NH$_2$/ COOH	112

  X = NH$_2$/ COOH	120
  X = NH$_2$/ COOH	108, 111a, 134
  X = NH$_2$/ COOH	121,122
  X = NH$_2$/ COOH	123
	124
	125

HOOC—⟨⟩—O—⟨⟩—C(cyclohexyl-t-Bu)—⟨⟩—O—⟨⟩—COOH	139j
H₂N—⟨⟩—O—⟨(CH₃)₂⟩—SO₂—⟨(CH₃)₂⟩—O—⟨⟩—NH₂	126
H₂N—⟨⟩—O—⟨CH₃⟩—⟨CH₃⟩—O—⟨⟩—NH₂	127
H₂N—⟨⟩—O—(adamantyl)—O—⟨⟩—NH₂	139i
X—⟨⟩—O—⟨⟩—C(tricyclic)—⟨⟩—O—⟨⟩—X X = NH₂/ COOH	139k,139l
H₂N—⟨⟩—O—(naphthyl)—O—⟨⟩—NH₂	128
H₂N—⟨⟩—⟨R,R⟩—⟨⟩—NH₂ R = ⟨biphenyl⟩ , ⟨terphenyl⟩ , ⟨naphthyl⟩	271

	129
	130
	131
	132
	133

2,6-naphthalenedicarboxylic acid has been employed in the synthesis of soluble polyamides.[108,111a,134] Compared to the polyamides derived from isophthalic and terephthalic acid, the polyamides derived from the naphthalic acid gave higher T_g and T_d (decomposition temperature). Vernekar et al.[117a] in their study of polyamides from a m-sulfone ether diamine (Figure 1.2) showed that the T_g decreases in the order a> c> b and T_d decreases in the order b> c>a. Vernekar et al. [47] also showed that the solubility of polyamides synthesized from p-sulfone ether diamines can be increased by the incorporation of a pendant pentadecyl group.
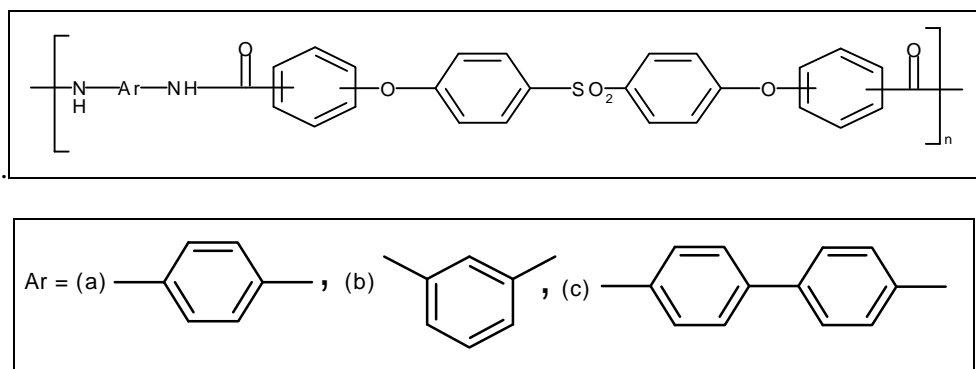
Figure 1.2. Polyamides synthesized from m-sulfone ether diamine

Several monomers containing flexible linkages between the aromatic rings have also been studied by Yang et al.[106] Imai et al.[112a] synthesized some soluble polyamides with flexible linkage and showed that the influence of different flexible links, can be very large, but it does depend on the nature of each polyamide.

Incorporation of aromatic silane functions[135] into the polymer backbone can also improve the solubility of polyamides. Vernekar et al.[136] reported the synthesis of some silane containing polyamides with improved solubility prepared from diacid chlorides having dimethyl silyl and diphenyl silyl bridging groups. Ji et al.[137] recently reported the synthesis of polyamides with pendant dendritic fragments (Figure 1.3). These polyamides were found to have improved solubility and those with second generation dendritic blocks were soluble in common organic solvents like ethyl acetate, acetone, ether, hexane etc.
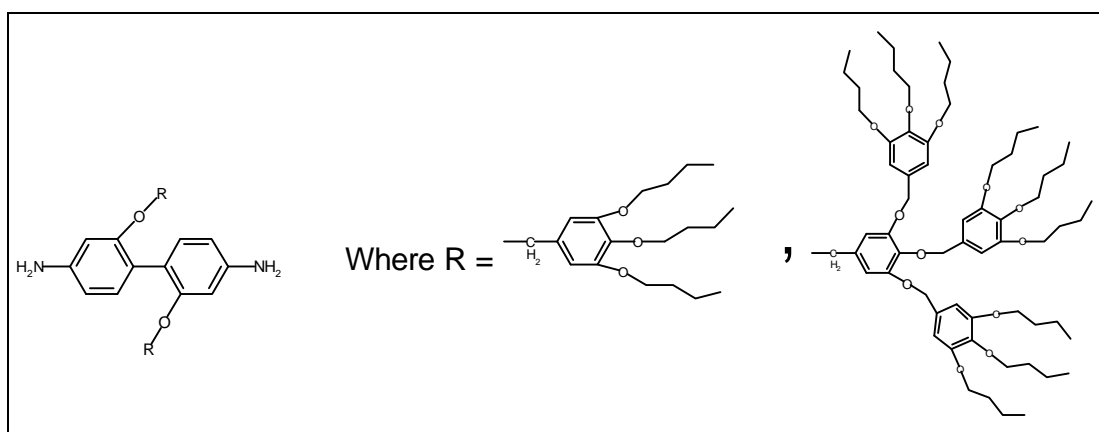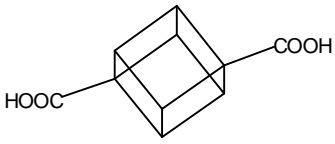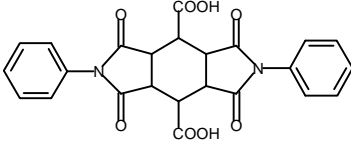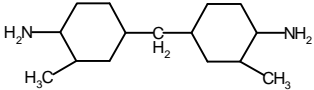
Figure 1.3. Polyamides containing pendant dendritic blocks

Mikroyannidis et al.[138] investigated the synthesis of several polyamides containing oligophenyls in the main chain and with highly phenylated side groups. Aromatic polyamides from diamines or diacids containing backbone cardo groups,[139] such as fluorene, phthalidimine, phthalide, adamantane, tricyclo[5.2.1.02,6] decane, norbornane, cyclohexyl with diamines or dicarboxylic acids containing large spiro units,[140] and with methyl, tert-butyl, and phenyl substituted ether linked dianilines or dibenzoicacids[141] have been reported in literature.

Polyamides with alicyclic units like cubane in the backbone have been investigated by Mehrdad et al.[142] Park et al.[143] investigated the synthesis of cycloaliphatic-aromatic polyamides having pendant N,N'-diphenylimido groups. Some of the monomers for polyamides containing alicyclic units are given in Table 1.3.

Table 1.3. Some monomers for polyamides containing alicyclic units

Diacids/Diamines	Refs
	142
	143
	144

1.2.2.3 Heterocyclic monomers

The use of heterocyclic monomers in the synthesis of polyamides is another approach towards improving the processability and thermal stability of the polyamides. It is well known that a large number of polymers, in which aromatic and heterocyclic rings are linked together in chains, are resistant to high temperature.[145] In most cases the connecting groups are less thermally stable than the rings themselves and the overall thermal stability of the polymer is determined largely by the nature of these groups. It is evident that the thermal stability

increases considerably with a decreasing number of single connecting groups in the polymer backbone. Imai et al.[146] studied the thermal stability of polyamides with phenoxathiin rings in place of open-chain diphenyl ether linkages and found that the polyamides synthesized from 2,8-diaminophenoxathiin and 2,8-diaminophenoxathiin-10,10'-dioxide were more stable than those synthesized from open-chain diphenyl ether linkages. These polymers were found to be soluble in polar aprotic solvents, but were not soluble in common low boiling organic solvents. Literature reports several other polyamides synthesized from tricyclic fused ring heterocycles containing dibenzo-p-dioxins,[147] thianthrene,[147] phenoxaphosphine,[148a] phenothiophosphine,[148b] phenoxasilin[149] and phenaxasiline rings.[150] These polyamides were found to be more thermally stable than the corresponding polyamides having open chain linkages. Imai et al.[151] reported the synthesis of polyamides from several highly phenylated heterocyclic diamines like 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene, 3,4-bis(4-aminophenyl)-2,5-diphenylfuran and 3,4-bis(4-aminophenyl)-2,5-diphenylpyrrole and from heterocyclic diacid chlorides like 2,5-bis(4-chloroformylphenyl)-3,4-diphenylthiophene. These polyamides were characterized by their high thermal stability and solubility in organic solvents. Some polyamides containing pyrazole[152] and oxadiazole[153] rings have also been reported recently.

1.2.3 Applications

Aromatic polyamides are resistant to alkali and have good hydrolytic stability as compared to nylons and polyesters. Due to these properties aromatic polyamides are used as filter bags for hoot stake gases, press cloths for industrial presses, home ironing board covers and sewing thread for high-speed sewing.[154] The resistance of aramids to ultra-violet and ionizing radiations is superior to that of nylons.

The 'Nomex' fiber (poly (m-phenyleneisophthalimide) retains 76% of its original strength after exposure to 155°C/g in a Vande Graft generator, where as nylon-6,6 is destroyed by the same exposure. Hence, the aramids are used as tyre cord in car casses and as the belts in bias-belted and radical-belted tyres. They are also used in cables, parachutes, body armour, in rigid reinforced plastics and also in high performance boats and aircrafts, circuit boards, filament wound vessels, fan blades and sporting goods.[155] Aromatic polyamides have

high volume resistivity and high dielectric strength as compared to nylons. At elevated temperatures they retain their properties and hence have high potential as high temperature dielectrics particularly in motors and transformers.[156] Aromatic polyamide fibers burn with difficulty. The limiting oxygen index which is a measure of heat resistance of polymers is very high for polyamide.[157] Hence aramids are used as industrial protective clothing, welders clothing and protective shields, fire department turnout coats, pants and shirts, jump suits for forest fighters, flight suit for pilots of the armed services, autoracing drivers suits, mailbags, carpets, cargo covers, boat covers etc.

Aramids have good permselective properties and are used as hollow-fiber permeation separation membranes to purify sea and brackish water or for the evaporation of numerous types of salts from water.[158] Many polyamides having pendant alkyl groups have been synthesized to improve the selectivity and permeability of the resulting membranes.[159] Polyamides are well known for reverse osmosis membranes but less for gas separation.[160] Aromatic polyamides also offer excellent thermal and mechanical properties, show good chemical resistance and are easily spun into hollow fibers for high performance gas separation modules.[161]

Polyamides have also been used as liquid crystal alignment layers. But only a few reports are available in this area and most of them are regarding the polyamides having pendant alkyl groups.[162,329h]

1.3 Polyimides

Polyimides constitute another important class of thermally stable polymers. They are condensation polymers incorporating the imide group in $-OC-\overset{|}{N}-CO-$ their repeating units either as an open chain or as rings and are generally derived from the reaction of organic diamines with organic tetracarboxylic acids or their dianhydrides. However, only cyclic polyimides are of genuine interest from a practical viewpoint and will be discussed in detail.

The first reference to a polyimide was dated at the beginning of the century in a work done by Bogert and Renshaw.[163] They disclosed that 4-aminophthalic anhydride, a relatively stable compound, does not melt upon heating but evolves water at elevated temperature with the formation of a 'polymolecular imide'. The initial impetus to develop high performance

polymers to satisfy the demands of electrical and aerospace industries resulted in the emergence of polyimides as an important class of polymers.[164] Actual commercial application of these polymers appeared in the form of aromatic-aliphatic polyimides prepared in analogy to nylon chemistry utilizing preformed monomer salts.[165] These materials were typically based on pyromellitic dianhydride and were insoluble. But they were melt processable if the aliphatic diamine was composed of nine or more atoms or a branched carbon chain of atleast seven atoms. Only a few family of high performance polymers are commercially available today. Due to intensive research done for heat resistant polymers in 1960's, polyimides soon became highly important because of their excellent thermal stability, along with good mechanical and electrical properties. However they do not lie at the top of the list of thermally stable polyheterocycles. Indeed, other polyheterocycles, such as polybenzimidazoles, polybenzoxazoles and polyquinolines, show better heat resistance than polyimides.[166] But polyimides soon gained a prominent position due to their excellent properties-price-processability balance and they virtually stand alone with respect to providing useful, available, technological materials. In the beginning, polyimides found application in rather restricted variety of technologies, mainly in the form of films or resins for aerospace and electrical industries.[167,168] Extensive studies have been carried out on polyimides than all other high temperature polymers combined, due to the availability of monomers, the ease of polymer synthesis and their excellent properties. The discovery of copolyimides and addition polyimides widened the range of properties and application possibilities of polyimides and made them versatile polymers for advanced technologies.[169] Du Pont is the world leader in polyimides. Their products include Kapton®(films, contains pyromellitic dianhydride-4,4'-oxydianiline (PMDA-ODA)), Vespel®(moldings, has PMDA-ODA structure and is prepared by special processing), Pyralin®(coatings, contains PMDA-ODA) and Avimid ®(composite matrices, contains PMDA and 50/50 mixtures of 1,3-bis(3-aminophenoxy)benzene and 2,2-bis(4-(4-aminophenoxy)phenyl)propane). The polyimides make up approximately 40% of the commercially available nonmetallic materials for use at temperatures up to 300°C. Polyimide products find use in a variety of applications such as films, coatings, medical devices, separation systems, structural components in airplanes including jet engines, high modulus fibers, binders in abrasive and cutting discs, automotive components, liquid crystal displays,

household appliances, electronic/microelectronic components, wire insulation and many other applications. Thus polyimides touch our lives in many different ways. Polyimides have been studied and reviewed extensively in several books, monographs and review articles.[170]

1.3.1 Synthetic methods for the preparation of polyimides

The earlier attempts to prepare aromatic polyimides were unsuccessful because they attempted the direct synthesis of the final polyimide from the starting monomers. Edwards and Robinson[171] in early Du Pont patents described the procedures related to polyimide salt technique. Starting with pyromellitic acid or related diesters, salts were prepared with diamines like m-phenylene diamine followed by heating to temperatures in excess of 300°C. Intractable polyimide powders resulted from the aromatic diamines and also from short chain aliphatic diamines. Thereafter considerable research work had been done to explore the different routes for the synthesis of polyamides and now, a number of synthetic methods are available for the synthesis of polyimides.[169] The important ones are

- Polycondensation of diamines and dianhydrides
- Polycondensation via ester derivatives of poly(amic acid)s
- Polycondensation of dianhydrides and diisocyanates
- Transition metal catalyzed polycondensation of diamines and di/tetrahalides
- Polymerization by cycloaddition reaction

1.3.1.1 Polycondensation of diamine and dianhydride

This is the most widely used method for the synthesis of polyimides. The polymerization of diamines and dianhydrides can be carried out in two different ways

a. Two-step method via poly(amic acid)s

b. One-step method

a. Two step method *via* poly (amic acid)s from dianhydrides and diamines

The polycondensation of an aromatic dianhydride and a diamine is the traditional method employed in the synthesis of polyimides and is shown in Scheme 1.6.
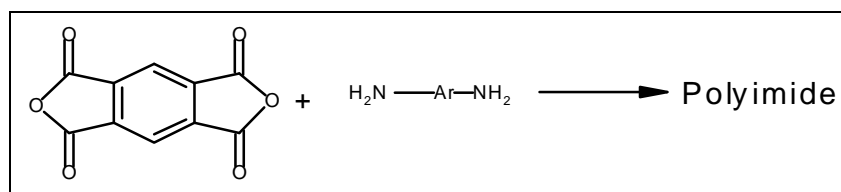
Scheme 1.6. Condensation of dianhydride with diamine

A successful route to the synthesis of high molecular weight polyimide was described first by Endrey in 1962 and successive Du Pont patents.[172] The patents were followed by publications in the U. S. and in Great Britain.[173,164b] In this method, the synthesis was conducted in two stages. First a soluble poly(amic acid) was prepared which was then converted to the desired polyimide (Scheme 1.7).
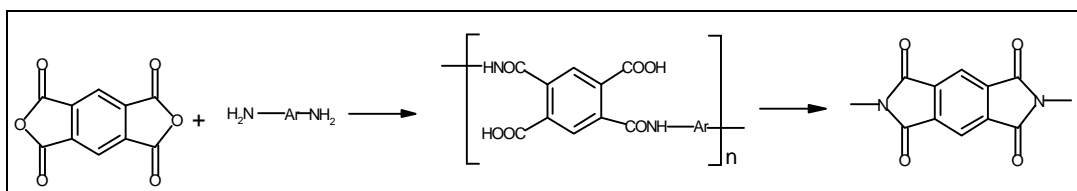
Scheme 1.7. Two step synthesis of polyimides

The first step is crucial to attain high molecular weight chains and the second one has a great influence on the final nature of the polymer since a quantitative conversion in the cyclodehydration process has to be there to obtain fully cyclized polyimide. This two-step reaction initiated enormous research and industrial activity in the field of polyimides. Thus this highly elegant process made it possible to bring the first significant commercial polyimide products into the market and it is still the method of choice in majority of applications. This process involves several elementary reactions interrelated in a complex scheme, which are discussed in the following section.

(i) Formation of poly (amic acid)s

When a diamine and a dianhydride are added into a dipolar aprotic solvent such as N,N-dimethylacetamide, N,N-dimethylformamide, or N-methylpyrrolidone, poly(amic acid) is rapidly formed at ambient temperatures. The reaction mechanism involves the nucleophilic attack of the amino group on the carbonyl carbon of anhydride group, followed by opening of the anhydride ring to form the amic acid group. This reaction is an equilibrium reaction, where the forward reaction is favored by the high concentration of monomers. Formation of

high molecular weight polyamic acid is dependant upon the purity of monomers, reactivity of monomers, strict stoichiometric balance, rigorous exclusion of moisture, choice of solvents and low to moderate temperatures.[174] Since the acylation of amine is a highly exothermic reaction, the equilibrium is usually favored at lower temperatures. The progress of polycondensation reactions largely depends on the nature of the monomers. Since the poly (amic acid) formation is a nucleophilic substitution reaction it is expected that the reaction rate is governed by the electrophilicity of the carbonyl groups of the anhydride and the nucleophilicity of the amino nitrogen atom of the diamine. In general high value of amine basicity and dianhydride electronic affinity will result in a higher reaction rate. Soviet researchers[175] have studied the acid/base relationships of some dianhydrides and diamines used in the synthesis of poly(amic acid)s. In general, the reaction in aprotic solvents is favored by increased electron affinity of the dianhydride and by the increased basicity of the diamine.

Solvents used in the formation of poly (amic acid)s also play an important role. Most commonly used solvents are dipolar aprotic solvents such as N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP), and tetramethyl urea (TMU). Solvents like hexamethyl phosphoramide (HMPA), pyridine and m-cresol can also be used. More recently[176] solvents like diglyme and ethylcarbitol have been used in cases where the polyamic acid solubility permits their use. They can be used alone or in combination with other solvents such as benzene, dioxane, toluene, cyclohexane, xylene etc. Sulphoxide solvents like dimethylsulphoxide can also be used. However, lower thermal stability and difficulty in removing it in the process of imidization stands against its use. Best solvents are dipolar aprotic amide solvents since they are 'Lewis bases'. The orthoamic acid formed in the reaction medium is a strong carboxylic acid and the interaction between the amide solvent and the amic acid is a major cause for the exothermicity of the reaction and is one of the most important driving forces. Therefore the rate of poly (amic acid) formation is faster in more polar and more basic solvents. However the rate is even faster in acidic solvents like m-cresol than in DMAc, indicating that the acylation of amine is catalyzed by the acid. When weakly basic amines were used in dipolar aprotic amide solvents, generally only low molecular weight polyimides were obtained. Egli et al.[177] reported that the reactions of BTDA (benzophenone tetracarboxylic acid dianhydride) and weakly basic diamines such as 3,3' and

4,4'-diaminodiphenylsulfones afforded high molecular weight poly (amic acid)s in solvents like tetrahydrofuran (THF) and diglyme. This may be due to the interaction of ether group with the hydrogen of the amino group, resulting in its enhanced basicity and because of reduced rate of reverse reaction, which requires the proton abstraction from the amic acid to generate carboxylate group. In order to obtain a successful polymerization, a fixed mode of monomer addition has been suggested. Thus, the addition of the dianhydride (preferably as a solid) to the diamine solution has been recommended as the right mode of addition to ensure high molecular weight polyimides.[178] Poly (amic acid)s are known to undergo hydrolytic degradation even at ambient temperatures. In the presence of water the anhydride groups can hydrolyze to form ortho dicarboxylic groups. The ortho dicarboxylic acid groups thus formed remain as one of the end groups of the poly(amic acid) and does not revert to the anhydride. The effect of water on the molecular weight of the already polymerized poly(amic acid)s in solution is well documented.[179]

(ii) Conversion of poly (amic acid)s to polyimides

Conversion of poly (amic acid)s to polyimides is generally carried out by thermal or chemical imidization methods

> *Thermal imidization of poly(amic acid)*

The conversion of poly (amic acid)s to the corresponding polyimides is usually performed thermally in solid state. The films cast from the poly (amic acid) solutions are dried and gradually heated up to 250-350°C, depending upon the stability and glass transition temperature of the polymer. The imidization process may be followed by a variety of means and has been studied on poly (amic acid)s, as well as in molecular models, by IR[180] and NMR[181] spectroscopy. Thermal imidization reaction does not take place in a true solid state but rather in a very concentrated viscous solution, and therefore, the presence of residual solvents play an important role. The imidization proceeds faster in the presence of dipolar aprotic solvents. This may be due to the specific solvation, which allow the favorable conformation of the amic acid group to cyclize.[182] It may also be explained by the plasticizing effect of the solvent, which helps to increase the mobility of the reacting functional groups. The basicity of the amide solvent, which helps it to accept protons, may also be responsible

for this effect.[183] The imidization proceeds rapidly at the initial stage and slows down in later stages. The initial rapid stage imidization is attributed to the ring closure of the amic acid in the favorable conformation (a) as shown in Scheme 1.8.[184] The lower rate in the later stage is attributed to the unfavorable conformation (b), which has to rearrange to conformation (a) before the ring closure.
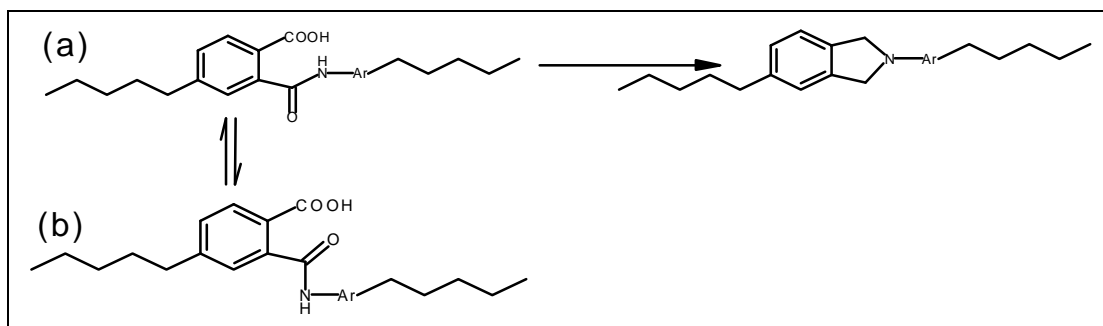
Scheme 1.8. Ring closure of poly (amic acid) to polyimide in the favorable conformation

➢ *Chemical imidization of poly (amic acid)*

The cyclodehydration of the poly (amic acid)s to polyimides can be readily achieved by means of chemical dehydration at ambient temperature. Commonly used reagents are acid dianhydrides in dipolar aprotic solvents or in the presence of tertiary amines.[185] Among the dehydrating agents used were acetic anhydride, propionic anhydride, n-butyric anhydride, benzoic anhydride, and others. Among the amine catalysts used were pyridine, methylpyridines, lutidine, N-methylmorpholine, trialkylamines, and others. The cyclizing agent was most effective when an optimum ratio of acetic anhydride/pyridine (4:3.5 moles per repeat unit of polyamic acid) was employed. Vinogradova et al.[186] showed that the pKa value of the base has a significant effect on the conversion of poly (amic acid) to polyimide. In the presence of trialkylamines with pKa >10.65, high molecular weight polyimides were obtained. The use of less basic tertiary amines resulted in the formation of lower molecular weight polyimides. However, different results were obtained for heteroaromatic amines. Despite lower basicity, high molecular weight polymers were obtained when pyridine, 2-methylpyridine and isoquinoline (pKa 5.23-5.68) were used as catalysts. Depending on the conditions and the nature of the dehydrating agents, the intermediate can evolve towards imide or isoimide. For example, the use of acetyl chloride as dehydrating agent afforded isoimides.[187] The use of triethylamine practically eliminated the isoimide formation and

provided significantly faster reaction rates.[188] The use of N,N'-dicyclohexylcarbodiimide (DCC) lead to the conversion of poly(amic acid)s to isoimides instead of imides.[189] Combinations of trifluoroacetic anhydride-triethylamine and ethylchloroformate-triethylamine also afforded high yields of isoimides.[189a]

b. One step method

A single-stage homogeneous solution polymerization technique can be employed for polyimides, which are soluble in organic solvents at polymerization temperatures. In this process, a stoichiometric mixture of monomers is heated in a high boiling solvent or a mixture of solvents in a temperature range of $140^{o}C$-$250^{o}C$ where the imidization reaction proceeds rapidly. This method is also used in the case of sterically hindered monomers having lower reactivity and that cannot be polymerized to high molecular weight polyimides by the two step method.[190] Commonly used solvents are nitrobenzene, benzonitrile, α-chloronaphthalene, o-chloronaphthalene, trichlorobenzenes, and phenolic solvents such as m-cresol and chlorophenols in addition to dipolar aprotic amide solvents. Toluene is often used as a cosolvent to facilitate the removal of water of condensation. Gerashchenko et al.[191] studied one-step solution polymerization in nitrobenzene employing a soluble polyimide system based on 9,9-bis(4-aminophenyl)fluorene with PMDA (pyromellitic dianhydride) or 4,4'-oxydiphthalic anhydride (ODPA). Vinogradova et al.[192] and Lavrov et al.[193] studied the imidization of a model compound N-phenylphthalamic acid to N-phenylphthalimide and showed that the rates were lower in basic aprotic amide solvents and faster in acidic solvents like m-cresol. In general, imidization reaction has been shown to be catalyzed by acid.[193,194] High temperature solution polymerization in m-cresol is often performed in the presence of high boiling tertiary amines such as quinoline as catalyst. Dialkylaminopyridines and other tertiary amines were effective catalysts in neutral solvents like nitrobenzene.[195] Alkali metal and zinc salts of carboxylic acids,[196] and salts of certain organophosphorus compounds[197] were also found to be efficient catalysts in one step polycondensation of polyimides.

1.3.1.2 Polycondensation *via* ester derivatives of poly(amic acid)s

Poly(amic acid)s in solution are inherently unstable and their shelf life is limited unless they are stored under refrigeration. However their ester derivatives, poly(amic ester)s, are significantly more stable. Inability to form carboxylate anion prevents them from undergoing the reverse reaction, which is the key reaction step of poly(amic acid) degradation. In addition, ester derivatives are generally more soluble in a wide variety of common organic solvents. 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 ester derivatives of polyamic acids can be classified into two categories

a. Alkyl esters of poly(amic acid)s

b. Silyl esters of poly(amic acid)s

a. Alkyl esters of poly(amic acid)s

Taking advantage of the property of poly(amic ester)s that do not undergo reverse reaction, mixtures of a rigid rod like poly(amic ester) and poly(amic acid) were used to form polyimide-based molecular composites.[198] The diacid esters obtained by the reaction of PMDA and short chain alcohols were characterized by low solubility. To overcome this problem, Flaim et al.[199] synthesized various rigid rod like poly(amic acid ester)s, possessing nonplanar structure or bulky substitutents, such as one shown in Scheme 1.9 to improve the solubility.
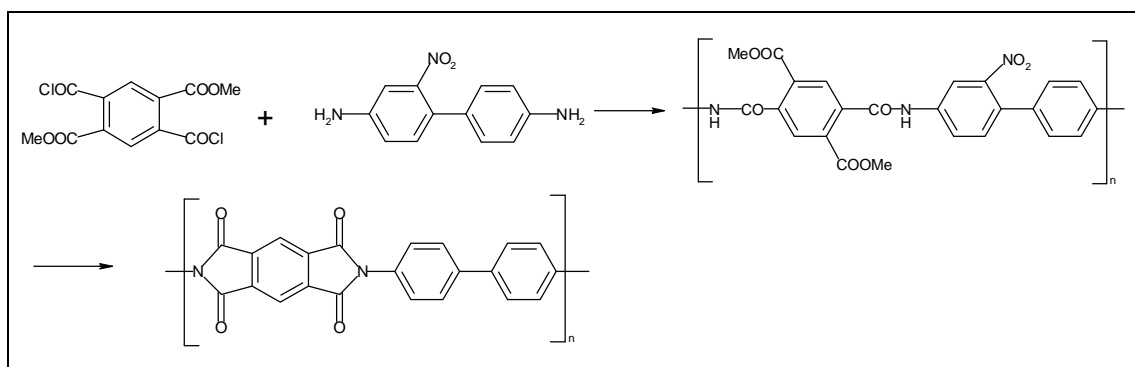
Scheme 1.9. Synthesis of polyimides from alkyl esters of poly (amic acid)s

Becker and Schmidt[200] reacted 2,5(bisethoxycarbonyl) terephthaloyl chloride with substituted p-pheylenediamines and 2,2'-disubstituted 4,4'-diaminobiphenyls to prepare various p-catenated rigid-rod poly(amide ester)s, which were then thermally converted to the corresponding rigid-rod polyimides. In contrast to the unsubstituted polyamides, majority of ethoxycarbonyl-substituted polyamides were soluble in dipolar solvents. Kakimoto et al.[201] also prepared similar para diester diacid chloride of PMDA with long chain alcohols. The polymerization of these diacid chlorides with p-phenylenediamine was performed in the presence of propylene oxide as acid acceptor in a mixture of hexamethyl phosphoramide and benzene to obtain high molecular polyamide precursor, which was then imidized to form polyimides.

b. Silyl esters of poly(amic acid)s

N-silylated diamines are more reactive than the amine itself. Hence N-silylated amines are used for the synthesis of polyimides, particularly when the diamines are less reactive. The N-silylated diamine method has several advantages over the conventional methods.

- High purity N-silylated aromatic diamines can be obtained by simple distillation
- N-silylated aromatic diamines exhibit excellent solubility in organic solvents

Boldebuck and Klebe[202] found that N,N'-bis(trialkylsilyl)diamines reacted rapidly at room temperature with various aromatic dianhydrides to form high molecular weight silyl esters of poly(amic acid)s soluble in less polar or non polar solvents. Homogeneous solutions of various polyamic silyl esters can also be prepared in aromatic hydrocarbon solvents containing small amounts of dipolar solvent. Like alkyl esters from poly (amic acid)s, the resulting silyl esters were also stable than the poly(amic acid)s. The imidization of poly(amic silylester)s to the corresponding polyimides required temperatures higher than 200°C and proceeded with the elimination of trimethylsilanol.[202] Silylated amines can also be reacted with acyl chlorides to form poly(amide amic acid)s with the elimination of trimethyl silylchloride. Oishi et al. [203] reported the reaction between 4-chloroformylphthalic anhydride with silylated diamines to form the silylated poly(amide amic acid)s. Polyimides were also prepared by the reaction of PMDA and N,N,N',N'-tetrasilyldiamine.[204]

1.3.1.3 Polycondensation of dianhydrides and diisocyanates

Polyimides can be prepared by the direct reaction of a dianhydride and a diisocyanate.[205] The reaction proceeds in the presence of a tertiary amine catalyst. Initial phase of the synthesis proceeds at 50-60°C with the evolution of CO_2. High temperatures are required in nonpolar solvents whereas the reaction proceeds in dipolar solvents at moderate temperatures. Protic compounds such as water, alcohols and amines can serve as catalysts. Meyers[205d] obtained polyimides from PMDA and diphenylmethanediisocyanates (MDI) in DMF. It was observed that the polymerization proceeds through a soluble intermediate as represented in Scheme 1.10. Upon heating, this soluble intermediate eliminates CO_2 and form the imide. Carleton et al.[206] prepared high molecular weight polyimides in DMAc and DMSO.
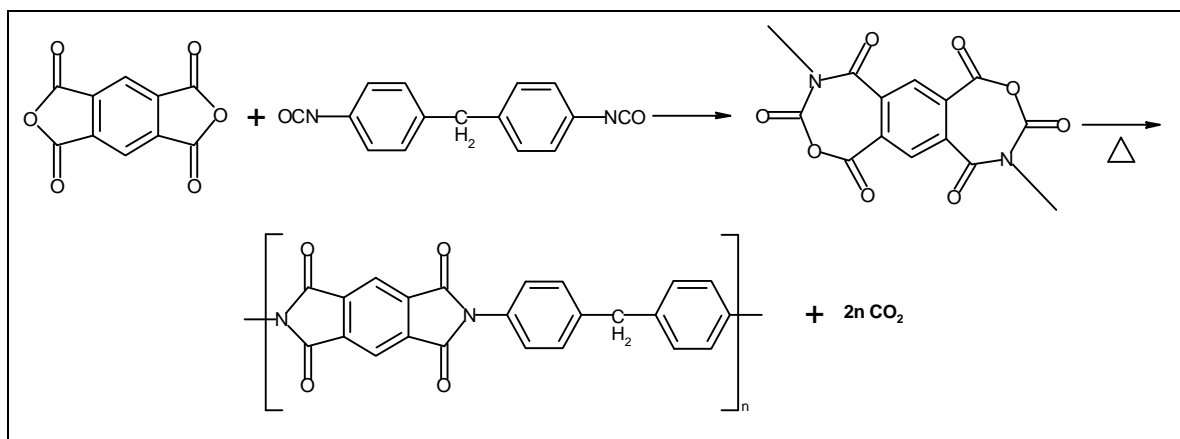
Scheme 1.10. Polycondensation of dianhydride and diisocyanate

Alvino and Edelman,[207] investigated the reaction of PMDA and MDI in dipolar solvents in the presence of tertiary amine as catalyst. High molecular weight poyimides were obtained when a controlled amount of water was added and it was found that the catalytic function of water enhanced in dipolar amide solvents. Ghatge and Mulik[208] obtained soluble polyimides from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and various aromatic diisocyanates. Similar results were also observed by Khune.[209] Kilic et al.[210] also reported polymerization of BTDA and PMDA with MDI and dicyclohexylmethyl diisocyanate in dipolar solvents. However, high molecular weight polyimides could not be obtained under these conditions. Onder[211] demonstrated that dianhydride and diisocyanate polymerization was catalyzed in dipolar solvents by alkali metal alkoxides and phenoxides. High molecular weight polyetherimides were synthesized from bis(ether anhydride)s and diisocyanates by

melt polymerization or high temperature solution polymerization in nonpolar aromatic solvents.[212] In the absence of polar solvents the reaction rate was extremely slow. However, in the presence of stable bases such as alkali carbonates, the polymerization proceeded efficiently at temperatures above 200°C to form high molecular weight polyetherimides. More recently Kakimoto et al.[213] polymerized PMDA and an aromatic diisocyanate with bulky substituents to form a soluble polyimide. High molecular weight polymers were also formed in non-polar aromatic solvents such as nitrobenzene, benzonitrile and anisole, while polymers with only moderate molecular weight were obtained in dipolar solvents such as NMP.

1.3.1.4 Transition metal catalyzed polycondensation of diamines and di/tetrahalides

Palladium catalyzed C-C coupling reaction can also be employed for the synthesis of polyimides (Scheme 1.11).[214] Rigid rod like polyimides were synthesized from N, N'-bis(4-bromo-2,5-diido-decylphenyl) pyromellitimide and 2,5-di dodecyl-1,4-benzenediboronic acid.[215] Perry et al.[216] synthesized poly (amic amide)s from bis(o-iodobenzamides) and diamines and then subsequently ring closed them to polyimides. This method usually gives only low molecular weight polyimides and therefore is not a very popular method.
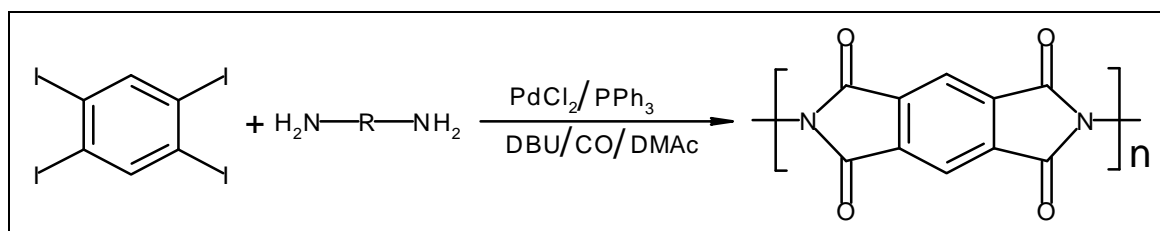
Scheme 1.11. Palladium catalyzed polycondenzation of diamines and tetra halides

1.3.1.5 Polymerization *via* the cycloaddition reaction

Bisimides and oligoimides capped with reactive unsaturations such as maleimide, acetylene and xylylene groups can be chain extended by cycloaddition reaction with proper bisdienes. In 1964, a patent was granted to Rhone Poulenc, France for cross linked polyimides obtained through the homo- and/or copolymerization of bismaleimides.[217] Later a large amount of work was done in this area and research organizations involved in aircraft/aerospace material developments recognized the potential of thermosetting imide

oligomers as resins for high temperature composites and adhesives. Further developments in the area of addition polyimides have been extensively reviewed by Stenzenberger et al.[218]

1.3.2 Structure-property relationship of aromatic polyimides

Polyimides are a class of polymers known for their excellent thermal stability, favorable dielectric properties and chemical resistance and have found application in a variety of advanced technologies.[169a] However these polymers are not easily processable in the fully imidized state due to their extreme structural rigidity. Therefore for many years the aromatic homopolyimides could be applied only in the form of films or coatings.[219] The processability is an important criteria without which the polymer becomes merely a laboratory curiosity. Several structural modifications were envisioned early, to overcome these limitations. A first improvement was outlined by preparing copolymers, which are soluble in the fully imidized state, mainly poly (ester imide)s and poly(amide imides)s.[164,219a,170a] As an alternative to these copolymers, addition polyimides were developed in the 1970's as a new class of thermosetting materials. Thus bismaleimides, bisnadimides, and end-capped thermocurable polyimides were successfully developed and marketed.[169] These resins were precursors of the modern PMR (polymeric monomer reactants) formulations.[220]

Further improvements in the chemistry of polyimides during the last few years have been directed towards the development of polyimides that are soluble in organic solvents or melt processable while fully imidized. Thus, the chemical structure of polyimides has to be modified to adapt the behavior and performance of these specialty polymers to the demands of the new technologies. The strategies to develop novel processable aromatic polyimides are mainly focussed on chemical modifications, by preparing new monomers with less molecular order, torsional mobility and lower intermolecular bonding.

Of the various alternatives to design novel processable polyimides, some general approaches have been universally adopted.

- Introduction of flexible segments or flexible groups, which reduce the chain stiffness
- Introduction of bulky side substituents, which help for the separation of polymer chains and hinder the molecular packing and crystallization
- Use of enlarged monomers containing angular bonds, which suppress coplanar structures

- Use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers, which lower regularity and molecular ordering
- Preparation of copolyimides from two or more dianhydrides and diamines

1.3.2.1 Polyimides containing flexible spacers or flexible groups

In recent years, polyimides containing flexible spacers have gained importance as technical materials. Thus some segmented, fluorinated polyimides[221] and copolyimides containing oligoethylene glycol[222,223] sequences and some polyimides containing oligosiloxane[224] and silane[225] segments have been presented as processable polyimides with potential application as thermally stable adhesives and thermoplastics. The thermal stability of these segmented polyimides is dependant on their chemical structure, and mainly on the flexible chain. It was found that the polyimides containing polyethylene glycol[222] sequences are thermally unstable, whereas polysiloxane[236] and perfluoroalkanes[226] and even alkanes[227] provide a reasonable thermal stability. For the preparation of segmented polyimides or block polyimides, diamines rather than dianhydrides are preferred as the monomer bearing the flexible segment.

Introduction of flexible linkages into the polymer backbone is a general approach used to lower transition temperatures and to improve the solubility of intractable polyimides. Most of the commercially available fully aromatic polyimides contain ketone or ether linkages in their repeating units and earlier works demonstrated that dianhydrides having two phthalic anhydride moieties joined by bonding groups gave more tractable polyimides.[160 1,228] Many different linkages like $-O-$,[229] $-C=O$,[230] $-S-$,[229a] $-SO_2-$,[231] $-Si(CH_3)_2-$,[236] $-C(CH_3)_2-$,[230] $-CH_2-$,[232] $-CHOH-$,[232,229b] and $-C(CF_3)_2-$,[233,229b] $-Ph-P=O-$,[234] etc. have been introduced into the polyimide backbone to improve the solubility of the polyimides. These bonding groups may be located on the dianhydride, on the diamine, or on both the monomers, or they can be formed even during the polycondensation reaction when some functional monomers containing preformed phthalimide groups are used as condensation monomers.[235] It has also been shown that the incorporation of diphenyl silane units in the polyimide backbone can lead to polymers with improved solubility.[236] The presence of these flexible groups has a dramatic effect on the properties of the final polymers. These linkages cause a breakdown in the

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planarity and an increase of the torsional mobility. These bonds also result in separation of the imide rings, whose relative density is actually responsible for the polymer tractability. The suppression of the coplanar structure is maximal for sulfonyl or hexafluoroisopropylidene groups or when the monomers are enlarged by more than one flexible linkage. The analysis of the T_g values and solubility of some of the polyimides prepared from these monomers show that the combination of non-planar dianhydrides and non-planar, meta-oriented aromatic diamines containing flexible linkages provide the structural elements needed for solubility and melt processability.[237] Falcigno et al.[238] explored the synthesis of non-coplanar dianhydrides like 2,2'-dichloro-4,4',5,5'-benzophenonetetracarboxylic dianhydride in the synthesis of soluble polyimides. Scola[239] first reported the synthesis of 2,2,2-trifluoro-1-phenylethylidene)diphthalic anhydride (3-FDA) which can be incorporated into polyimides in the place of 6-FDA (4,4'-hexafluoroisopropylidene bis(phthalic anhydride).

Another rational approach to improve tractability of aromatic polyimides consists of extending the length of the diamine and/or the dianhydride by incorporating more phenylene rings and more connecting flexible groups. Using the same chemical functions previously mentioned for bridged diamines and dianhydrides, a wide variety of new enlarged monomers have been prepared and used for the synthesis of processable polyimides.[240,229a,235b,233b,138f] Some optically active polyimides were synthesized from optically active diamine and dianhydride monomers.[241] These polyimides were soluble in a variety of solvents and the good solubility of these monomers was attributed to the incorporation of flexible aryl ether groups and non-coplanirity in the 2,2'-substituted 1,1'-dinaphthyl unit. Song et al.[242] reported the synthesis of two new 1,1'-binaphthyl-2,2'-diyl-based dianhydrides, i.e., 2,2'-bis(3,4-dicarboxybenzamido)-1,1'-binaphthyl dianhydride and 2,2'-bis (3,4-dicarboxybenzoyloxy)-1,1'-binaphthyl dianhydride and the corresponding polyimides. These polyimides showed high solubility in solvents like THF, dichloroethane and chloroform.

1.3.2.2 Polyimides with bulky substitution

Structural modifications to attain soluble aromatic polyimides have also been carried out by introducing bulky substituents, aryl or heterocyclic rings. One of the first references to this approach was made by Korschak and Rusanov[243], who synthesized soluble aromatic
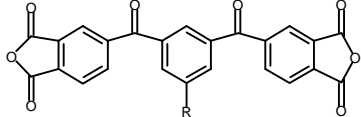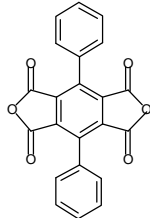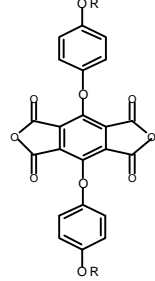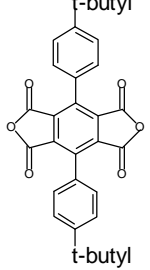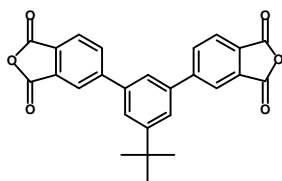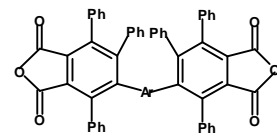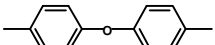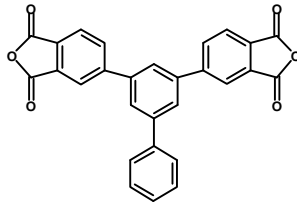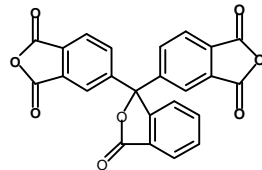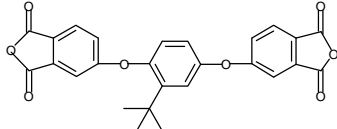
polyimides containing side phthalimide groups. More recently Rusanov et al. [244] reported polyimides containing pendant imide groups. As a continuation of the pioneering work done by Russian researchers, many attempts have been made to prepare new monomers, diamines and dianhydrides, with bulky pendant groups for novel processable polyimides and some of these monomers are shown in Tables 1.4 and 1.5. Among the different substituents, pendant phenyl groups are the most promising since they does not reduce the thermal stability and help in the disruption of the chain packing by increasing the free volume.[245,247b] David et al.[246] reported the synthesis of several dianhydrides containing t-butyl and phenyl pendant groups. The polyimides prepared from these dianhydrides and commercially available diamines showed good solubility, glass transition temperature, thermal properties and mechanical properties. Literature reports the synthesis of several polyimides containing p-terphenyl or p-quinquephenyl moieties in the backbone and highly phenylated bulky pendant groups.[247,138] These polymers showed solubility even in solvents like 1,2,2,2-tetrachloroethane. The bulky rigid monomer 3,6-diphenylpyromellitic dianhydride (DPPMDA) was investigated as a replacement for pyromellitic dianhydride (PMDA) in several systems incorporating both rigid and flexible diamines with the aim of increasing polymer solubility.[248] Indeed, increased solubility was observed in all systems containing DPPMDA relative to those containing PMDA. Several polyimides having bulky pendant ether groups have been synthesized from diamines having pendant methoxy, phenoxy and biphenoxy moieties.[249] It was found that the thermal stability and the melt processability of the polyimides did not depend on these substituents but their solubility in organic solvents was improved. Some rigid-rod polyimides having p-terphenyl and p-quinquephenyl moieties in the backbone and naphthyl pendant groups were synthesized by Mikroyannidis.[138c] Even though these polyimides were expected to give good solubility and thermal stability, they showed poor solubility and comparatively low thermal stability. Yufei et al.[137b] reported the synthesis of novel aromatic polyimides having pendant dendritic fragments from the corresponding diamines having pendant dendritic fragments (Figure 1.4). These polyimides were found to have good solubility in common organic solvents, but the glass transition temperatures were lower than the conventional polyimides.
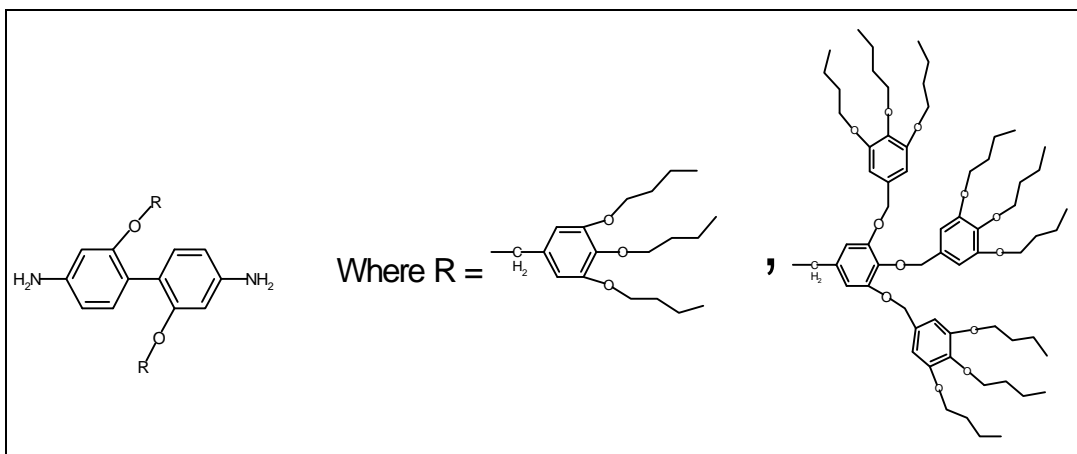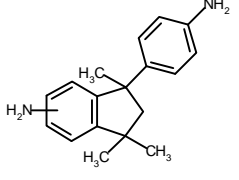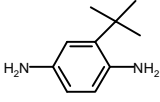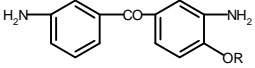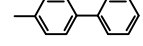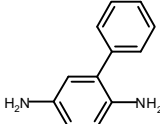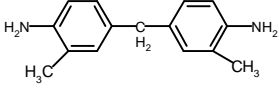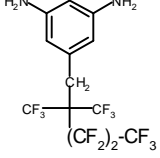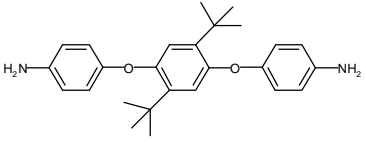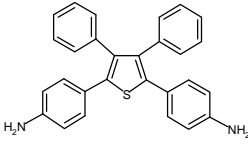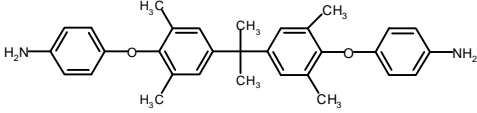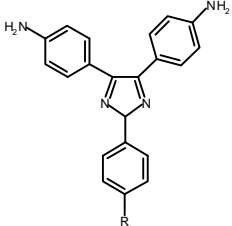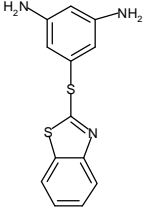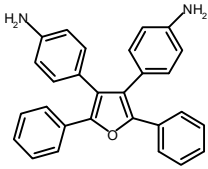
Figure 1.4. Diamine having pendant dendritic fragments
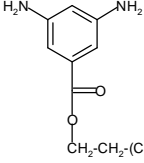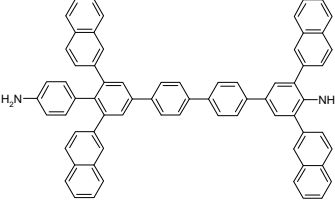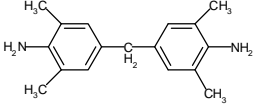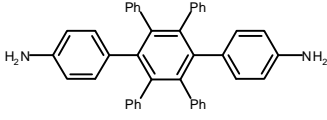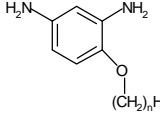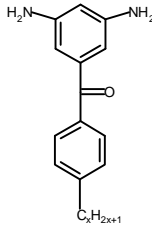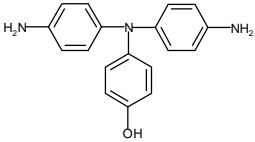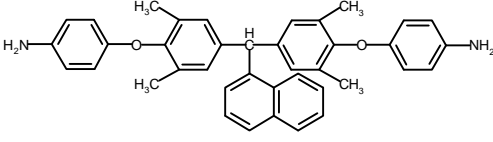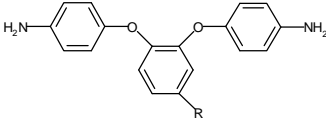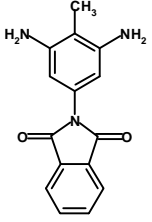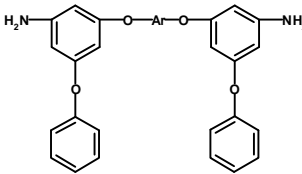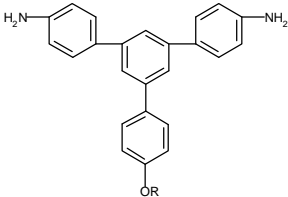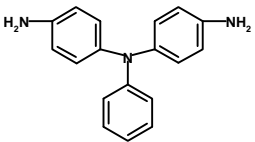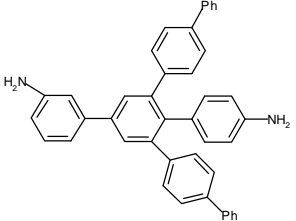
Pendant alkyl groups were also known to give soluble polyimides. Tsuda et al.[250] reported the synthesis of an alkyldiaminobenzophenone which gave soluble polyimides with anhydrides like 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCA-AH) and benzophenone tetracarboxylic acid dianhydride. Polyimides containing pendant methyl[265] and dipentadecyl[46] groups were also reported in literature. The polyimides containing pentadecyl groups were more soluble and had lower T_g than those containing methyl groups. The polyimides synthesized from 1,2-bis(4-aminophenoxy)-4-ter-butylbenzene[251] showed good solubility and showed no appreciable decomposition up to 500°C in the thermogravimetric analysis. The polyimides containing symmetric, bulky di-*tert*-butyl substituents[261] were found to be more crystalline and less soluble than the polyimides containing mono-*tert*-butyl substituent. These polyimides were found to have good thermal stability also.
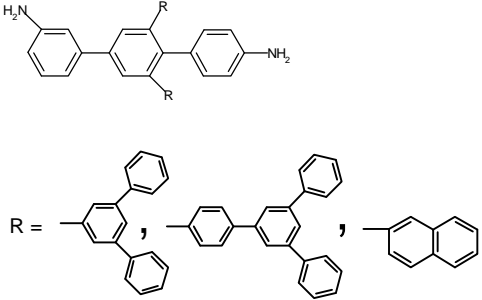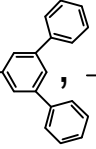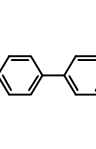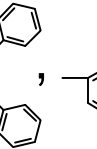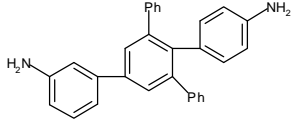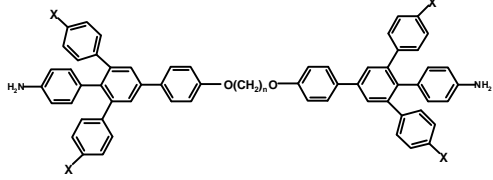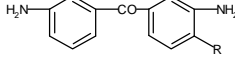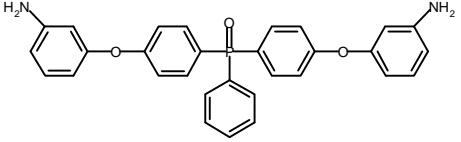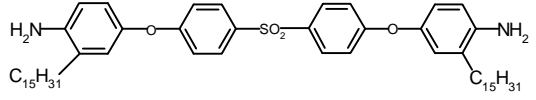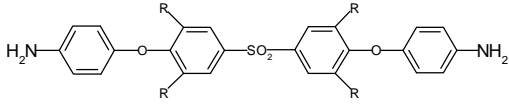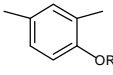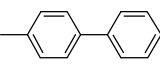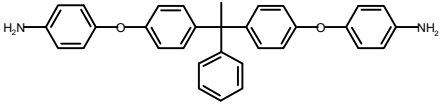
Table 1.4. Dianhydrides containing bulky pendant substitution

Dianhydrides	Refs	Dianhydrides	Refs
R: t-butyl, Ph, NO₂Ph	246		248
	252	t-butyl / t-butyl	253
	254	Ph Ph Ph Ph Ph / Ar / Ph Ph Ar:	255
	254		256
	257		

45

Table 1.5. Diamines containing bulky pendant substitution

	258		200
R = —CH₃	249		200
	259		260
	261		245b
	262	R: H, CH₃	245c
	263		299c

46
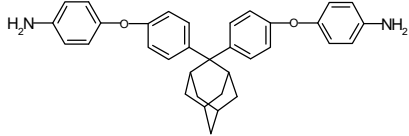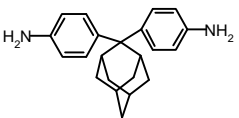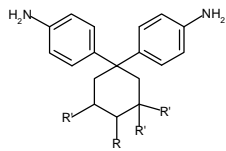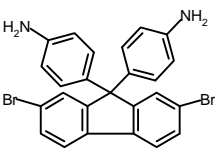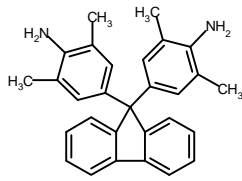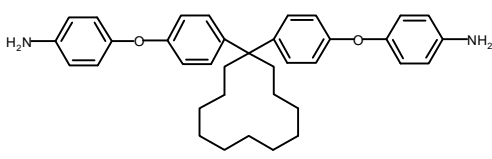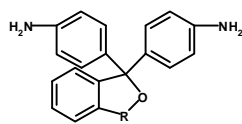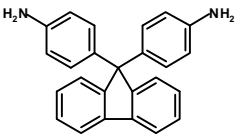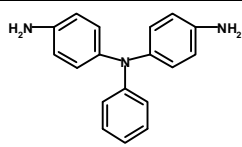
H$_2$N, NH$_2$ (structure) ester with CH$_2$-CH$_2$-(CF$_2$)$_5$-CF$_3$	264	(naphthalene-substituted diamine structure)	138c
H$_3$C, CH$_3$ H$_2$N, NH$_2$ H$_3$C, CH$_3$ (methylene-bridged structure)	265	Ph Ph H$_2$N, NH$_2$ Ph Ph (tetraphenyl structure)	266
H$_2$N, NH$_2$ O (CH$_2$)$_n$H Where n = 8, 10, 12, 14, 16	267	H$_2$N, NH$_2$ O C$_x$H$_{2x+1}$ X = 9-14	250
H$_2$N, N, NH$_2$ OH	268	H$_2$N, H$_3$C, CH$_3$ O O NH$_2$ H$_3$C, CH$_3$ (naphthyl structure)	269
H$_2$N, O O NH$_2$ R R = H, t-butyl	251	H$_2$N, CH$_3$ NH$_2$ N O O	244
H$_2$N, O Ar O NH$_2$ (diphenoxy structure)	244	H$_2$N, NH$_2$ OR	138d
H$_2$N, NH$_2$ N (triphenylamine structure)	270	Ph H$_2$N, NH$_2$ Ph	247a

R = (three structures)	271	(structure with Ph groups)	247a
X = Ph, H ; n = 6,10	272	R = C$_1$ - C$_9$ alkyl	273
(structure)	274	(structure with C$_{15}$H$_{31}$)	46
(structure with R groups)	275	R = (naphthyl, biphenyl)	97
(structure)	276		
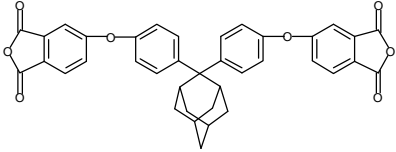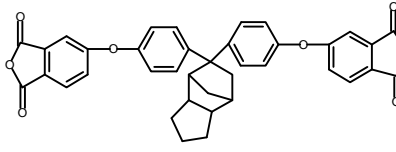
Fluorene diamines and the so called "cardo" monomers are also important alternatives for the preparation of processable polyimides.[277] Several "cardo" monomers used in the synthesis of soluble polyimides are given in Table 1.5. Several new monomers containing "cardo" groups such as cyclododecylidene, adamantane, tricyclodecane, norbornane, t-butylcyclohexylidene, phenylcyclohexylidene and diphenyl methylene were synthesized through the aromatic nucleophilic substitution of cardo bisphenols with p-chloronitrobenzene, followed by catalytic hydrogenation.[278] All these polyimides showed good solubility in

solvents like NMP, DMAc, DMF, DMSO and THF. The polyimide bearing adamantane group had the highest T_g value. Polyimide having diphenylmethylene group showed the highest thermal stability and polymer containing cyclododecylidene group showed lowest solubility than the others.

Table 1.6. Cardo monomers used in the synthesis of soluble polyimides

Diamines	Refs	Diamines	Refs
	279		280
R, R' = H R = CH₃, R' = H R = H, R' = CH₃	281		282
	283		284
R =O, NH	285		285
	270		

Dianhydrides	Refs
	286
	287

1.3.2.3 Other processable polyimides

Literature reports some meta-oriented monomers like 3,3'-diaminobiphenyl[288] for the synthesis of soluble polyimides. These polyimides were found to be more soluble than the corresponding para-oriented monomers. Tong et al.[289] reported the synthesis of polyimides having rigid but non-coplanar and nonlinear conformation from a non-coplanar dianhydride like 2,2',3,3'-biphenyltetracarboxylic dianhydride. Genies et al.[290] reported the synthesis of sulphonated naphthalenic polyimides and their use as materials for proton exchange membranes. Synthesis of novel copolyimides from a diamine containing tetrahydro[5]helicene unit and the effect of this group on the solubility of the resulting polyimides was investigated by Bender et al.[291] Fully imidized soluble polyimides have been prepared using monomers derived from diphenylindane and aromatic dianhydrides. Technical polymers (XU218, for instance), prepared from 1,1,3-trimethyldiaminophenylindane and benzophenone tetracarboxylic acid dianhydride, have been marketed over the last decade. The polyimides containing indane group showed good thermal property, with T_g values over $300^\circ C$.[292] Apart from indane group, other heterocycles have also been introduced in combination with imides in order to produce soluble aromatic copolyimides.[293] These polymers showed high thermal stability but were insoluble in organic solvents. But polyimides containing heterocyclic moieties like phenylquinoxaline,[294] oxadiazole[295] or benzimidazole[296] show an acceptable degree of solubility, high T_g values and excellent thermal stability. Soluble polyimides containing pyrazoline moieties have been synthesized from diamines like 3-(4-aminophenyl)-5-(3-aminophenyl)-2-pyrazoline.[297] These polyimides

were even soluble in solvents like dichloromethane and chloroform and had T_g's in the range 127^oC-163^oC. High molecular weight polyimides were synthesized from thianthrene-2,3,7,8-tetracarboxylicacid-5,5,10,10-tetraoxide via the Yamazaki-Higashi phosphorylation method.[298] These polyimides were found to have poor thermal stability. Several other polyimides containing tetraphenyl heterocycles have also been reported in the literature.[299]

Among the various attempts to improve the solubility of polyimides, the incorporation of alicyclic monomers seems to be a promising route. [300] Todate, a lot of alicyclic diamines and dianhydrides for the synthesis of polyimides have been developed.[301] Hore et al.[300c,d,302] investigated the thermal properties, solubility and UV-visible absorption of polyimides synthesized from some alicyclic diamines. Some polyimide resins were manufactured from cyclobutane-1,2,3,4-tetracarboxylic dianhydride and aromatic diamines.[303] Chern et al.[304] extensively studied polyimides and polyamides containing adamantyl and diadamantyl moieties. Improved solubility has also been reported for polyimides containing pendant alicyclic units.[305] Matsumoto et al.[306] reported the synthesis of different tetracarboxylic acid dianhydrides bearing a polyalicyclic structure, along with their polycondensation with aromatic diamines in NMP or DMAc. The resulting polyimides were soluble at room temperature in aprotic polar solvents and gave flexible and tough films. These polymers showed excellent thermal stability and possess good mechanical properties. Dianhydrides having a spiral carbon have also been used in the synthesis of soluble polyimides.[307]

One of the most attractive and successful attempts in obtaining processable aromatic polyimides is the introduction of fluorine atoms in the polymer backbone or the introduction of hexafluoroisopropylidene group in the main chain of the polymer.[308] Most of these fluorine containing polyimides are soluble, have high T_g and excellent thermal properties. These polymers show some improved properties like

- Low dielectric constant
- High optical transparency
- Excellent mechanical properties
- Low moisture absorption
- Increased solubility
- Low optical loss and low refractive index

The synthesis of polyimides from several fluorinated monomers have been reviewed by Sasaki and Nishi.[309]

1.3.3 Applications

Aromatic polyimides are of great interest as high performance materials because of their excellent oxidative, thermal and mechanical properties. Films of aromatic polyimides represent the largest end-use area for the polyimides because of their useful properties over an extremely broad temperature range. Several polyimide films like Kapton[®], Upilex R[®], Upilex S[®], Novax[®] etc., have been commercialized. Kapton[®] is used extensively in aerospace wire and cable, traction motors, flexible printed circuits, magnet wire, transformers and capacitors and also in many other applications. The area of electronic industry has become increasingly important in recent years with increasing polyimide use not only as film base, but also as laminates, particularly with copper. It is particularly in circuitry applications that Upilex S[®] appears to offer significant potential competition to Kapton[®]. Novax[®] has lower coefficient of thermal expansion and lower water absorption as compared to Kapton[®]. Vespel[®], the polyimide molded material manufactured by Du Pont, has been used for making polyimide bushings, roller guides, gears and bearings.[310] Polyimide fibers find application in protective clothings and filter bags. Polyimides have played an increasing role in electronics for a variety of applications. These include use as base sheet film for flexible circuitry, planarization coatings for computer chips, interlayer dielectrics and alpha particle barriers. The cross-linked polyimides have found significant application in circuit boards. Several photosensitive polyimide precursors have been used directly in circuits in order to reduce the cost of multi step processing.[311] A number of companies including Du Pont and Monsanto have developed polyimide foams. These foams find application in aircraft/aerospace, acoustical and thermal insulation, vibrational insulation etc.[312] The other product areas include electronic instrument protection, marine uses and cryogenic blankets. Polyimide adhesives and coatings are used in electrical and electronics industry. Some of the main applications of polyimides are discussed below in detail.

1.3.3.1 Polyimides as gas separation membranes

Gas separation by selective permeation through membranes of polymeric materials has attracted considerable attention for commercial exploitation and presently it is one of the fastest growing branches of separation technology.[313] The technique offers many advantages such as low energy requirement, low investment cost, easy fabrication of modules of desired size and shape etc. as compared to other techniques. The molecular structures of polymers strongly affect the permeability and permselectivity[314] and aromatic polyimides are an important class of membrane materials for gas separation because of their high permselectivity and excellent thermal and physical properties.[315] Polyimides are one of the most important high gas permselective polymers used for the separation of common gases. For example, separation factor for N_2/O_2 varies in the range of 3.25-9 depending on the chemical structure of the polyimide.[316] However there is still a general trend in the family of polyimides that compounds having high permeability show low permselectivity and those having high permselectivity show low permeability.[317] Thus, the control of the gas permeability and permselectivity has become a subject of strong research interest because of its importance in the development of new membrane materials. The relationship between the structure and gas permeation properties of aromatic polyimides has been investigated extensively in order to prepare gas separation membranes with high gas permeability and permselectivity simultaneously.[318] Now it has been recognized that simultaneous improvement in permeability and permselectivity can be achieved by attaching bulky groups onto the backbone of aromatic polyimides which restricts the motion of phenyl ring around the linkages (increases selectivity) and increases the free volume (increases permeability).[319] It has also been reported in the literature that gas permeability and permselectivity of many polymers can be increased by tailoring the chemical structure of the diamine.[320] By analyzing the permeability data for various polyimides reported in literature some broad generalities can be drawn as to how the diamine structure can affect the gas permeability properties of these polyimides.[321] The m,m' linkages generally decrease the permeability and increase the selectivity compared to p,p' placement of the diamine functions. Increasing the monomer rigidity decreases permeability and increases selectivity. Increasing alkylation ortho to amine increases permeability. Presence of CF_3 or hexafluoroisopropylidene groups either on the

rings or as linking groups increases permeability. The presence of dimethylsiloxy component in the polyimide, either in the main chain or as a graft substituent, increases permeability and decreases selectivity. Thus the key principle for achieving high selectivity and high permeability in the same material is to design polymer repeat units that minimize back bone or segmented mobility (intramolecular) and to avoid dense packing (intermolecular) of chains. A number of polyimides incorporating the above mentioned structural modifications have been employed in the synthesis of gas separation membranes.[321]

1.3.3.2 Polyimides as liquid crystal orientation layers

Another area, which has received relatively little attention in the polyimide literature, excluding patent publications, concerns the use of polyimides as liquid crystal orienting layers for display devices. Alignment and tilting of the liquid crystal molecules along the surfaces of the display substrates is an important aspect of liquid crystal technology. A tilt angle between the long molecular axes of the liquid crystal (pretilt angle) and the substrate is necessary to achieve stable electro-optical characteristics. These pretilt angles are necessary to ensure uniform unidirectional LC motion, otherwise defects called reverse tilt disclinations, can occur in twisted nematic LCD or non-twisted nematic LCD. These defects will degrade the quality of twisted nematic LCDS and without the so-called 'tilt bias angle', a twisted nematic display will have a patchy appearance.[322] The tilt bias angle required for the twisted nematic LCD's is 1° to 3° and for super twisted nematic LCD's is 5° to 14°. In almost every LCD made today, alignment and tilting are controlled by mechanically brushing the polymer film, about 100 nm thick with a velvet cloth. Several methods for measuring the tilt bias angle are reported in literature. These include, (1) crystal-rotation method[323] (2) destructive capacitive method[324] and magneto null method and (4) optical retardation method.[325] Many investigations have been done to understand the relationship between the alignment layer polymer surface structures and liquid crystal display parameters.[326] These investigations revealed that twisted nematic displays, prepared with a low pretilt angle, showed undesirable light-scattering effects and displays with a large pretilt angle on the other hand, often showed disturbing interference colors and have a reduced multiplexing capacity. In general pretilt angle depends on the properties of the LC and molecular structure and properties of the orienting polymer (especially the surface polarity and molecular orientation of the polymer

surface). Therefore to optimize the display performance, it is important to control the pretilt angle. Although many theoretical and experimental studies on LC alignment have been performed, the actual alignment mechanism on the rubbed films is still not fully understood.[327] Here the thermal requirements are not stringent and therefore the use of polyimides derived from alicyclic monomers[328] and monomers having pendant alkyl[329] groups have gained importance. Liu et al.[330] in their study of molecular design of liquid crystal alignment polyimide layer (LCAL) showed that LCAL should have flexible moieties in the polymer backbone and some long-chain alkyl groups should be introduced into the main chain or the side chain so as to raise the LC pretilt angle. In addition, some researchers have found that polyimides with long alkyl and fluorinated alkyl side branches generate high pretilt angles of LCs by rubbing.[331] They suggested that the high pretilt angles are due to steric interactions between LCs and neatly aligned branched chains. Soluble polyimide resins obtained from aliphatic tetracarboxylic dianhydride and an aromatic diamine like 3,5-diamino-N-butylbenzamide having a substituted amide group have been known to yield liquid crystal alignment agents with superior heat-resistance, transparency and liquid crystal alignment capacity.[332]   Tsuda[333] reported the synthesis of soluble polyimides based on alkyldiaminobenzophenones, which gave pretilt angles in the range of 5-20 degrees probably due to the hydrophobic interaction with the alkyl groups. Thus the main emphasis of the earlier studies in this area has been to develop polyimide alignment layers having improved alignment properties by the introduction of long pendant groups as side chains. Requirement of a polyimide to be used in LCD application is good solubility in common organic solvents, high monomer purity, high pretilt angles and low cost. It is therefore necessary to develop a polyimide alignment layer having good alignment properties and high solubility in common organic solvents and that can be readily prepared on an industrial scale from a cheap resource.

1.3.3.3 Polyimides as low dielectric constant materials

Polyimides are a class of polymers extensively used in microelectronics. They are particularly attractive as interlayer dielectrics in integrated circuit fabrication, because of their low relative permittivity,[334] low losses over a wide frequency range[335] and high breakdown voltages.[336] In addition polyimides tend to be chemically inert in the presence of many solvents, mechanically tough and flexible and many are thermally stable up to 450°C. The

dielectric constant of the conventional polyimides are in the order of 3.0 or higher[337] which is much lower than the most conventional interlayer dielectric silicon dioxide, which has a dielectric constant of 4.1. But there are problems associated with polyimide dielectrics like moisture absorption, which acts to increase the dielectric constant.[338] Development of low dielectric constant polyimides that exhibit facile processing and good thermal and mechanical behavior represent one research area that needs attention. In this regard fluorine-containing polyimides have attracted the interest of researchers since they show low moisture absorption and have low dielectric constant. The synthesis of a variety of fluorine containing polyimides has been reviewed by Rusanov et al.[339] The dielectric properties of polyimides are also dependant on the hydrophobicity[340] and the introduction of hydrophobic alkyl group in the polymer chain reduces the dielectric constant of the resulting polymer.[341] Introduction of silicon is also known to reduce the dielectric constant.

1.4   Scope and objective

From the foregoing discussions it is understood that aromatic polyamides and polyimides constitute a major class of thermally stable polymers having excellent thermal, mechanical and electrical properties over a wide range of temperature.[342, 343] However these polymers are processable only under extreme conditions which limit their application areas. Thus the enhancement of solubility of these polymers without sacrificing their excellent properties became the object of wide spread study. [344, 345] Literature reports many attempts to improve the solubility of these polymers by making use of structurally modified monomers. Various approaches have been suggested to improve the solubility of these polyamides and polyimides. These include (1) introduction of flexible segments or flexible groups, which reduce the chain stiffness, (2) introduction of bulky side substituents, which help for the separation of polymer chains and hinder the molecular packing and crystallization, (3) use of enlarged monomers containing angular bonds, which suppress coplanar structures (4) use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers, which lower regularity and molecular ordering, (5) preparation of copolyimides from two or more dianhydrides and diamines. Various monomers synthesized based on these approaches have been discussed in detail in the previous sections. The aim of the present work is to make use

of one or more of these structural modifications together to have a combined effect on the properties of the resulting polymer. With this objective in mind we decided to synthesize m-substituted monomers having bulky pendant groups like long alkyl group and phenyl group along with polar groups like ether, ester and/or amide connecting groups. Even though alkyl groups are known to improve solubility, they reduce the thermal stability of the resulting polymer to some extent. But such alkyl group containing polymers are commonly used in a variety of applications like alignment layers for liquid crystal,[330,331] gas separation membranes[346] and as materials for interlayer dielectrics in integrated circuit fabrication[334,335,336] where the thermal properties are not very stringent. Moreover, the bulky substitutions tend to disrupt the charge transfer interactions in these polymers resulting in excellent transparency and low color, which is important if the polymer has to be used in displays. Polyimides have gained more importance than polyamides in these areas because of their long term durability and low moisture absorption as compared to polyamides. Incorporation of silicon enhances solubility, improves gas permeability and dielectric properties of polyimides and polyamides. Hence it was also an objective of present work to incorporate silicon in polyimides and polyamides containing bulky pendant side chain.

There have been constant searches for new cost-effective renewable natural resources that can be used in the synthesis of polymers for specialty applications. In this regard cashew nut shell liquid, an agricultural by-product of the cashew industry, which is one of the few major and economic sources of long chain phenols, holds considerable promise as a versatile and valuable raw material for polymer production. Cardanol, a pentadecenyl phenol is one of the major constituents of cashew nut shell liquid. Though there have been few attempts on the synthesis, chemical modification, and functionalization of cardanol and its polymers, there are no reports available on the use of cardanol in the synthesis of high value polymers that can be used in specialty applications such as alignment layers for liquid crystals, gas separation membranes, and as interlayer dielectrics. Thus the main objective of this work was to make use of CNSL (Cashew Nut Shell Liquid) as a starting material for the preparation of useful compounds like polyimides and polyamides having specialty applications. Based on these objectives the following specific problems were chosen for the present work.

- Synthesis and characterization of new m-phenylene diamines containing pendant pentadecyl group along with phenoxy, benzoate or benzamide pendant group from cardanol (Figure 1.5).
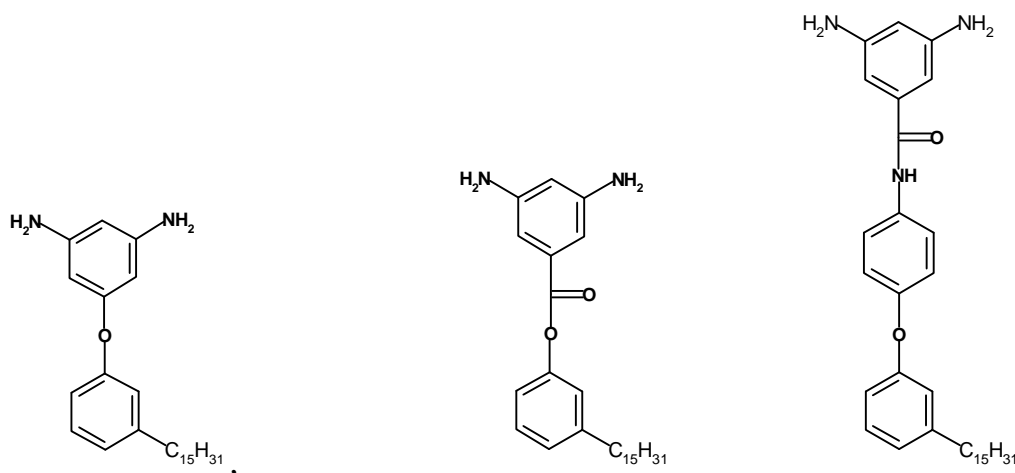
Figure 1.5. Diamines synthesized form cardanol

- Synthesis and characterization of silicon containing diacid chloride and dianhydride (Figure 1.6).
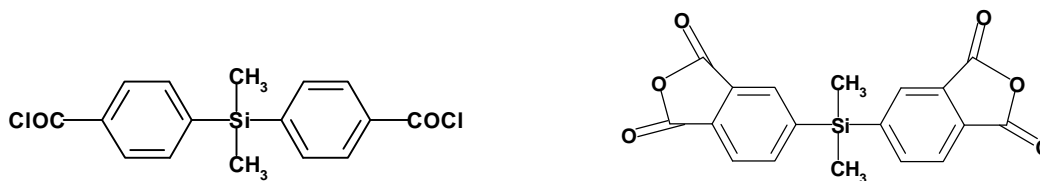
Figure 1.6. Silicon containing monomers

- Synthesis and characterization of polyamides from these diamines having long pendant groups and to study the effect of these groups on the permeability properties of these polymers
- Synthesis and characterization of polyimides and copolyimides from these diamines having long pendant groups and to study their application as alignment layers for liquid crystal and gas separation membranes and as low dielectric constant materials that can be used as interlayer dielectrics. Another objective is to study the optical transparency of these polyimide films, since this is an important property for the polyimide films to be used in electronics industry.

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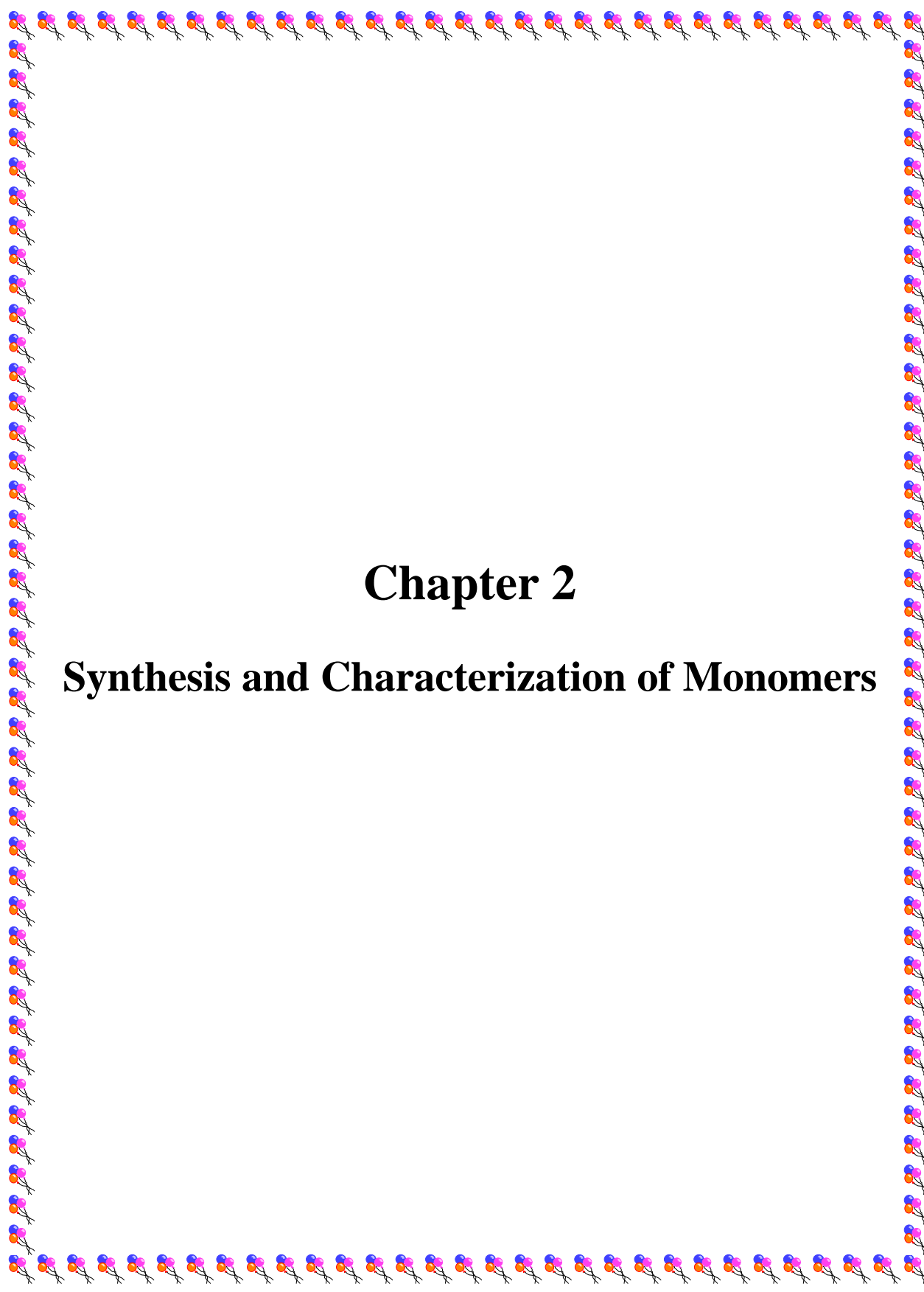
Chapter 2

Synthesis and Characterization of Monomers

2.1 Introduction

One of the important criteria that decide the final properties of a polymer, is the structure of monomers and by selecting a suitable monomer the existing properties of a polymer can be modified. Therefore in the synthesis of polymers the first step constitute the synthesis of desired monomers, which can give rise to polymers with expected/aimed properties. In the case of polyimides the commonly used monomers are diamine and dianhydride and in the case of polyamides diamine and dicarboxylic acid or acid chlorides.

Amines are derivatives of ammonia, where one, two or three of the hydrogen atoms are replaced with alkyl, cycloalkyl, aromatic or heterocyclic group. Diamines possess two primary amino groups and form a very distinct class of organic compounds. They are useful as dye intermediates, as antioxidants in the rubber industry and in the synthesis of diisocyanates. Aromatic diamines are important starting materials for the preparation of a large number of products having a wide variety of end uses. In recent years the use of diamines as building blocks for heat resistant polymers viz. polyimides, polyamides, polyamideimides and polyesterimides, has shown a marked increase. These polymers find application in different fields, such as (1) high temperature mechanical and electrical parts, (2) protective clothing for military, (3) electrical insulation, (4) desalination and gas separation membranes (5) aerospace industry and (6) optical devices.

Phenylene diamines are one of the most widely used aromatic diamines for the synthesis of polymers. There are three phenylene diamines namely ortho, meta and para. Out of these the meta isomers are the least expensive and are extensively used in synthesis of polyurethanes. Polymers from meta isomer have gained importance because of their high heat and flame resistance and polymers from para-isomer are noted for their high tensile strength and high modulus.

Even though phenylene diamines are used in the synthesis of polyamides and polyimides with exceptionally high tensile strength and high heat resistance, polymers made from them are not easily processable. Therefore it is necessary to synthesize structurally modified diamines to fine-tune the existing properties of the polymers without sacrificing

their excellent properties like thermal stability. Structurally modified phenylene diamines can be prepared by introducing flexible and/or bulky pendant substituents. The interest in these type of phenylene diamine monomers lies in the fact that they improve the solubility/processability of the resulting polymers while retaining superior properties like thermal stability as compared to other diamine monomers having flexible groups in the main chain. Among phenylene diamines, m–phenylene diamines are most suitable for improving the solubility of the resulting polymers because the m-linkages act as kinks, and helps in the disruption of symmetry and hence the synthesis of substituted m-phenylene diamines have gained importance.

A variety of starting materials have been used for the synthesis of diamines through different synthetic routes. Diamines are generally prepared by ammonolysis route or by the reduction of dinitro compounds, dioximes or dinitriles by means of suitable reducing agents. In ammonolysis route functional groups like halogen,[1] hydroxyl,[2] keto and aldehyde[3] are replaced with amino group and therefore a new bond is formed between carbon and nitrogen, whereas in reduction route a bond between carbon and nitrogen already exists in the molecule. Other methods used in the synthesis of diamines include (1) Hofmann degradation[4] (2) Schmidt reaction[5] (3) condensation of sodium salt of aminophenol with dihalo diphenyl sulfone[6] and (4) condensation of amine or its hydrochloride with a ketone or aldehyde.[7]

Among the above mentioned methods the most widely used one is the reduction route. Earlier reports on synthesis of amines by reduction were based on stoichiometric reagents like (1) metal and acid (Fe or Zn or Sn along with hydrochloric acid, sulphuric acid, acetic acid or formic acid), (2) metal and alkali (Zn or Fe in alkaline solutions), (3) sulfides in alkaline solutions (sodium sulfide or disulfide, ammonium sulfide, polysulfides or hydrosulfides), (4) sodium hydrosulfite in alkaline solution, (5) metal hydrides like lithium aluminium hydride or lithium hydride or sodium borohydride and (7) amalgams.[8] The substrates used for reduction include (1) nitro compounds, (2) amides, (3) oximes, (4) isocyanates, isothiocyanates, azides, or N-nitroso compounds, and (5) azo, azoxy and hydrazo compounds.[8,9] The stoichiometric reagents mentioned above produce large amounts of salts as by-products posing environmental problems. Therefore catalytic hydrogenation processes are gaining particular attention as they provide environmentally friendly and cleaner synthetic routes.

Catalytic hydrogenation is the most efficient route for the synthesis of diamines and can be carried out using gaseous hydrogen[9] or using hydrogen donors like hydrazine hydrate[9] and formic acid[10] (transfer hydrogenation) in presence of a catalyst. The catalysts used for transfer hydrogenation include Raney Nickel, platinum and palladium black. The transfer hydrogenation reactions are widely used in the reduction of nitro compounds, since they don't need any specific reactors and are considered as an alternative for direct hydrogenation. But hydrogenation using gaseous hydrogen is more effective and requires shorter reaction times. Extensive studies have been carried out on different types of catalyst, pressures, temperatures, solvent, concentration of reactants and mode of reaction. A number of patents are available on the synthesis of aliphatic,[11] cycloaliphatic[12] and aromatic diamines[13] by catalytic hydrogenation.

The diamines used in the synthesis of polymers are mainly synthesized by the catalytic hydrogenation of the respective dinitro compounds. This is due to the fact that many substituted dinitro compounds can be readily prepared by simple substitution reactions of dinitro or mononitro halides and acid chlorides with compounds having an active hydrogen atom like bisphenols, phenols or amines. The most widely used catalysts for these reductions include palladium and platinum catalysts. Ruthenium and rhodium catalysts have also been used, but they have only limited and specialized use. Most of the diamines discussed in Chapter 1, Sections 1.2.2 and 1.3.2, which are used in the synthesis of high performance polymers like polyamides and polyimides are in turn synthesized by catalytic hydrogenation of respective dinitro compounds.

From the above discussions it is evident that substituted aromatic nitro compounds are useful substrates for the synthesis of substituted diamines, which in turn are important intermediates for the synthesis of soluble polymers and can be synthesized by simple substitution reactions. It is also evident that, the reduction of these nitro compounds by catalytic hydrogenation is the most popular and efficient route used in the synthesis of diamines. Among different diamino compounds known, the phenylene diamines have gained particular attention because of the excellent properties they impart to the resulting polymers. Substituted m-phenylene diamines are known to improve the solubility of thermally stable polymers like polyamides without affecting their thermal properties. Structurally modified m-

phenylene diamines can be synthesized from dinitro compounds obtained by the reaction of 2,4-dinitrochlorobenzene or 3,5-dinitrobenzoyl chloride with compounds having an active hydrogen atom, like monoamines, alcohols or phenols. [14,15,16] Even though these substituted phenylene diamines can be made by simple condensation reactions, not many reports are available on their synthesis.

The objective of the present work was to synthesize different substituted phenylene dinitro compounds and diamino compounds having flexible connecting groups and pendant bulky substituents .To achieve this objective, a naturally available phenol, 3-pentadecylphenol (cardanol) having a pendant long alkyl group and a functional group like –OH, having an acidic hydrogen that can be easily replaced in substitution reactions is made use of.

Phenylene diamines have to be reacted with other difunctional monomers like diacid chlorides or dicarboxylic acids to give polyamides and with dianhydrides to give polyimides. Structure of both monomers influence the final properties of polymers. The commercially available and most widely used diacids/diacid chlorides include terephthalic and isophthalic acids/diacid chlorides and dianhydrides include pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylicacid dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylicacid dianhydride (BTDA), 3,3',4,4'-oxydiphthalic dianhydride (ODPA) and 4,4'-hexafluoroisopropylidenebis (phthalic anhydride) (6-FDA). There are literature reports on some silicon containing diacid chloride and dianhydride monomers useful in the synthesis of soluble polyamides[17] and polyimides[18]. But silicon containing diacid chlorides and dianhydrides are not commercially available and have to be synthesized. Incorporation of silicon in polyamides and polyimides enhances solubility/processability of these polymers without affecting other properties and hence synthesis of silicon containing diacid chlorides and dianhydrides has gained special importance.

In this chapter the synthesis of new substituted phenylene dinitro compounds and the corresponding diamino compounds from cardanol is discussed. The dinitro compounds and the corresponding diamino compounds were designed to have flexible connecting groups like ether, ester and amide along with bulky pendant substituents like pentadecylphenyl and pentadecyldiphenylether, to improve the solubility of foreseen polymers. The dinitro compounds synthesized by reacting cardanol with 2,4-dinitrochlorobenzene or 3,5-

dinitrobenzoyl chloride were then catalytically reduced to diamino compounds in presence of gaseous hydrogen using supported palladium catalyst like Pd/C. Silicon containing diacid chloride and dianhydride that can be condensed with these diamines to give polyamides and polyimides with an additional enhancement in solubility were also synthesized.

2.2 Experimental

2.2.1 Materials

2,4-dinitrochorobenzene was recrystallized from ethanol (Fluka, Switzerland). Tetrahydrofuran (S.D. Fine Chem., India), diethyl ether (S.D. Fine Chem., India), benzene (S.D. Fine Chem., India) and n-hexane (S.D. Fine Chem., India) were first dried over $CaCl_2$, then refluxed with sodium and distilled. Dichloromethane (S.D. Fine Chem., India) and carbon tetrachloride (S.D. Fine Chem., India) were dried over $CaCl_2$, refluxed with P_2O_5 and fractionally distilled. Dichlorodimethylsilane (Fluka A.G., Switzerland), acetic anhydride (S. D. Fine Chem., India) and thionyl chloride (S. D. Fine Chem., India) were distilled prior to use. Rectified spirit was distilled twice before use. Dimethylformamide was dried over CaH_2 and vacuum distilled. Potassium carbonate (S. D. Fine Chem., India), was dried at $120^{o}C$ prior to use. Bromine (S. D. Fine Chem., India), xylene (S. D. Fine Chem., India), bromotoluene (S. D. Fine Chem., India), lithium metal (Aldrich, USA), p-chloronitrobenzene (Fluka, Switzerland), N-methyl imidazole (Fluka, Switzerland), methyl ethyl ketone (S. D. Fine Chem., India), petroleum ether $(60-80^{o}C)$ (S. D. Fine Chem., India), petroleum ether $(40-60^{o}C)$ (S. D. Fine Chem., India), 5%Pd/C (Aldrich, USA), 10%Pd/C (Aldrich, USA), methanol (S. D. Fine Chem., India), 3,5-dinitro benzoic acid (S. D. Fine Chem., India), potassium permanganate (S. D. Fine Chem., India), pyridine (S. D. Fine Chem., India), hydrochloric acid (S. D. Fine Chem., India) and sodium bicarbonate (S. D. Fine Chem., India) were used as received.

Cardanol was obtained by the vacuum distillation of cashew nut shell liquid at $220^{o}C/1mm$ Hg. (Lit. bp $230-235^{o}C/3-4$ mm Hg).[19]

81

2.2.2 Analytical methods

The elemental analysis was carried out by CHNS-O, EA 1108-Elemental Analyser of Carlo-Erba Instruments, Italy. The FT-IR spectra were recorded on a Perkin-Elmer 599B spectrophotometer in nujol mull and KBr pellets. ^{1}H NMR spectra were recorded on a Bruker NMR instrument at 200 and 300 MHz and ^{13}C NMR spectra were recorded on a Bruker NMR instrument at 200MHz. The mass spectra were recorded on AI MS 30 double beam mass spectrometer.

2.2.3 Synthesis of new substituted phenylene diamines

2.2.3.1 Synthesis of 4-(3-pentadecylphenoxy)benzene-1,3-diamine

This diamine was synthesized in two steps starting from a nucleophilic substitution reaction of 2,4-dinitrochlorobenzene with 3-pentadecylphenol obtained by the hydrogenation of cardanol (3-pentadecenylphenol), in the presence of an acid acceptor like N-methyl imidazole, followed by catalytic reduction of the resulting dinitro compound with Pd/C. The various steps involved in the synthesis of this diamine is outlined in Scheme 2.1.

(i) Synthesis of 3-pentadecylphenol (1a)

500 g (1.64 mol) of 3-pentadecenylphenol obtained from cashew nut shell liquid was distilled twice and hydrogenated in presence of 1.5 g 5%Pd/C catalyst at 70°C in a Parr autoclave under 600 psi hydrogen pressure. When no more hydrogen absorption was noticed, the hydrogenation was stopped and the product filtered and recrystallized from petroleum ether (40-60^{0}C) to obtain 3-pentadecylphenol (tetrahydroanacardol) (THA).

Yield: 480 g (86.5%)

Melting point: 50-51^{0}C (Lit. [20] mp: 51°C).

FT-IR (KBr, cm^{-1}): 3342 (-OH stretching), 2925, 2849 (aliphatic –CH).

^{1}H NMR (CDCl$_3$, δ ppm): 7.18 (t, 1H, H$_d$), 6.65-6.85 (m, 3H, H$_c$, H$_b$ and H$_e$), 5.5-5.85 (s, 1H, H$_a$), 1.15-1.7 (m, 26H, -(CH$_2$)$_3$), 2.59 (t, 2H, -CH$_2$), 0.95 (t, 3H, -CH$_3$).

Elemental analysis:	C%	H%
Calculated	82.89	11.84
Observed	82.5	11.62

(ii) Synthesis of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b)

To a 100 mL three necked round bottom flask equipped with a reflux condenser, thermowell and magnetic stirrer was added 5 g (0.016 mol) of 3-pentadecylphenol, 1.35 g (1.3 mL, 0.016 mol) of N-methyl imidazole and 50 mL methyl ethyl ketone and the solution was stirred for 1.5 h. Then 3.33 g (0.016 mol) of 2,4-dinitrochlorobenzene was added to this and the reaction mixture was refluxed for 3 h. The solvent was then distilled off and the residue was dissolved in ether. The ether solution was then washed with water, 5% NaOH solution and again with water. Then the ether solution was dried with sodium sulphate and the ether distilled off to get the crude product. This was then recrystallized from petroleum ether 40-60°C to obtain pure dinitro compound.

Yield: 7.3g (94.7%)

Melting point: 63-64°C

FT-IR (KBr, cm^{-1}): 1532, 1346 (-NO$_2$ stretching), 1280 (-C-O-C-).

^{1}H NMR (CDCl$_3$, δ ppm): 8.82-8.93 (d, 1H, H$_a$), 8.26-8.41 (dd, 1H, H$_b$), 7.38 (t, 1H, H$_e$), 7.11-7.23 (d, 1H, H$_c$), 6.87-7.10 (m, 3H, H$_d$, H$_f$ and H$_g$), 2.64 (t, 2H, benzylic –CH$_2$), 1.20-1.73 (m, 26H, -(CH$_2$)$_3$), 0.88 (t, 3H, -CH$_3$),

Mass spectrum: Molecular ion peak (M$^+$) at 470.

Elemental analysis:	C%	H%	N%
Calculated:	68.93	8.08	5.95
Observed:	68.97	8.21	5.77

(iii) Synthesis of 4-(3-pentadecylphenoxy)benzene-1,3-diamine (1c)

3 g (0.0063 mol) of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene was dissolved in 100 mL methanol in a Parr autoclave and reduced using 0.1 g 5%Pd/C catalyst at 70^{0}C and 600 psi hydrogen pressure. When the absorption of hydrogen was complete the solution was filtered to remove the catalyst and the methanol distilled off. The residue was then dissolved in ether and treated with activated charcoal. After the removal of ether the residue was recrystallized from petroleum ether (40-60°C) to obtain the pure diamine.

Cashew nut shell liquid $\xrightarrow{\text{220}^0\text{C /1mm Hg}}$ **3-pentadecenylphenol** ($C_{15}H_{27}$)

$\xrightarrow[\text{Pd/C, 600psi}]{\text{70}^o\text{C, H}_2}$ **3-pentadecylphenol (1a)** ($C_{15}H_{31}$)

Pd/C, MeOH

1-chloro-2,4-dinitrobenzene $\xrightarrow{\text{NMI, MEK, Reflux}}$

1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b) ($C_{15}H_{31}$)

$\xrightarrow[\substack{\text{600 psi, 70}^o\text{C} \\ \text{MeOH}}]{\text{H}_2\text{, Pd/C}}$ **4-(3-pentadecylphenoxy)benzene-1,3-diamine (1c)** ($C_{15}H_{31}$)
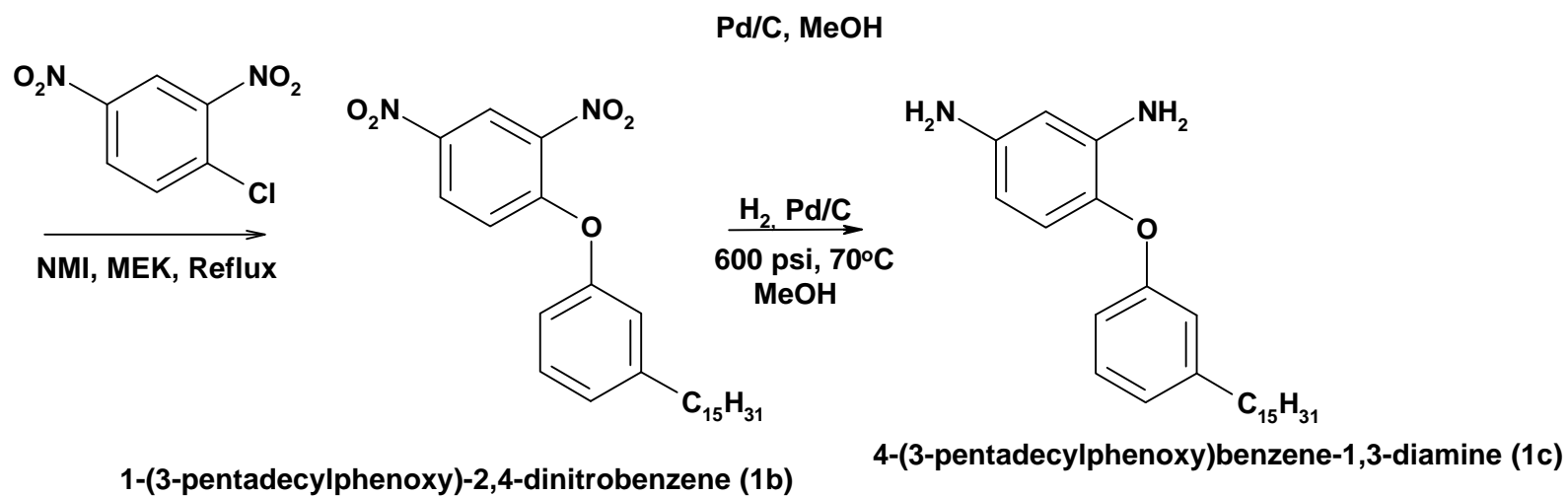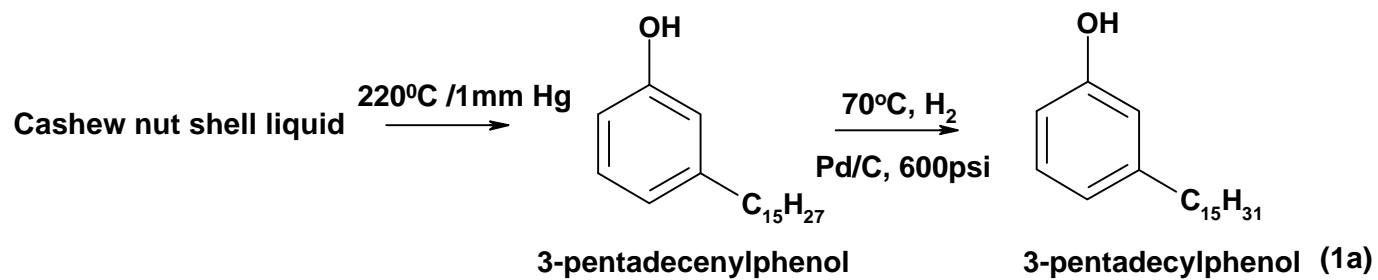
Scheme 2.1. Synthesis of 4-(3-pentadecylphenoxy)benzene-1,3-diamine

Yield: 2.23g (86%)

Melting point: 55°C

FT-IR (KBr, cm^{-1}): 3400-3456 (-N-H stretching), 1620 (-N-H deformation), 1510, 1488 (-C-C- stretching of aromatic ring), 1218 (-C-O-C-), 1244 (-C-N stretching).

^{1}H NMR (CDCl$_3$, δ ppm): 7.17 (t, 1H, H$_e$), 6.7-6.8 (m, 4H, H$_c$, H$_d$, H$_f$, H$_g$), 6.05-6.2 (m, 2H, H$_a$, and H$_b$), 2.65-3.5 (s (broad), 4H, -NH$_2$), 2.55 (t, 2H, benzylic –CH$_2$), 1.2-1.7 (m, 26H, -(CH$_2$)$_3$), 0.89 (t, 3H, -CH$_3$).

^{13}C NMR (CDCl$_3$, δ ppm): 158.39 (C$_7$), 144.65 (C$_{11}$), 143.65 (C$_3$), 139.65 (C$_6$), 135.09 (C$_1$), 129.06 (C$_9$), 121.86 (C$_5$,C$_{10}$), 115.94 (C$_{12}$), 112.89 (C$_8$), 105.53 (C$_4$), 103.11 (C$_2$).

Mass spectrum: Molecular ion peak (M$^+$) at 410

Elemental analysis:	C%	H%	N%
Calculated:	79.02	10.24	6.82
Observed:	79.88	9.91	6.62

2.2.3.2 Synthesis of 3-pentadecylphenyl-3,5-diaminobenzoate

This diamine was synthesized by a simple condensation reaction of 3,5-dinitrobenzoyl chloride with 3-pentadecylphenol in the presence of an acid acceptor like N-methyl imidazole, followed by catalytic reduction of the resulting dinitro compound with Pd/C. The various steps involved in the synthesis of this diamine are outlined in Scheme 2.2.

(i) Synthesis of 3,5-dinitrobenzoylchloride (2a)

To a single necked round bottom flask equipped with a reflux condenser, guard tube and magnetic stirrer was added 20 g (0.094 mol) of 3,5-dinitrobenzoic acid and 80 mL of thionyl chloride. The solution was then refluxed with stirring for 6-8 h (till the solution became clear) and excess thionyl chloride was distilled out. Then 50 mL of dry benzene was added to the product and distilled to remove traces of thionyl chloride. After the complete removal of benzene, 3,5-DNBC formed was recrystallized from carbon tetra chloride after charcoal treatment.

Yield: 20.65 g (95%)

Melting point: 69.5^{0}C

FT-IR (KBr, cm^{-1}): 1757 ($-\overset{\overset{O}{\|}}{C}-$), 1538, 1346 (-NO$_2$ stretching).

^{1}H NMR (CDCl$_3$, δ ppm): 9.02-9.57 (m, 3H)

(ii) Synthesis of 3-pentadecylphenyl-3,5-dinitrobenzoate (2b)

To a 500 mL three necked round bottom flask equipped with a magnetic stirrer, reflux condenser, thermowell, nitrogen gas inlet and guard tube was added 10 g (0.032 mol) of 3-pentadecylphenol, 2.68 g (2.61 mL, 0.032 mol) N-methyl imidazole and 150 mL dry THF under a stream of nitrogen and the solution was stirred well and cooled to 0°C. Then a solution of 8 g (0.034 mol) 3,5-dinitrobenzoyl chloride in 30 mL dry THF was added dropwise to this with constant stirring over a period of 1 h, maintaining the temperature at 0°C throughout the addition. Then the reaction mixture was stirred at room temperature for 5 h and then at 70°C for 3 h. Then THF was distilled off under a stream of nitrogen to obtain a dark yellow residue. This was then dissolved in diethyl ether and the ether layer washed with a 5% solution of sodium bicarbonate to remove any residual acid. After this, it was thoroughly washed with distilled water to remove the alkali, dried with anhydrous sodium sulphate and the ether distilled off. The crude product obtained was then recrystallized from ethanol.

Yield: 14.67 g (90%)

Melting point: 73-74°C

FT-IR (KBr, cm^{-1}): 1742 ($-\overset{\overset{O}{\|}}{C}-$), 1548, 1344 (-NO$_2$ stretching), 1268 ($-C-\overset{\overset{O}{\|}}{C}-O-$), 1162 (-O-C-C-).

^{1}H NMR (CDCl$_3$, δ ppm): 9.27-9.37 (m, 3H, H$_a$, H$_b$, H$_c$), 7.39 (t, 1H, H$_e$), 7.04-7.23 (m, 3H, H$_d$, H$_f$, H$_g$), 2.68 (t, 2H, benzylic –CH$_2$), 1.16-1.81 (m, 26H, (-CH$_2$)$_{13}$), 0.89 (t, 3H, -CH$_3$).

Mass spectrum: Molecular ion (M$^+$) peak at 498.

Elemental analysis:	C%	H%	N%
Calculated:	67.46	7.63	5.62
Observed:	67.60	7.54	5.55

(iii) Synthesis of 3-pentadecylphenyl-3,5-diaminobenzoate (2c)

3 g (0.006 mol) of 3-pentadecylphenyl-3,5-dinitrobenzoate was dissolved in 20 mL ethanol in a Parr autoclave and reduced using 0.1 g 10%Pd/C catalyst at 40^0C and 40 psi hydrogen pressure. When the absorption of hydrogen was complete the solution was filtered to remove the catalyst and the diamine recrystallized from the filtrate.

Yield: 2.41 g (91.6 %)

Melting point: 80^oC

FT-IR (KBr, cm^{-1}): 3366-3456 (-N-H stretching), 1716 ($-\overset{\overset{\text{O}}{\|}}{\text{C}}-$), 1604 (-N-H deformation), 1374 (-C-N stretching), 1210 ($-\text{C}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-$), 1151 (-O-C-C-).

^{1}H NMR (CDCl$_3$, δ ppm): 7.32 (t, 1H, H$_e$), 6.96-7.11 (m, 3H, H$_d$, H$_f$, H$_g$), 6.8-6.96 (s, 2H, H$_b$, H$_c$), 6.26 (s, 1H, H$_a$), 3.52-3.91 (s, 4H, -NH$_2$), 2.64 (t, 2H, benzylic –CH$_2$), 1.12-1.81 (m, 26H, -(CH)$_2$)$_{13}$), 0.89 (t, 3H, -CH3).

^{13}C NMR (CDCl$_3$, δ ppm): 165.49 (C$_7$), 150.86 (C$_8$), 147.62 (C$_1$, C$_3$), 144.50 (C$_{12}$), 131.19 (C$_5$), 128.84 (C$_{10}$), 125.57 (C$_{11}$), 121.34 (C$_{13}$), 118.66 (C$_9$), 106.93 (C$_6$, C$_4$), 105.94 (C$_2$).

Mass spectrum: Molecular ion peak (M$^+$) at 438

Elemental analysis:	C%	H%	N%
Calculated:	76.6	9.58	6.39
Observed:	77.56	8.69	6.29
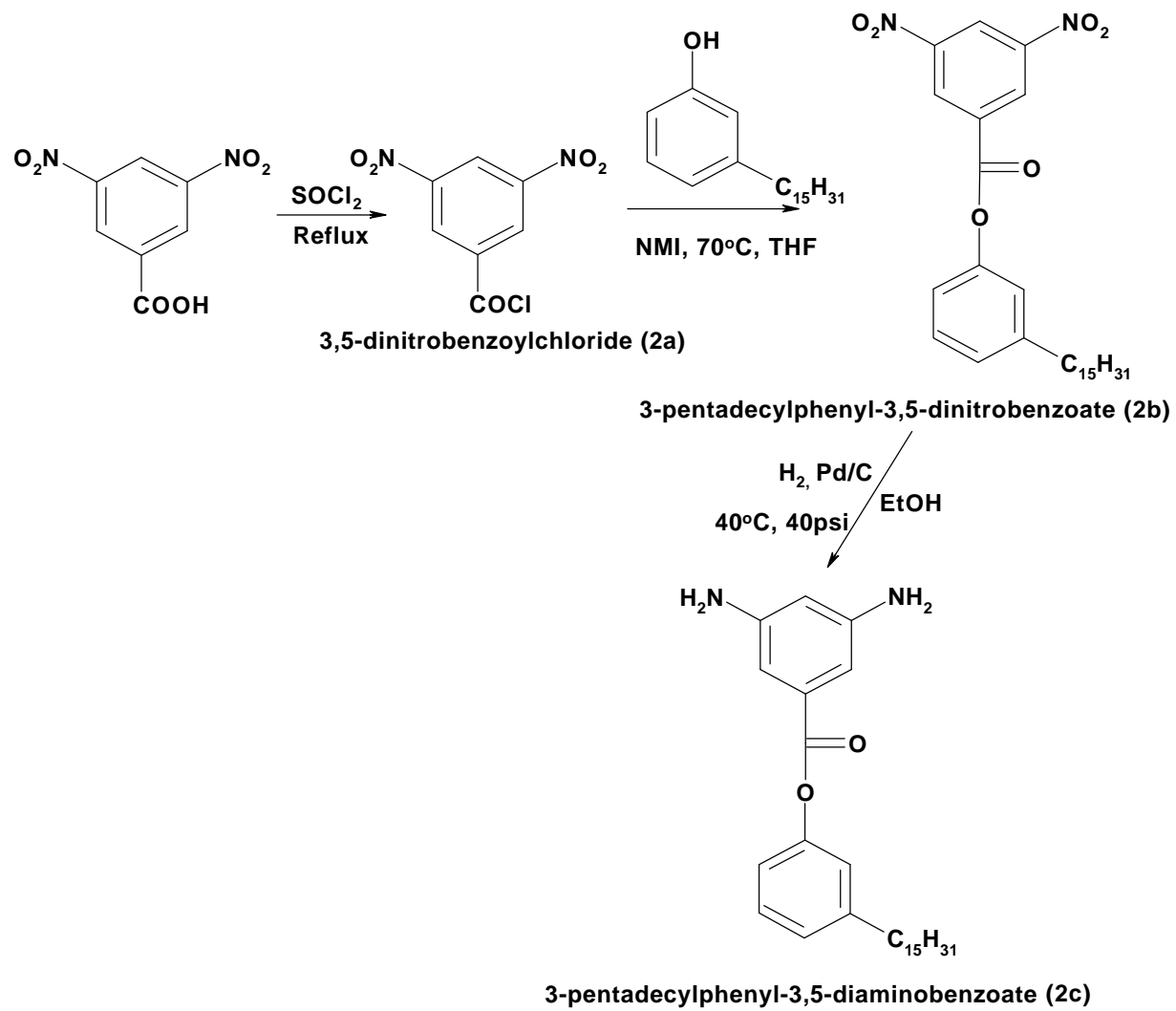
Scheme 2.2. Synthesis of 3-pentadecylphenyl-3,5-diaminobenzoate

2.2.3.3 Synthesis of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide

This diamine was synthesized in four steps from 3-pentadecylphenol. In the first step 3-pentadecylphenol was condensed with 1-chloro-4-nitrobenzene in presence of K_2CO_3 and the resulting 4-nitro-3'-pentadecyldiphenyl ether was catalytically reduced to 4-amino-3'-pentadecyldiphenyl ether using Pd/C in the second step. Then 4-amino-3'-pentadecyldiphenyl ether was reacted with 3,5-dinitrobenzoyl chloride in presence of an acid acceptor like N-methyl imidazole, to give 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl)benzamide. This was then catalytically reduced with Pd/C to the corresponding diamine. The various steps involved in the synthesis of this diamine are outlined in Scheme 2.3.

(i) Synthesis of 4-nitro-3′-pentadecyldiphenyl ether (3a)

To a 100 mL three necked round bottom flask equipped with a magnetic stirrer, reflux condenser, thermowell, nitrogen inlet and guard tube was added 3 g (0.0098 mol) of 3-pentadecylphenol, 1.55 g (0.0098 mol) of 1-chloro-4-nitrobenzene, 1.36 g (0.0098mol) of K_2CO_3 and 15 mL DMF at room temperature under a stream of nitrogen. The reaction mixture was then heated to 140^0C and the reaction continued for 8 h at this temperature. Then the reaction mixture was cooled to room temperature and poured into excess water to precipitate the product. The crude product was filtered and then washed with large excess of water, dried and recrystallized from ethanol.

Yield: 3.79 g (91%)

Melting point: 45-47°C

FTIR: IR (KBr, cm^{-1}): 1520, 1344 (-NO$_2$ stretching), 1247 (-C-O-C-), 850 (-C-N stretching).

^{1}H NMR (CDCl$_3$, δ ppm): 8.16-8.28 (d, 2H, H$_a$, H$_b$), 7.28 – 7.41 (t, 1H, H$_g$), 6.86-7.15 (m, 5H, H$_f$, H$_e$, H$_c$, H$_d$, H$_h$), 2.63 (t, 2H, benzylic –CH$_2$), 1.10 – 1.77 (m, 26H, -(CH$_2$)$_{13}$), 0.89 (t, 3H, -CH$_3$)

Elemental analysis:	C%	H%	N%
Calculated:	76.23	9.17	3.29
Observed:	76.19	9.20	3.10

(ii) Synthesis of 4-amino-3′-pentadecyldiphenyl ether (3b)

0.3 g (0.007 mol) 4-nitro-3'-pentadecyldiphenyl ether was dissolved in 20 mL ethanol in a Parr autoclave and reduced using 0.1 g 10%Pd/C catalyst at 70^0C and 600 psi hydrogen pressure. When the absorption of hydrogen was complete the solution was filtered to remove the catalyst and the product recrystallized from the filtrate.

Yield: 2.44 g (90.4%)

Melting point: $63 - 65^0$C

FT-IR (KBr, cm^{-1}): 3360-3444 (-N-H stretching), 1614 (-N-H deformation), 1336 (-C-N stretching), 1248 (-C-O-C-).

^{1}H NMR (CDCl$_3$, δ ppm): 7.19 (t, 1H, H$_g$), 6.62-6.94 (m, 7H, H$_f$, H$_a$, H$_e$, H$_b$, H$_h$ H$_d$, H$_c$), 3.01–3.93 (s (broad), 2H, -NH$_2$), 2.56 (t, 2H, benzylic –CH$_2$), 1.16–1.71 (m, 26H, -(CH$_2$)$_{13}$), 0.9 (t, 3H, -CH$_3$)

Elemental analysis:	C%	H%	N%
Calculated:	82.02	10.37	3.54
Observed:	82.00	10.36	3.51

(iii) Synthesis of 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (3c)

To a 250 mL three necked flask equipped with a magnetic stirrer, reflux condenser, a nitrogen gas inlet and a guard tube was added 3 g (0.0075mol) of 4-amino-3'-pentadecylphenyldiphenylether, 0.61 mL (0.0076 mol) N-methyl imidazole, and 18 mL dry dichloroethane and the reaction mixture was cooled to 0^oC. Then 1.84 g (0.008 mol) of 3,5-dinitrobenzoyl chloride in 5 mL dry dichloroethane was added drop wise over a period of 0.5 h under a stream of nitrogen, maintaining the temperature at 0^oC. After the addition the reaction mixture was stirred at room temperature for 3 h and then at 70^oC for 3 h. Then dichloroethane was distilled off and the crude product obtained was washed with saturated sodium bicarbonate solution and then with water, dried and recrystallized from ethanol.

Yield: 4.1 g (91.7%)

Melting point: 110-112°C

FT-IR (KBr, cm^{-1}): 3296 (-N-H stretching), 1652 ($-\overset{\overset{\displaystyle O}{\|}}{C}-$), 1539, 1342 (-NO$_2$ stretching), 1252(-C-O-C-).

^{1}H NMR (CDCl$_3$, δ ppm): 9.18-9.23 (s, 1H, H$_a$), 9.03-9.10 (s, 2H, H$_b$, H$_c$), 8.14-8.23 (s, 1H, -NH), 7.54-7.65 (d, 2H, H$_e$, H$_d$), 7.20-7.29 (t, 1H, H$_j$), 6.99-7.09 (d, 2H, H$_f$, H$_g$), 6.91 – 6.99 (d, 1H, H$_k$), 6.77-6.89 (m, 2H, H$_i$, H$_h$), 2.59 (t, 2H, benzylic –CH$_2$), 1.16 – 1.70 (m, 26H, -(CH$_2$)$_{13}$), 0.88 (t, 3H, -CH$_3$)

Mass spectrum: Molecular ion peak (M$^+$) at 589.

Elemental analysis:	C%	H%	N%
Calculated:	69.26	7.3	7.13
Observed:	69.35	6.9	6.52

(iv) Synthesis of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (3d)

3 g (0.005 mol) 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl)benzamide, was dissolved in 20 mL ethanol and reduced using 0.1 g 10%Pd/C catalyst at 40^{0}C and 40 psi hydrogen pressure until no more hydrogen was absorbed. The catalyst was then filtered and the diamine recrystallized from the filtrate.

Yield: 2.4 g (89.2%)

Melting point: 115-118°C

FT-IR (Nujol, cm^{-1}): 3408-3467 (-N-H stretching of amine), 3308 (-N-H stretching of amide), 1646 ($-\overset{\overset{\displaystyle O}{\|}}{C}-$), 1592 (-N-H deformation of amine), 1522 (-N-H deformation of amide), 1356 (-C-N stretching of amine), 1241 (-C-O-C-).

^{1}H NMR (CDCl$_3$, δ ppm): 7.98 (s, 1H, -NH), 7.47-7.62 (d, 2H, H$_d$, H$_e$), 7.15-7.24 (t, 1H, H$_j$), 6.94-7.01 (d, 2H, H$_f$, H$_g$), 6.87-6.92 (d, 1H, H$_k$), 6.72-6.86 (m, 2H, H$_i$, H$_h$), 6.50 (s, 2H, H$_b$, H$_c$), 6.07 (s, 1H, H$_a$), 2.97-3.92 (s (broad), 4H, –NH$_2$), 2.56 (t, 2H, benzylic –CH$_2$), 1.09 – 1.70 (m, 26H, -(CH$_2$)$_{13}$), 0.88 (t, 3H, -CH$_3$).

4-nitro-3'-pentadecyldiphenyl ether (3a)

4-amino-3'pentadecyphenyldiphenyl ether (3b)

3,5-dinitro-N-(4-(3- pentadecylphenoxy) phenyl) benzamide (3c)

3,5-diamino-N-(4-(3- pentadecylphenoxy) phenyl) benzamide (3d)
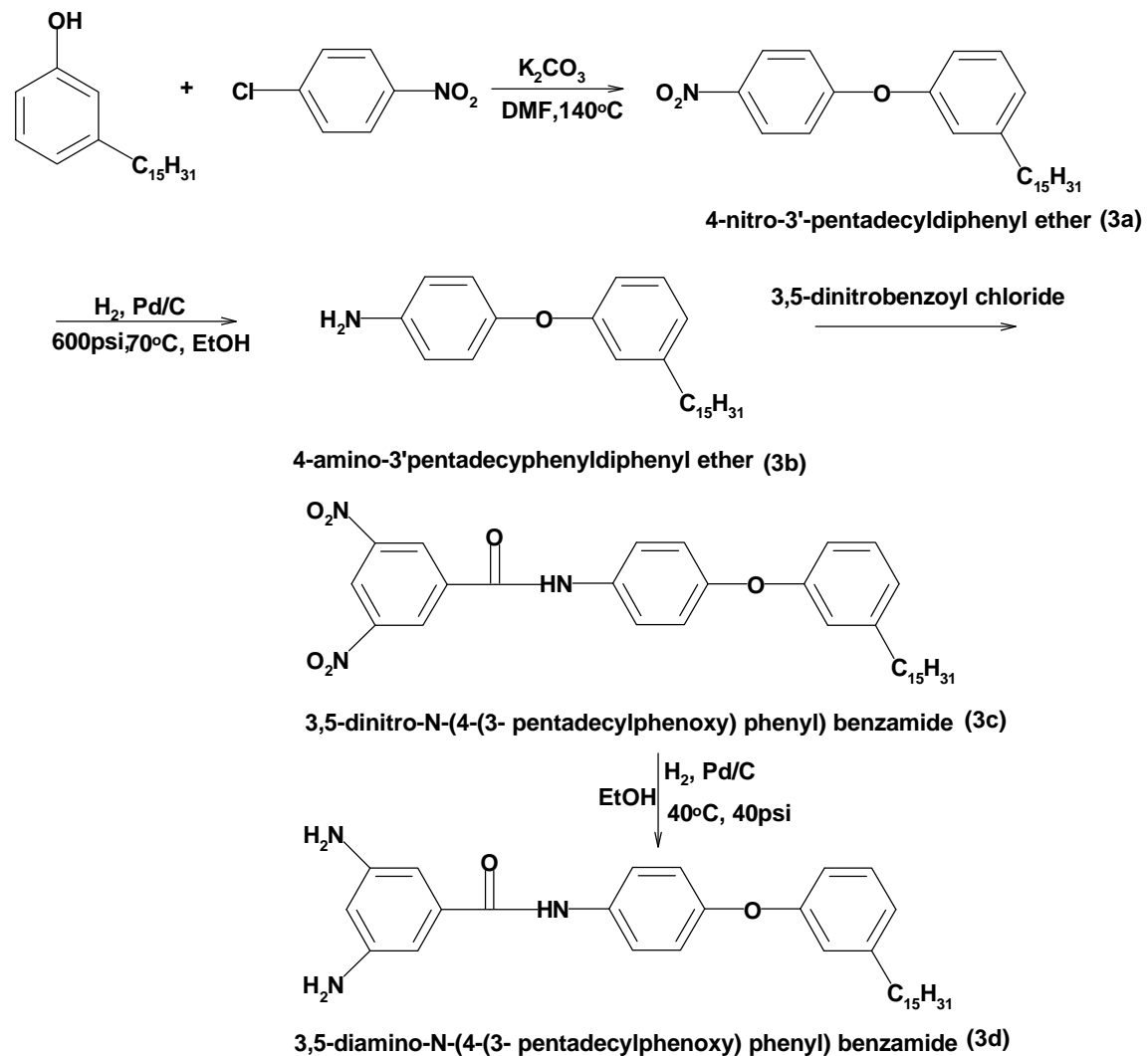
Scheme 2.3. Synthesis of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide

^{13}C NMR (CDCl$_3$ + DMSO, δ ppm): 166.52 (C7), 157.00 (C14), 151.92 (C11), 148.03 (C1, C3), 144.20 (C18), 136.63 (C5), 134.57 (C8), 128.77 (C16), 122.37 (C17), 121.27 (C9, C13), 118.51 (C10, C12), 117.52 (C15), 114.69 (C19), 103.07 (C2, C4, C6).

Mass spectrum showed a molecular ion peak (M$^+$) at 530

Elemental analysis:	C%	H%	N%
Calculated:	76.98	8.86	7.92
Observed:	77.28	8.32	7.68

2.2.4 Synthesis of silicon containing dianhydride

Silicon containing dianhydride was synthesized according to a reported procedure.[21]

2.2.4.1 Synthesis of bis(3,4–dicarboxyphenyl)dimethylsilane dianhydride (SiDA)

This compound was synthesized from o-xylene in 4 steps as shown in Scheme 2.4. In the first step o-xylene was brominated to obtain 4-bromo-o-xylene. The second step involved the lithiation of 4-bromo-o-xylene followed by reaction with dichlorodimethylsilane to give bis(3,4-dimethylphenyl)dimethylsilane. In the third step the tetramethyl compound from the second step was oxidized using potassium permanganate and pyridine to obtain the tetra acid and this tetra acid was treated with acetic anhydride in the fourth step to obtain the dianhydride.

(i) Synthesis of 4-bromo–o-xylene (4a)

To a 250 mL four necked round bottom flask equipped with a mechanical stirrer, dropping funnel, thermowell and reflux condenser, was added 15 g (0.14 mol, 17.2 mL) of o-xylene, 0.5 g of clean iron nails (washed with dilute HCl and then with alcohol) and a crystal of iodine. The top of the condenser was connected to a KOH trap and the reaction mixture was stirred and cooled to 0°C in an ice salt mixture. 19.8 g (0.12 mol, 6.36 mL) of Br$_2$ was added drop wise at this temperature over a period of 3.5 h. During this time the internal temperature was maintained at 0–5°C. After the addition of Br$_2$ was complete the reaction mixture was allowed to stand overnight. Next day, it was poured into water and washed successively with two 50 mL portions of water, two 50 mL portions of 3% NaOH and again with two 100 mL portions of water. The product was then steam distilled. The organic layer

was then separated from water and aqueous layer extracted with ether. The ether was removed and both organic layers were combined and dried over anhydrous sodium sulphate. The product obtained when distilled through a short column under reduced pressure afforded bromo-o-xylene, a mixture of 4 and 3-bromo-o-xylene in 80:20 ratio.

Yield : 19.96 g (89.9% based on Br_2)

FT-IR (Neat, cm^{-1}): 1085 (-C-Br)

^{1}H NMR (CDCl_3, δ ppm) 6.95- 7.55 (6H, m, aryl CH; 3 -CH from 3-bromo and 3 -CH from 4-bromo), 2.35 – 2.50 (6H, d, aryl CH_3 of 3-bromo), 2.25 - 2.35 (6H, d, aryl CH_3 of 4-bromo).

(ii) Synthesis of bis(3,4-dimethylphenyl)dimethylsilane (4b)

To a 250 mL four necked round bottom flask equipped with a mechanical stirrer, a thermowell, a nitrogen gas inlet, reflux condenser and guard tube, was added 3.8 g (0.59 mol) lithium metal and 108 mL dry ether. The solution was then cooled to –5°C and 40.0 g (0.22 mol, 29.1 mL) 4-bromo-o-xylene (80:20 mixture of 4 and 3-bromo) was added drop wise over a period of 1.5 h under nitrogen atmosphere. After a 6 h reaction period at room temperature, the reaction mixture was again cooled to 0^{0}C and 13.9 g (0.11 mol, 13.1 mL) of dichlorodimethylsilane was added drop wise over a period of 2 h. Then the mixture was allowed to stir overnight at room temperature. Unreacted lithium was removed by filtration and water was added to the reaction mixture. The ether layer was then separated and the aqueous layer extracted with ether thrice. All the ether layers were combined and dried over anhydrous sodium sulphate. Then ether was removed and the product vacuum distilled. The product obtained after distillation contained both bis(2,3-dimethylphenyl)dimethylsilane and bis(3,4-dimethylphenyl)dimethylsilane. Recrystallization of the vacuum distilled product from benzene yielded pure bis (3,4-dimethylphenyl)dimethylsilane.

Yield: 25.75 g (75.9%)

Melting point: 55-56^{0}C (Lit.[22] Reports m. p. 54.5-55.5^{0}C

FT-IR (KBr, cm^{-1}): 1247, 797 (silyl –CH_3).

^{1}H NMR (CDCl_3, δ ppm): 7.25-7.6 (6H,m, aryl -CH); 2.3-2.65 (12H, s, aryl –CH_3); 0.6-0.85 (6H, s, silyl –CH_3)

Elemental analysis: C%   H%

| Calculated: | 80.56 | 8.95 |
| Observed: | 80.59 | 8.90 |

(iii) Synthesis of bis(3,4-dicarboxyphenyl)dimethylsilane (4c)

To a three necked round bottom flask equipped with a mechanical stirrer, thermowell and reflux condenser was added 26.8g (0.1 mol) bis(3,4-dimethyl phenyl)dimethylsilane, 400 mL pyridine, and 110 mL water. The reaction mixture was then heated to $130^{\circ}C$ and to the refluxing solution, 205 g (1.29 mol) solid $KmnO_4$ was added portion wise to maintain a slow reflux. Water was added occasionally to replace the loss by evaporation and to wash down the permanganate. The solution was then refluxed for 1.5 h before methanol (100 mL) was added to destroy excess permanganate. The MnO_2 was suction filtered while hot and washed with boiling water. Filtrate and washings were combined and the pyridine was removed by vacuum distillation.

After cooling, the solution was acidified with concentrated HCl and kept in freeze to obtain the tetracarboxylic acid,

Yield: 29 g (74.7%)

Melting point: 216-220^{0}C

FTIR (KBr, cm^{-1}): 2959, 1710 (-COOH); 1256, 799 (silyl –CH$_3$)

^{1}H NMR (DMSO–d$_6$, δ ppm): 7.6-7.8 (6H, m, aryl -CH); 0.6 (6H,s, silyl -CH); carboxylic acid protons were not observed due to their exchange

Elemental analysis:	C%	H%
Calculated:	55.65	4.12
Observed:	55.02	3.95

CH₃ — Fe, Br₂ / 0°C → **4-bromo-o-xylene (4a)** — Li → — Si(CH₃)₂(Cl)₂ →

bis(3,4-dimethylphenyl)dimethylsilane (4b) — KMnO₄, Pyridine / Reflux → **bis(3,4-dicarboxyphenyl)dimethylsilane (4c)**

Acetic anhydride / Reflux → **bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (4d)**
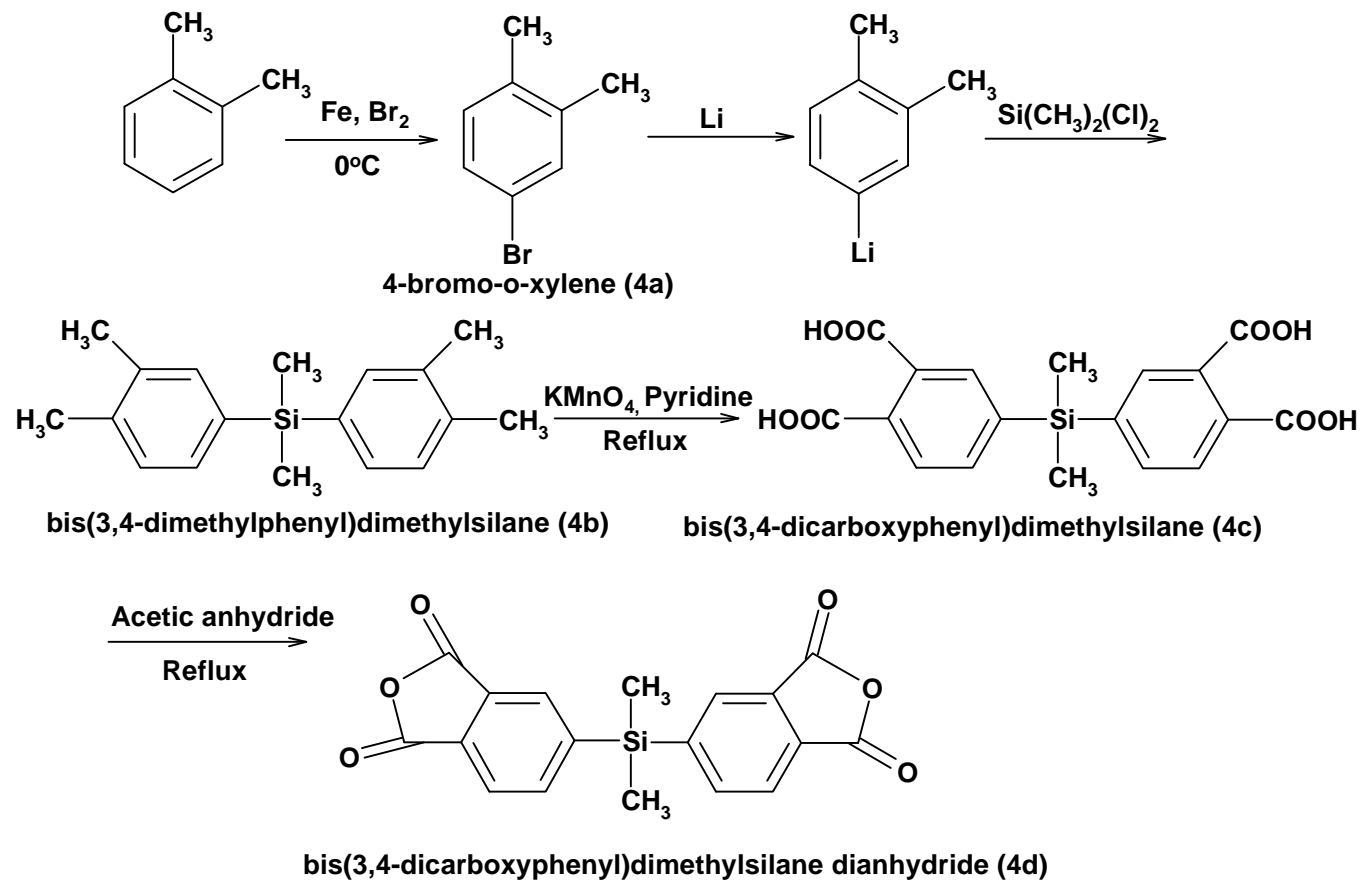
Scheme 2.4. Synthesis of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride

(iv) Synthesis of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (4d)

To a single necked round bottom flask equipped with a reflux condenser, a magnetic stirrer and a guard tube was added 12 g (0.03 mol) bis(3,4-dicarboxyphenyl)dimethylsilane and 39.56 mL (42.73 g) of acetic anhydride and the solution was slowly refluxed for 1.5 h, taking care to prevent decolorisation caused by over heating. Following a vacuum distillation of the solvent the product was recrystallized from 2:1 benzene-hexane mixture to obtain the dianhydride.

Yield: 7.4 g (68%)

Melting point: 180.10 - 180.15^{o}C.

FT-IR (KBr, cm^{-1}): 1854, 1778 (doublet anhydride carbonyl); 1248, 814, (silyl –CH$_3$)

^{1}HNMR (CDCl$_3$, δ ppm): 8-8.2 (6H, m, aryl -CH), 0.8 (6H, s, silyl -CH)

Elemental analysis: C%   H%

Calculated: 61.36   3.4

Observed: 61.64   3.12

2.2.5 Synthesis of silicon containing diacid chloride

2.2.5.1 Synthesis of bis(4-chlorocarbonylphenyl)dimethylsilane (DMSC)

Silicon containing diacid chloride was synthesized in three steps starting from 4-bromotoluene. Lithiated 4-bromotoluene was reacted with dichlorodimethylsilane to obtain bis(4-methylphenyl)dimethylsilane, which was then oxidized to the corresponding diacid using potassium permanganate and pyridine, followed by treatment with thionyl chloride to obtain the corresponding diacid chloride. Various steps involved in this synthesis are outlined in Scheme 2.5.

(i) Synthesis of bis(4-methylphenyl)dimethylsilane (5a)

To a 500 mL four necked round bottom flask equipped with a reflux condenser, a thermowell, a dropping funnel, a nitrogen gas inlet and a mechanical stirrer was added 2.4 g (0.3 mol) lithium wire in 120 mL dry ether and the solution was then cooled to 0°C. Then 4-bromotoluene (30 g, 0.17 mol) dissolved in 40 mL dry ether was added dropwise to this solution under nitrogen atmosphere over a period of 4 h. The reaction was then continued at

room temperature for 5 h and then again cooled to 0°C and a solution of 11.32 g (0.08 mol) dichlorodimethylsilane was added drop wise over a period of 2 h, and the reaction was then continued at room temperature overnight. The unreacted lithium was then removed by filtration and the filtrate poured into water. The ether layer was then separated, washed with water, 5% HCl, 5% NaOH and dried over sodium sulphate. The crude product was obtained by distilling off ether. Vacuum distillation (bp 127°C/0.5mm Hg) of the crude product gave pure bis(4-methylphenyl)dimethylsilane. (Lit.[17] reported bp 130°C/0.5mm Hg).

Yield: 34.5 g (82%)

FT-IR (Neat, cm^{-1}): 1250, 840 (silyl –CH_3).

^{1}H NMR (CDCl$_3$, δ ppm): 7.1- 7.40 (d, 4H, aryl, ortho to –CH_3), 6.7-7.10 (d, 4H, aryl, ortho to Si), 2.20 (s, 6H, aryl –CH_3), 0.60 (s, 6H, silyl –CH_3).

(ii) Synthesis of bis(4-carboxy phenyl)dimethylsilane (5b)

To a one litre three necked round bottom flask equipped with a thermowell, a reflux condenser and a mechanical stirrer was added 24.0 g (0.1 mol) bis(4-methyl phenyl)dimethylsilane, 65 mL water and 140 mL pyridine and the solution was heated to reflux. To this solution 100 g (0.65 mol) solid $KMnO_4$ was added at a slow rate with stirring to maintain a slow reflux. Water was added occasionally to replace the loss by evaporation and to wash down the permanganate. The solution was then refluxed overnight before 100 mL methanol was added to destroy excess permanganate. The MnO_2 was suction filtered while hot and washed with boiling water. Filtrate and washings were combined and the pyridine was removed by vacuum distillation.

After cooling, the solution was acidified with concentrated HCl and kept in freeze to obtain the diacid. The diacid obtained was again redissolved in aqueous sodium carbonate, treated with charcoal, filtered and acidified. The precipitated solid was dried at 80°C under vacuum and recrystallized from ethanol:water mixture.

Yield: 22.5 g (75%)

Melting point: 286 - 289°C

FT-IR (KBr, cm^{-1}): 2660, 1692 (-COOH), 1254, 830 (silyl –CH_3)

^{1}H NMR (DMSO-d$_6$, δ ppm): 7.85-8.0 (d, 4H, aryl, ortho to –COOH), 7.60-7.70 (d, 4H, aryl, ortho to Si), 3.0-4.7 (s, 2H, -COOH), 0.60 (s, 6H, silyl –CH$_3$),

Elemental analysis:	C%	H%
Calculated:	63.98	5.37
Observed:	64.11	5.50

(iii) Synthesis of bis(4-chlorocarbonylphenyl)dimethylsilane (5c)

To a single necked round bottom flask equipped with a magnetic stirrer, reflux condenser and a guard tube was added 10 g (0.03 mol) of bis(4-carboxyphenyl)dimethylsilane and 30 mL thionyl chloride and the solution was refluxed for 6 h. The resulting clear solution was concentrated to dryness and then dry benzene was added and distilled out to remove traces of thionyl chloride. The residue was recrystallized from dry n-hexane to obtain the product.

Yield: 7.9 g (80%)

Melting point: 80-82°C (Lit mp 81°C)

FT-IR (KBr, cm^{-1}): 1774, 1732 (aryl –COCl), 1212, 832 (silyl –CH$_3$).

^{1}H NMR (CDCl$_3$, δ ppm): 0.6 (s, 6H, silyl –CH$_3$), 7.62-7.77 (d, 4H, H$_b$, ortho to Si), 8.03-8.23 (d, 4H, H$_a$, ortho to –COCl).

bis(4-methylphenyl)dimethylsilane (5a)

bis(4-carboxy phenyl)dimethylsilane (5b)

bis(4-chlorocarbonylphenyl)dimethylsilane (5c)
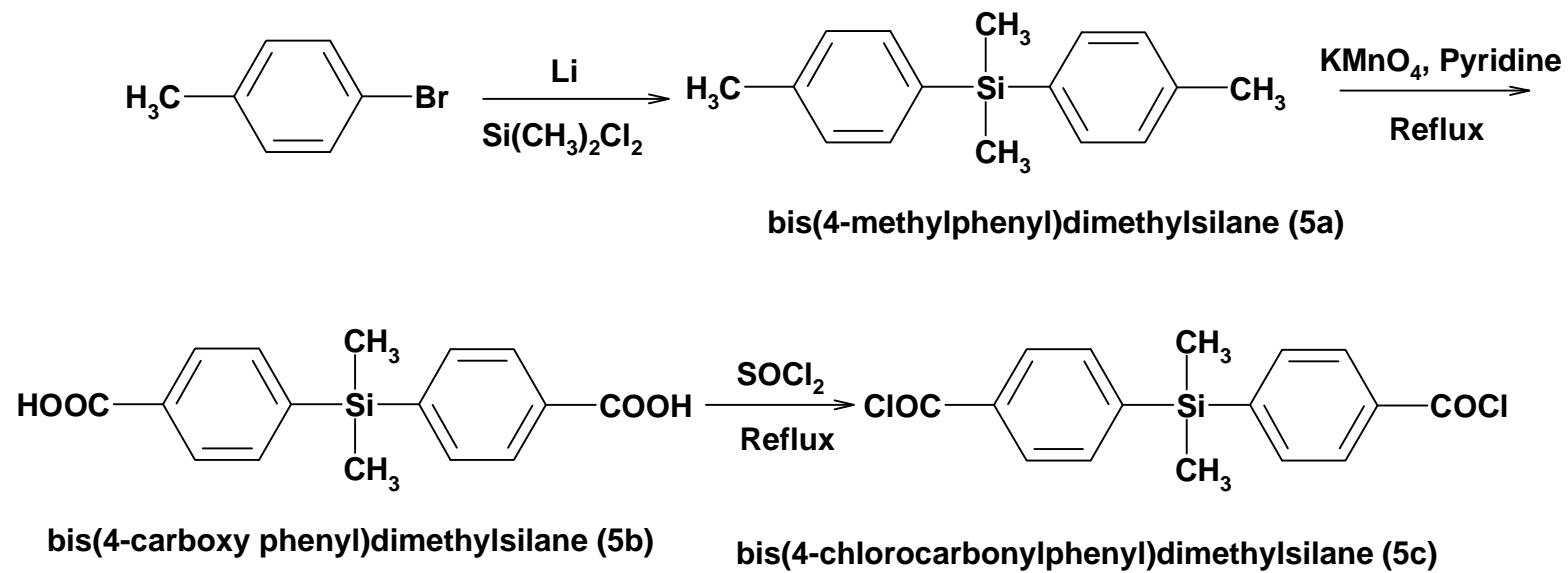
Scheme 2.5. Synthesis of bis(4-chlorocarbonylphenyl)dimethylsilane

2.3 Results and discussion

2.3.1 Synthesis and characterization of 4-(3-pentadecylphenoxy) benzene-1,3 -diamine

This diamine was synthesized from 3-pentadecenylphenol (cardanol) in three steps (Scheme 2.1). In the first step, 3-pentadecylphenol was synthesized by the hydrogenation of freshly distilled cardanol in presence of 5%Pd/C catalyst. The product obtained was recrystallized from petroleum ether 60-80°C and was characterized by ^{1}H NMR, FT-IR and elemental analysis. Elemental analysis values were in good agreement with the calculated values. FT-IR spectrum (Figure 2.1) and ^{1}H NMR spectrum (Figure 2.2) confirmed the structure of the product.

FT-IR spectrum of 3-pentadecylphenol (1a) (Figure 2.1) showed a broad band centered at 3342 cm^{-1} corresponding to the –OH group. The bands at 2925 and 2849 cm^{-1} were due to aliphatic –CH stretching vibrations. The disappearance of bands in the region 1667-1640 cm^{-1} corresponding to –C=C- stretching vibrations confirmed the completion of hydrogenation. The ^{1}H NMR spectrum of 3-pentadecylphenol (Figure 2.2) does not show a multiplet in the region 4.66-5.66 δ ppm corresponding to the olefinic proton in cardanol indicating complete hydrogenation of olefinic bonds. A broad singlet centered at 5.71 δ ppm is due to the hydroxyl group. The multiplet in the region 1.66-2.9 δ ppm, observed in the case of cardanol has disappeared and a new triplet has formed at 2.59 δ ppm. This triplet corresponds to the methylene protons attached to aromatic ring. All these observations show that the hydrogenation of the side group of cardanol is complete. Further the multiplet in the region 6.65-7.18 δ ppm, which integrated to four protons showed that the aromatic ring is intact.
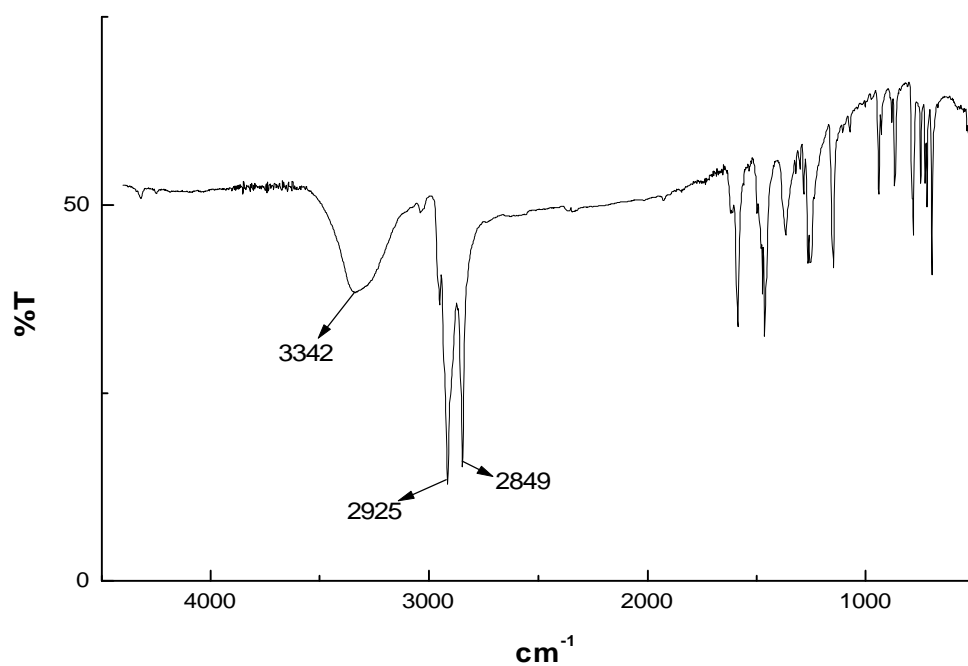
Figure 2.1. FT-IR spectrum of 3-pentadecylphenol (1a) (KBr)
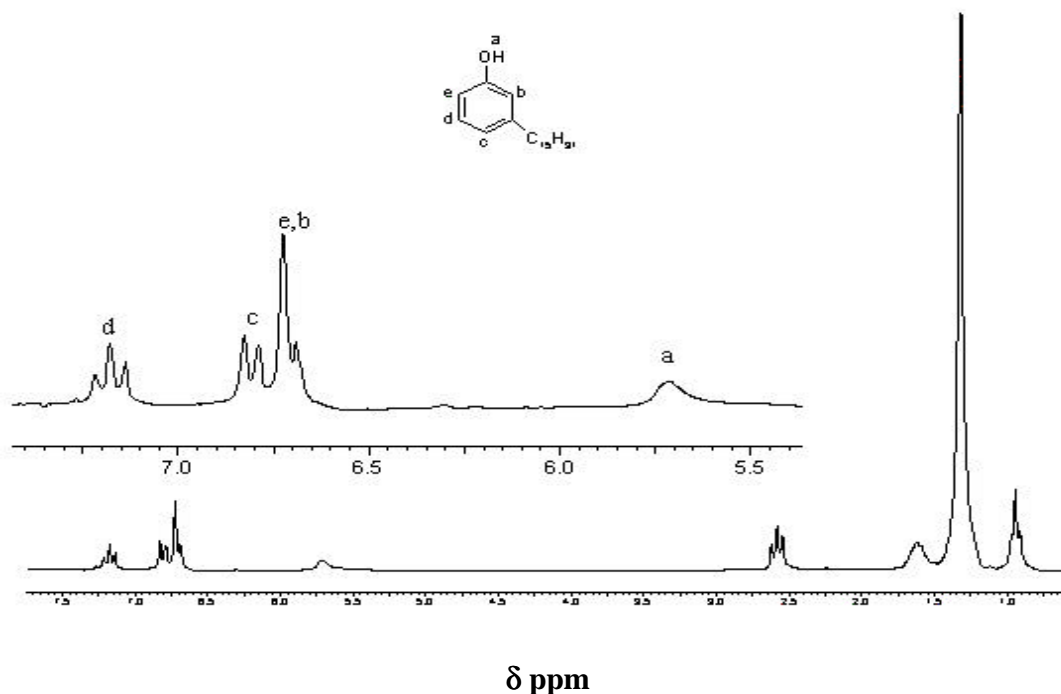
δ ppm
Figure 2.2. ^{1}H NMR spectrum of 3-pentadecylphenol (1a) in CDCl$_3$

Second step involved the synthesis of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b) from 3-pentadecylphenol. In this step 3-pentadecylphenol was reacted with 2,4-dinitrochlorobenzene in methyl ethyl ketone at reflux temperature, in the presence of an acid acceptor like N-methyl imidazole. The product obtained was purified by recrystallization from petroleum ether 40-60°C. Literature reports the use of acid acceptors like triethyl amine in ketonic solvents like acetone[23] and acid acceptors like sodium or potassium hydroxide in solvents like ethanol[24,14] or DMF, for the synthesis of aryl ethers from dinitrochlorobenzene. Both these methods were not useful in the synthesis of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene from a sterically hindered phenol like 3-pentadecylphenol. In both these cases the yields were comparatively low. In the case of triethyl amine, the reaction was not complete even after 48 h. On the other hand the use of strong bases like sodium and potassium hydroxide resulted in the formation of a substantial amount of 2,4-dinitrophenol by the hydrolysis of 2,4-dinitrochloro benzene, which in turn reduced the yield. In the present study it was found that the use of N-methyl imidazole as an acid acceptor gave better yields. Thus a new process for the synthesis of dinitrophenyl ethers was developed.

FT-IR and ^{1}H NMR spectra and elemental analysis confirmed the formation of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b). The elemental analysis values were found to be in good agreement with the calculated values. FT-IR spectrum of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b) (Figure 2.3) showed bands at 1532 and 1346 cm^{-1} due to asymmetric and symmetric –NO$_2$ stretching vibrations. The bands at 1280 and 1070 cm^{-1} are due to –C-O-C- asymmetric and symmetric stretching vibrations. The band at 870 cm^{-1} is due to the aromatic –C-N stretching vibration. ^{1}H NMR spectrum of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b) (Figure 2.4) showed signals at 0.88, 1.20-1.73 and 2.64 δ ppm corresponding to the protons of –CH$_3$, -(CH$_2$)$_{13}$ and -CH$_2$ of alkyl chain attached to the aromatic ring with the expected multiplicity, in addition to signals corresponding to aromatic protons in the region 6.87-8.93 δ ppm with expected multiplicity and integration equivalent to seven protons. These observations along with a molecular ion peak at m/z 470 in the mass spectrum (Appendix I, Figure A.1) confirmed the structure of the product.
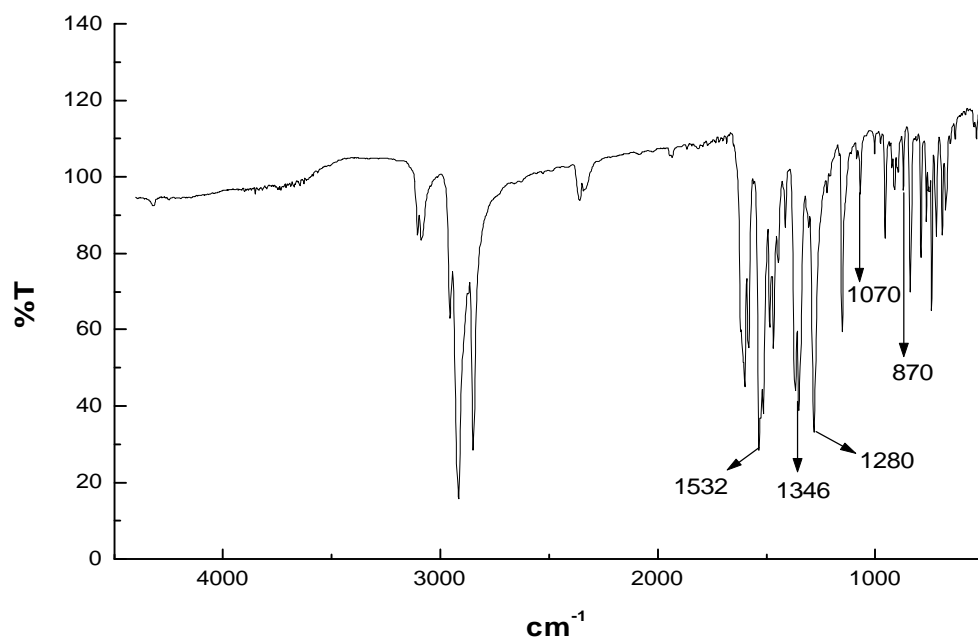
Figure 2.3. FTIR spectrum of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b)   (KBr)

δ ppm
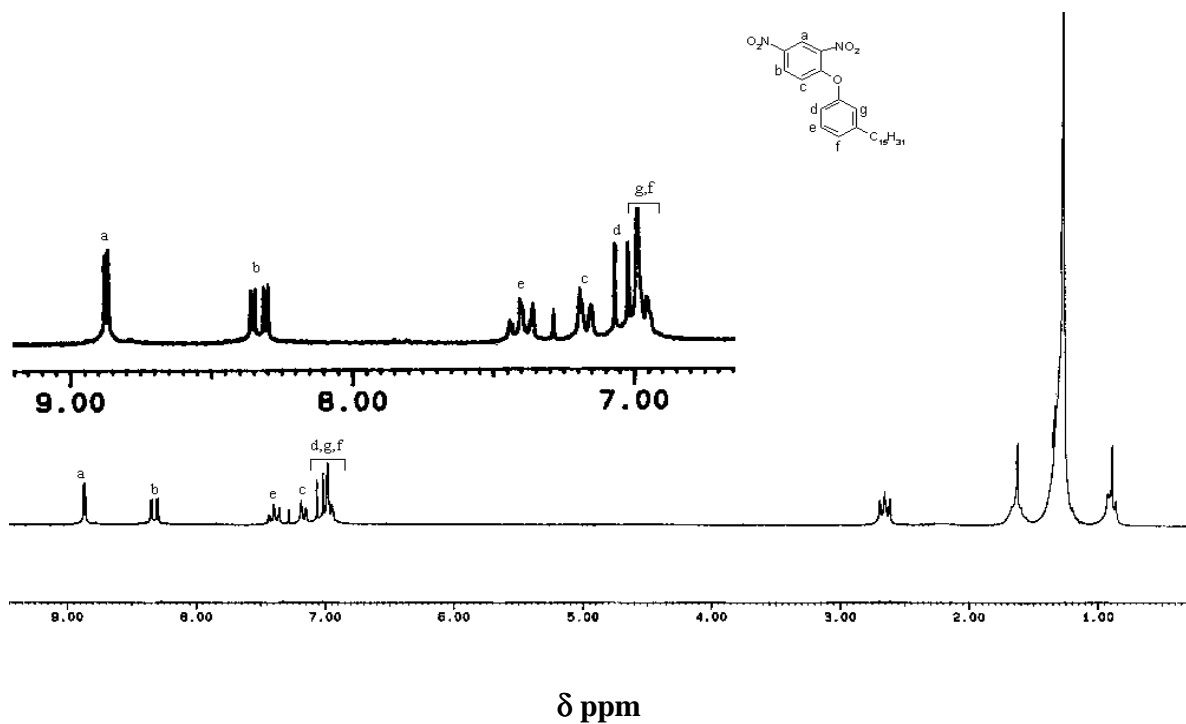
Figure 2.4. ^{1}H NMR spectrum of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b)   in CDCl$_3$

In the third step the dinitro compound was catalytically hydrogenated in presence of Pd/C to obtain the diamine, 4-(3-pentadecylphenoxy)benzene1,3-diamine (1c). The structure of diamine was confirmed by elemental analysis and FT-IR and ^{1}H NMR spectra. Elemental analysis values were in good agreement with the calculated values. The appearance of a doublet at 3400-3456 cm^{-1} corresponding to –N-H symmetric and asymmetric stretching vibrations and the disappearance of the bands at 1532 and 1346 cm^{-1} due to asymmetric and symmetric –NO$_2$ stretching vibration in the FT-IR spectrum of 4-(3-pentadecylphenoxy)benzene-1,3-diamine(1c) (Figure 2.5) showed that the hydrogenation was complete. Other characteristic bands of amine group were at 1620 (-N-H deformation) and 1244 cm^{-1} (-C-N stretching). The bands at 1510, 1488 cm^{-1} corresponding to carbon-carbon stretching of the aromatic ring showed that the aromatic ring was not affected by hydrogenation. The band at 1218 cm^{-1} was due to the ether linkage. ^{1}H NMR spectrum of 4-(3-pentadecylphenoxy)benzene-1,3-diamine(1c) (Figure 2.6) showed peaks at 0.89, 1.2-1.7 and 2.55 δ ppm corresponding to the
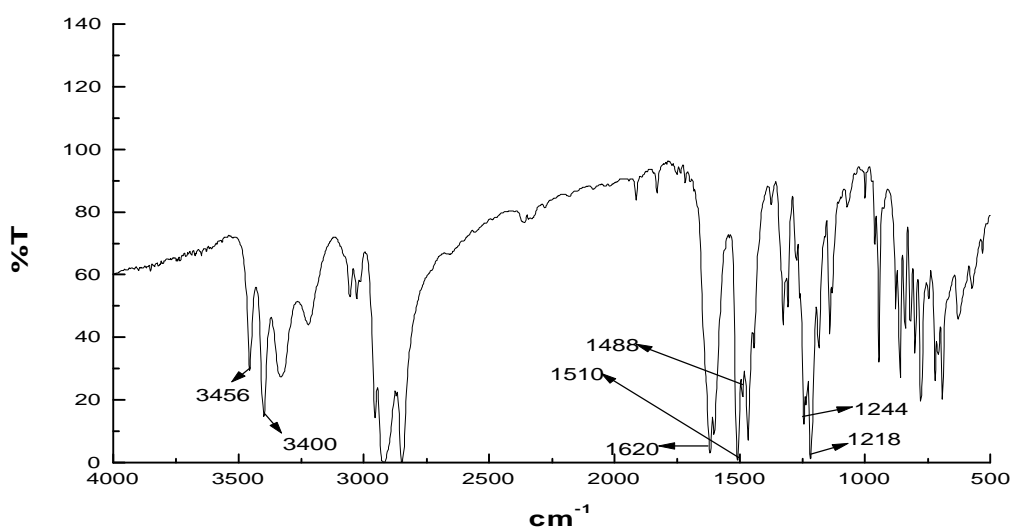
Figure 2.5. FT-IR spectrum of 4-(3-pentadecylphenoxy)benzene-1,3-diamine (1c) (KBr)

pentadecyl groups with the expected multiplicity and integration. The broad singlet at 2.65-3.5 δ ppm was due to the –NH$_2$ protons. Other aromatic protons in the region 6.05-7.17 δ ppm also showed the expected multiplicity and integration values. Further a molecular ion peak at

m/z 410 in the mass spectrum (Appendix I, Figure A.2) confirmed the formation of the product. Assignment of ^{13}C is shown in Figure 2.7 and the δ values obtained were in good agreement with the proposed diamine structure.

δ ppm
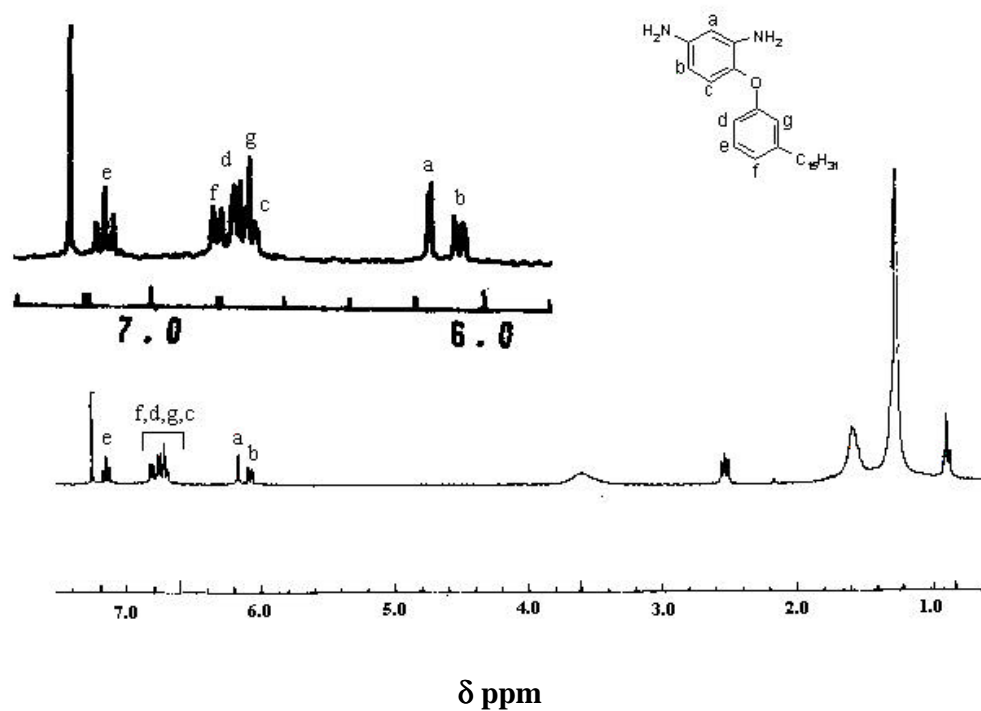
Figure 2.6. ^{1}H NMR spectrum of 4-(3-pentadecylphenoxy)benzene-1,3-diamine (1c) in CDCl₃

δ ppm
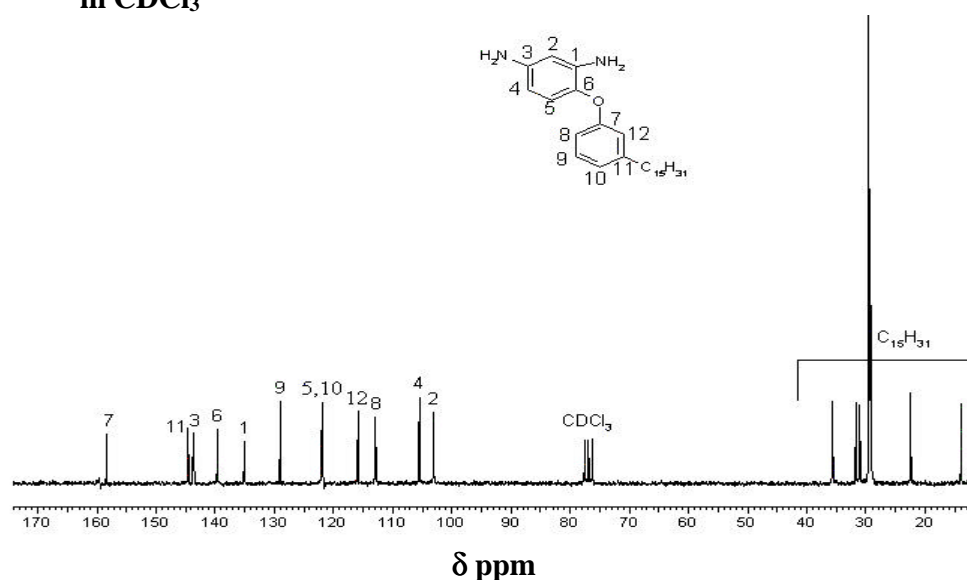
Figure 2.7. ^{13}C NMR spectrum of 4-(3-pentadecylphenoxy)benzene-1,3-diamine (1c) in CDCl₃

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2.3.2 Synthesis and characterization of 3-pentadecylphenyl-3,5-diamino benzoate

This diamine was synthesized by a simple condensation reaction of 3,5-dinitrobenzoyl chloride with 3-pentadecylphenol in presence of an acid acceptor like N-methyl imidazole, followed by catalytic reduction of the resulting dinitro compound with Pd/C as shown in Scheme 2.2.

In the first step 3,5-dinitrobenzoyl chloride (2a) was synthesized by refluxing 3,5-dinitrobenzoic acid with thionyl chloride and by recrystallizing the crude product from carbon tetrachloride. The formation of acid chloride was confirmed by FT-IR and ^{1}H NMR. FT-IR spectrum of 3,5-dinitrobenzoyl chloride (2a) (Figure 2.8) did not show any band in the region 2500-3000 cm^{-1} corresponding to the hydroxyl group of –COOH and this confirmed the complete conversion of acid to acid chloride. Other characteristic bands in the region 1757, 1538 and 1346 cm^{-1} were due to carbonyl group and nitro group respectively.
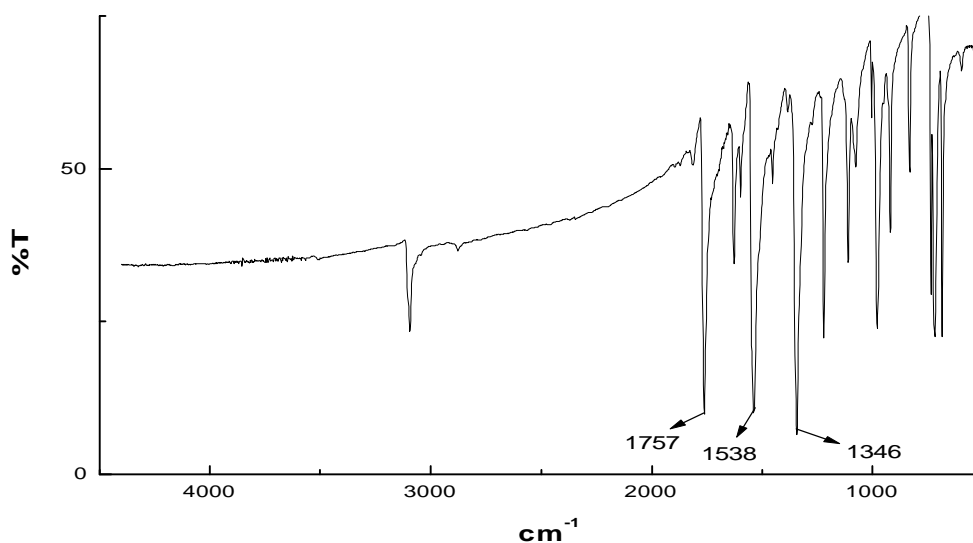
Figure 2. 8. FT-IR spectrum of 3,5-dinitrobenzoyl chloride (2a) (KBr)

^{1}H NMR spectrum of 3,5-dinitrobenzoyl chloride (2a) (Figure 2.9) showed two singlets in the region 9.02-9.57 δ ppm, which integrated into 3 protons corresponding to two protons ortho to –NO$_2$ and the one in between two -NO$_2$. These confirmed the formation of acid chloride.

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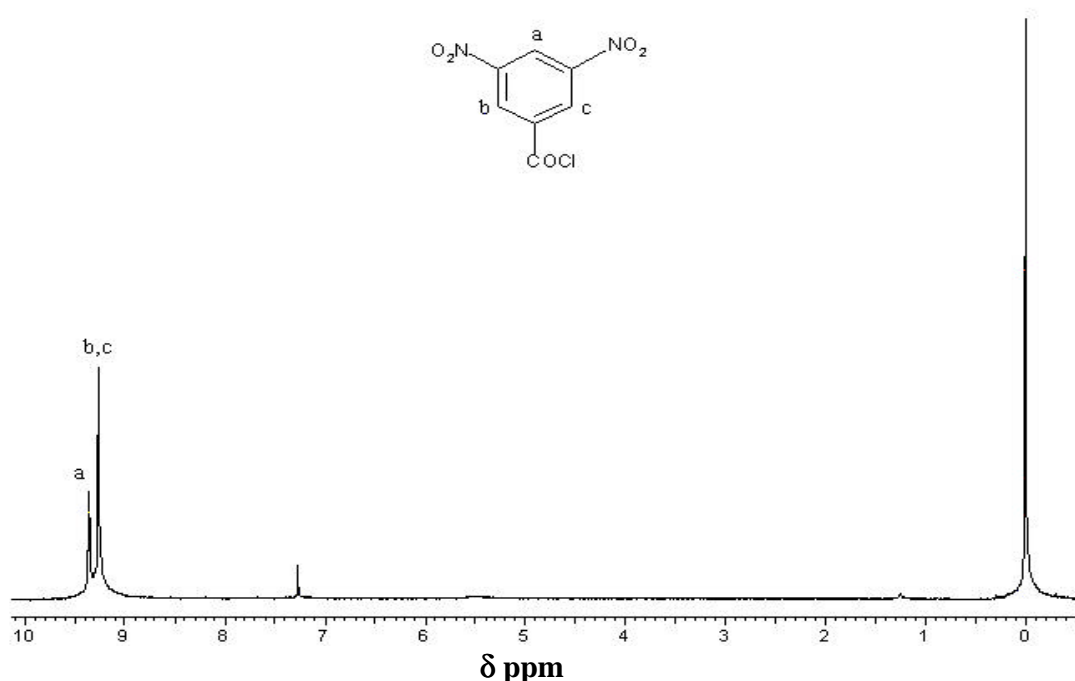
Figure 2. 9. ^{1}H NMR spectrum of 3,5-dinitrobenzoyl chloride (2a) in CDCl$_3$

In the second step 3,5-dinitrobenzoyl chloride was condensed with 3-pentadecylphenol in presence of an acid acceptor like N-methyl imidazole to obtain 3-pentadecylphenyl-3,5-dinitrobenzoate (2b). It was found that the use of N-methyl imidazole as an acid acceptor gave better yields as compared to the reported procedure for the synthesis of benzoic acid esters using triethylamine.[15] Elemental analysis, FT-IR, ^{1}H NMR and mass spectra confirmed the structure of the product. Elemental analysis values were in good agreement with the calculated values. FT-IR spectrum of 3-pentadecylphenyl-3,5-dinitrobenzoate (2b) (Figure 2.10) showed bands at 1548 and 1344 cm^{-1} due to –NO$_2$ asymmetric and symmetric stretching vibrations. The band at 1742 cm^{-1} was due to the ester carbonyl group and the bands at 1268 and 1162 cm^{-1} were due to other stretching vibrations of the ester group. The ^{1}H NMR spectrum of 3-pentadecylphenyl-3,5-dinitrobenzoate (2b) (Figure 2.11) showed signals at 0.89, 1.16-1.81 and 2.68 δ ppm with expected multiplicities and integration corresponding to the pentadecyl group. Aromatic region showed signals at 7.04-7.39 δ ppm corresponding to 4 protons in the aromatic ring of 3-pentadecylphenol with expected multiplicities and integration and a multiplet in the region 9.27-9.37 δ ppm

corresponding to 3 protons ortho to nitro group. Further a molecular ion peak at m/z 498 in the mass spectrum (Appendix I, Figure A.3) confirmed the structure of the product.
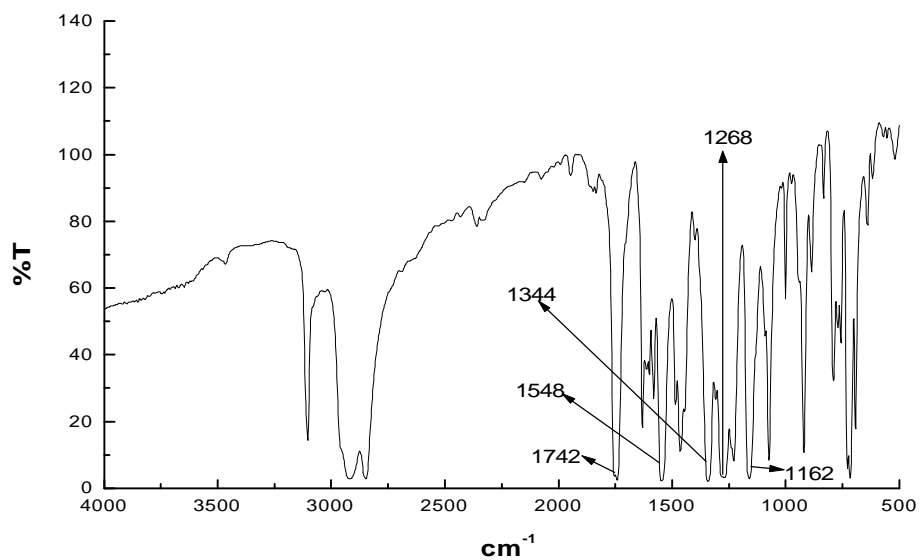
Figure 2.10. FTIR spectrum of 3-pentadecylphenyl-3,5-dinitrobenzoate (2b) (KBr)

δ ppm
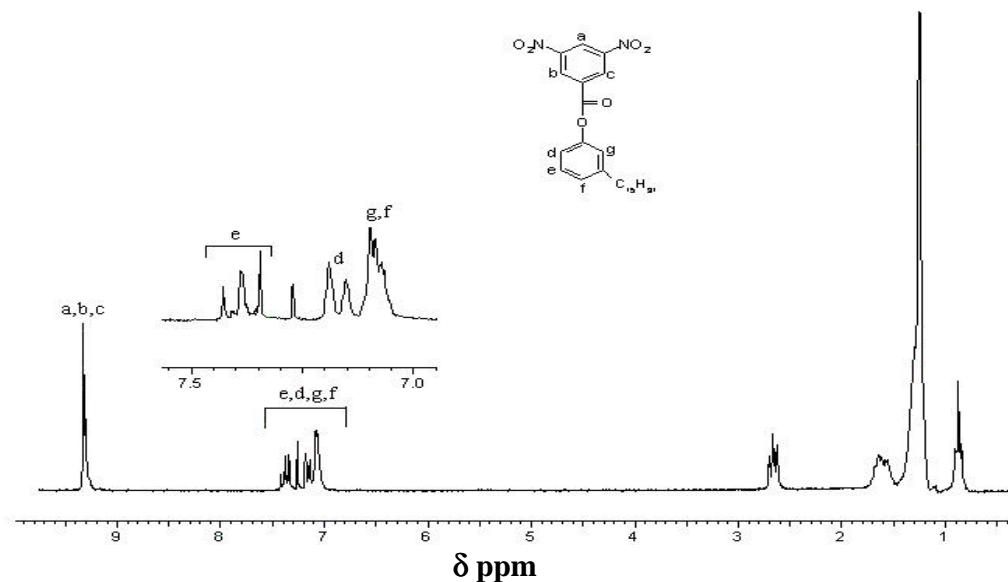
Figure 2.11. ¹H NMR spectrum of 3-pentadecylphenyl-3,5- dinitrobenzoate (2b) in CDCl₃

In the next step 3-pentadecylphenyl-3,5-dinitrobenzoate was reduced with Pd/C in presence of hydrogen at 40°C and 40 psi to the corresponding diamine, 3-pentadecylphenyl-3,5-diaminobenzoate (2c). Elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectra confirmed the structure of the product. Elemental analysis values were in good agreement with the calculated values. FT-IR spectrum of 3-pentadecylphenyl-3,5-diaminobenzoate (2c) (Figure 2.12) showed bands at 3366-3456 cm^{-1} and at 1604 cm^{-1} due to –N-H stretching vibration and –N-H deformation indicating the reduction of nitro group. The completion of hydrogenation was confirmed by the absence of bands at 1548 and 1344 cm^{-1}due to –NO$_2$ group. Another characteristic band of diamine was at 1374 cm^{-1} due to -C-N stretching vibration. The bands corresponding to ester group were at 1716, 1210 and 1151 cm^{-1}. ^{1}H NMR spectrum of 3-pentadecylphenyl-3,5- diaminobenzoate (2c) (Figure 2.13) showed two triplets at 0.89 and 2.64 δ ppm and a multiplet at 1.12-1.81 δ ppm corresponding to –CH$_3$, benzylic –CH$_2$ and -(CH$_2$)$_{13}$ of pentadecyl group.
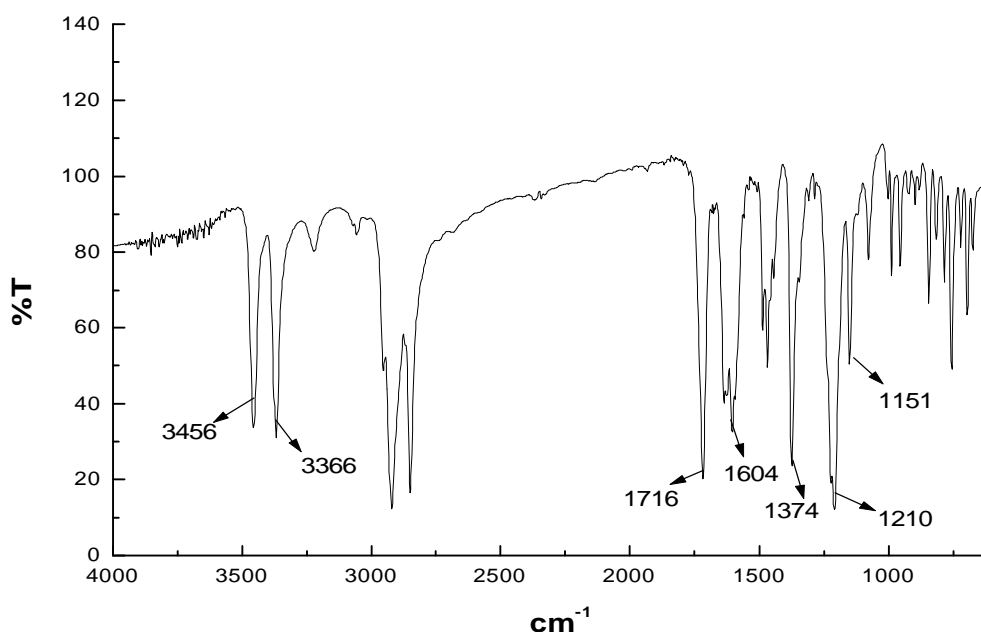
Figure 2.12. FT-IR spectrum of 3-pentadecylphenyl-3,5-diaminobenzoate (2c) (KBr)

A broad singlet at 3.52-3.91 δ ppm, which integrated to 4 protons showed the presence of two amino groups. A singlet at 6.26 δ ppm was due to the aromatic proton in between the amino groups. Other aromatic protons in the region 6.8-7.32 δ ppm also showed the expected multiplicities and integration corresponding to 6 protons. ^{13}C NMR spectrum of 3-pentadecylphenyl-3,5-diaminobenzoate (2c) (Figure 2.14) showed δppm values corresponding to 13 carbon atoms and were in good agreement with the proposed structure. The assignment is given in Figure 2.14. Mass spectrum (Appendix I, Figure A.4) showed a molecular ion peak at m/z 438. Thus the structure of the product was confirmed.

δ ppm
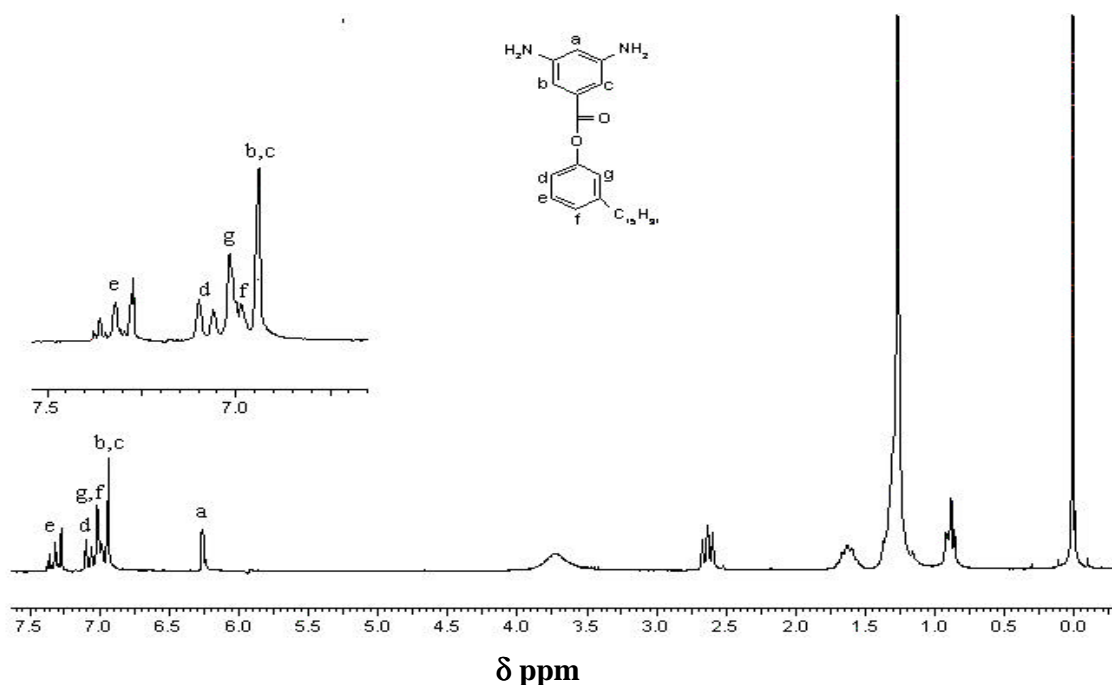
Figure 2.13. ^{1}H NMR spectrum of 3-pentadecylphenyl-3,5-diaminobenzoate (2c) in CDCl₃
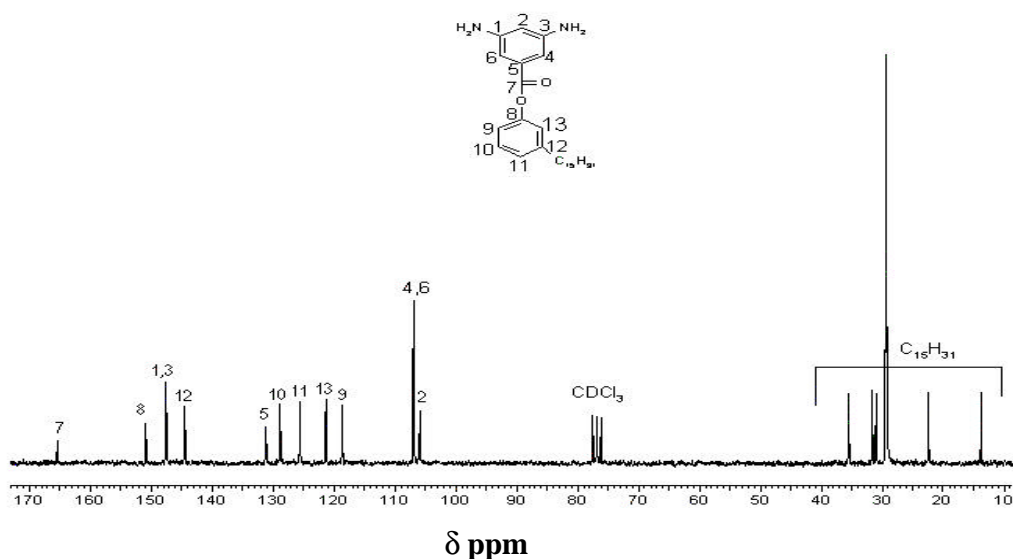
Figure 2.14. ^{13}C NMR spectrum of 3-pentadecylphenyl-3,5-diaminobenzoate (2c) in CDCl$_3$

2.3.3 Synthesis and characterization of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide

This diamine was prepared via a four step reaction scheme (Scheme 2.3) starting from 3-pentadecylphenol. Condensation of 3-pentadecylphenol with 1-chloro-4-nitrobenzene in presence of K$_2$CO$_3$ yielded 4-nitro-3'-pentadecyldiphenyl ether (3a). In the second step the catalytic hydrogenation of 3a to 4-amino-3'-pentadecyldiphenyl ether (3b) was accomplished using Pd/C as catalyst. Then 4-amino-3'-pentadecyldiphenyl ether was then reacted with 3,5-dinitrobenzoyl chloride, in presence of an acid acceptor like N-methyl imidazole to obtain 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (3c). It was found that the yields obtained were higher when N-methyl imidazole was used as an acid acceptor compared to that obtained in the procedure reported[16] for the synthesis of benzamides using triethylamine. The catalytic hydrogenation of 3c was accomplished with hydrogen in presence of Pd/C at 40°C and 40 psi to obtain 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (3d). The chemical structures of all the synthesized compounds were confirmed by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectra, and the results were in good agreement with the expected structures.

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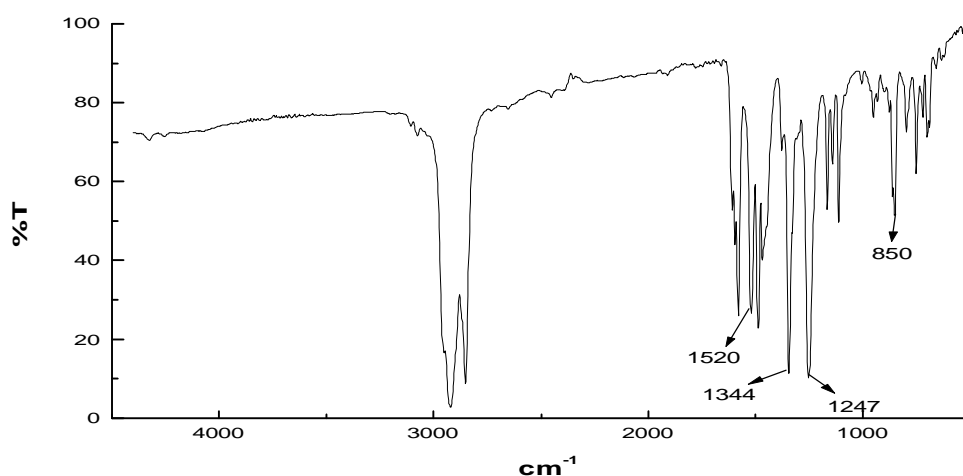
Figure 2.15. FT-IR spectrum of 4-nitro-3'-pentadecyldiphenyl ether (3a) (KBr)

FT-IR spectrum of 4-nitro-3'-pentadecyldiphenylether (3a) (Figure 2.15) showed bands corresponding to -NO_2 asymmetric and symmetric stretching vibrations at 1520 and 1344 cm^{-1}, in addition to a band at 850 cm^{-1} due to –C-N stretching vibration of aromatic nitro group. The band at 1247 cm^{-1} confirmed the presence of ether linkage. The ^{1}H NMR spectrum of 4-nitro-3'-pentadecyldiphenylether (3a) (Figure 2.16) showed the characteristic signals of pentadecyl group at 0.89, 1.10 – 1.77 and 2.63 δ ppm respectively. The doublet at 8.16-8.28 δ ppm is peculiar to the aromatic protons at the ortho position of the nitro group. Three doublets were found in the region 6.86-7.15 δ ppm corresponding to four hydrogens ortho to ether group and the one at the ortho position of pentadecyl group. The proton at the meta position of the pentadecyl group was found as a triplet in the region 7.28 – 7.41 δ ppm. These results confirmed the formation of 3a.
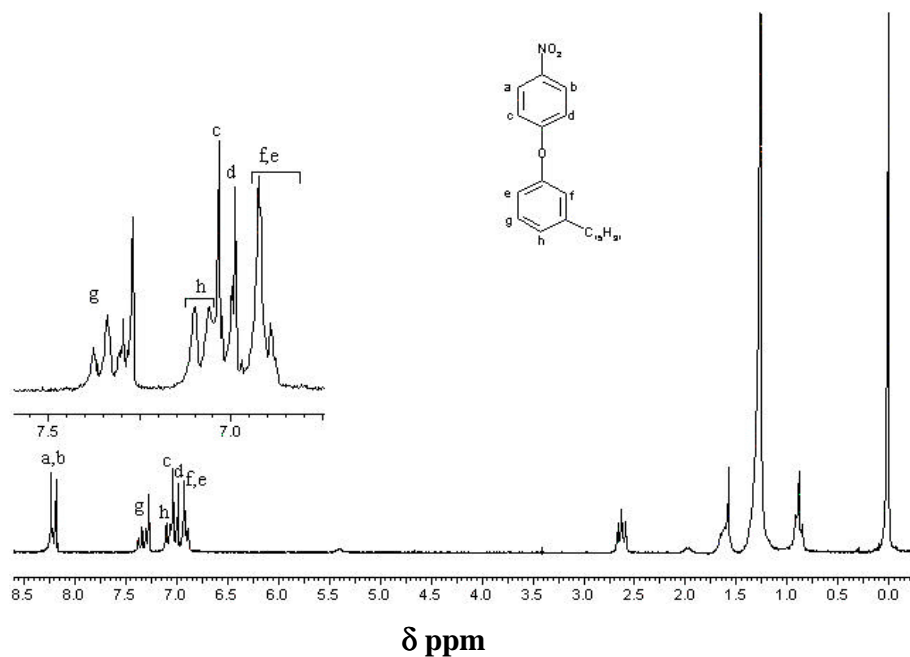
.**Figure 2.16. ^{1}H NMR of 4-nitro-3'-pentadecyldiphenyl ether (3a) in CDCl$_3$**

FT-IR spectrum of 4-amino-3'-pentadecyldiphenyl ether (3b) (Figure 2.17) showed new bands in the region 3360-3444 cm^{-1} (-N-H stretching) and at 1614 cm^{-1} (-N-H deformation) characteristic of –NH$_2$ group and lacked the absorptions at 1520 and 1344 cm^{-1} due to –NO$_2$ group. Further the –C-N stretching band of –NH$_2$ group was found at 1336 cm^{-1}. The absorption at 1248 cm^{-1} showed that the ether linkage is intact.
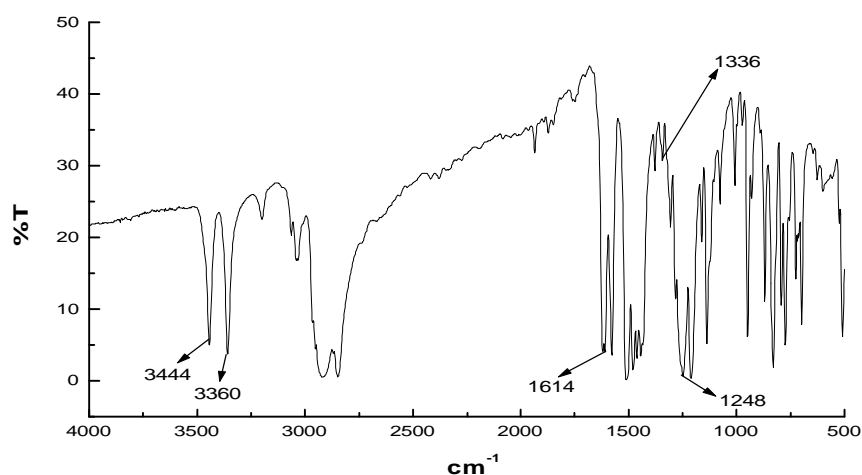
Figure 2.17. FT-IR spectrum of 4-amino-3'-pentadecyldiphenyl ether (3b) (KBr)

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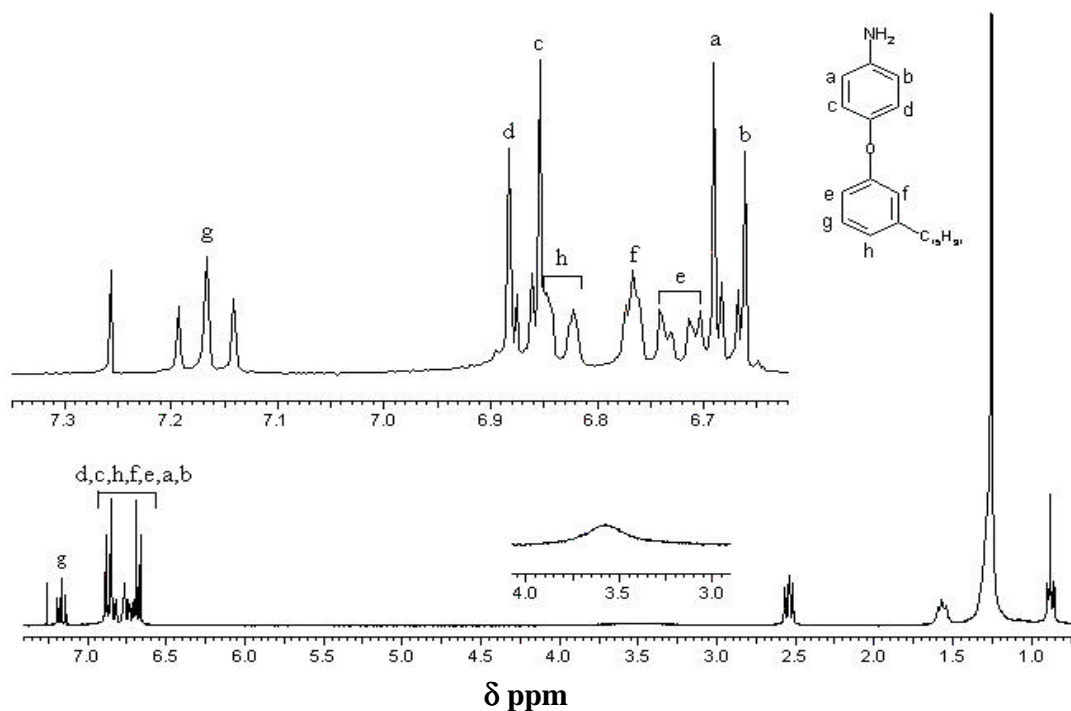
Figure 2.18. ^{1}H NMR spectrum of 4-amino-3'-pentadecyldiphenyl ether (3b) in CDCl₃

^{1}H NMR spectrum of 4-amino-3'-pentadecyldiphenyl ether (3b) (Figure 2.18) showed characteristic signals of pentadecyl group at 0.9, 1.16–1.71 and 2.56 δ ppm. The broad singlet at 3.01–3.93 δ ppm was due to $-NH_2$ group. The peaks in the region 6.62-6.94 δ ppm showed an integration of seven corresponding to seven aromatic protons. The triplet at 7.19 δ ppm was due to the aromatic proton at the meta position of pentadecyl group. These results strongly support the formation of 3b.

The FT-IR spectrum of 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3c) (Figure 2.19) showed new absorptions at 3296 and 1652 cm^{-1} due to amide $-N-H$ and carbonyl stretching vibrations. The bands at 1539 and 1342 cm^{-1} were due to asymmetrical and symmetrical stretching vibrations of $-NO_2$ group. The carbonyl group showed absorption at 1652 cm^{-1} and the ether group (-C-O-C-) showed absorption at 1252 cm^{-1}.
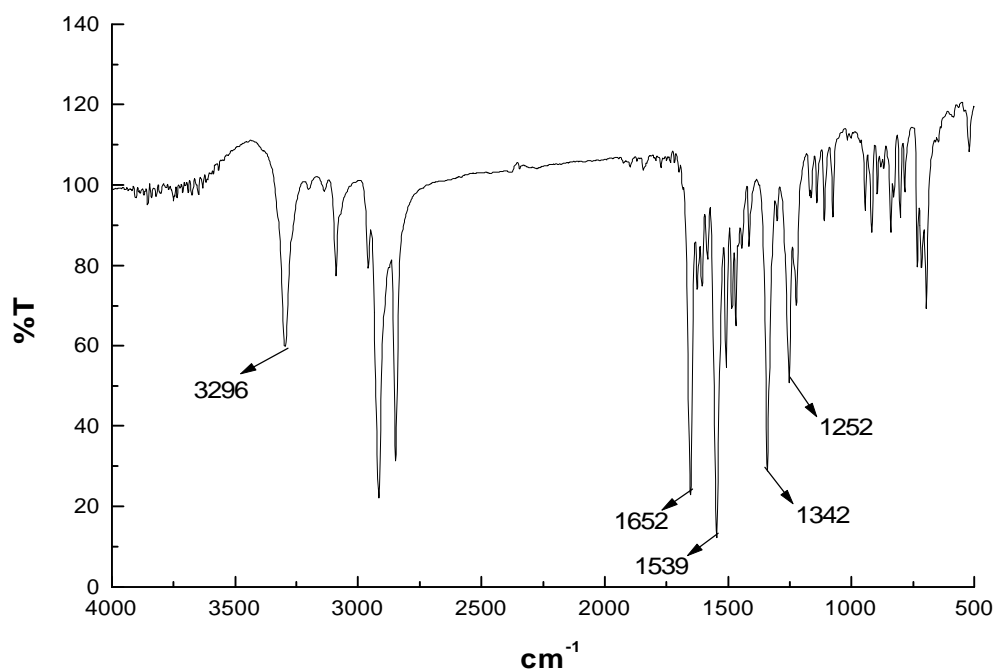
Figure 2.19. FT-IR spectrum of 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3c) (KBr)

The ^{1}H NMR spectrum of 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3c) (Figure 2.20) showed two triplets at 0.88 and 2.59 δ ppm and a multiplet at 1.16–1.70 δ ppm corresponding to pentadecyl group. Two protons ortho to –N-H group showed a doublet at 7.54-7.65 δ ppm and the protons ortho to both –NO$_2$ and –C=O group showed a singlet in the region 9.03-9.10 δ ppm. One proton in between the –NO$_2$ groups showed a singlet at 9.18-9.23 δ ppm. The –N-H proton was observed as a singlet at 8.14-8.23 δ ppm. All other protons showed peaks in the region 6.78-7.28 δ ppm with expected multiplicities and integration. These observations, along with a molecular ion peak at m/z 589 (Appendix I, Figure A.5) confirmed the structure of the product.

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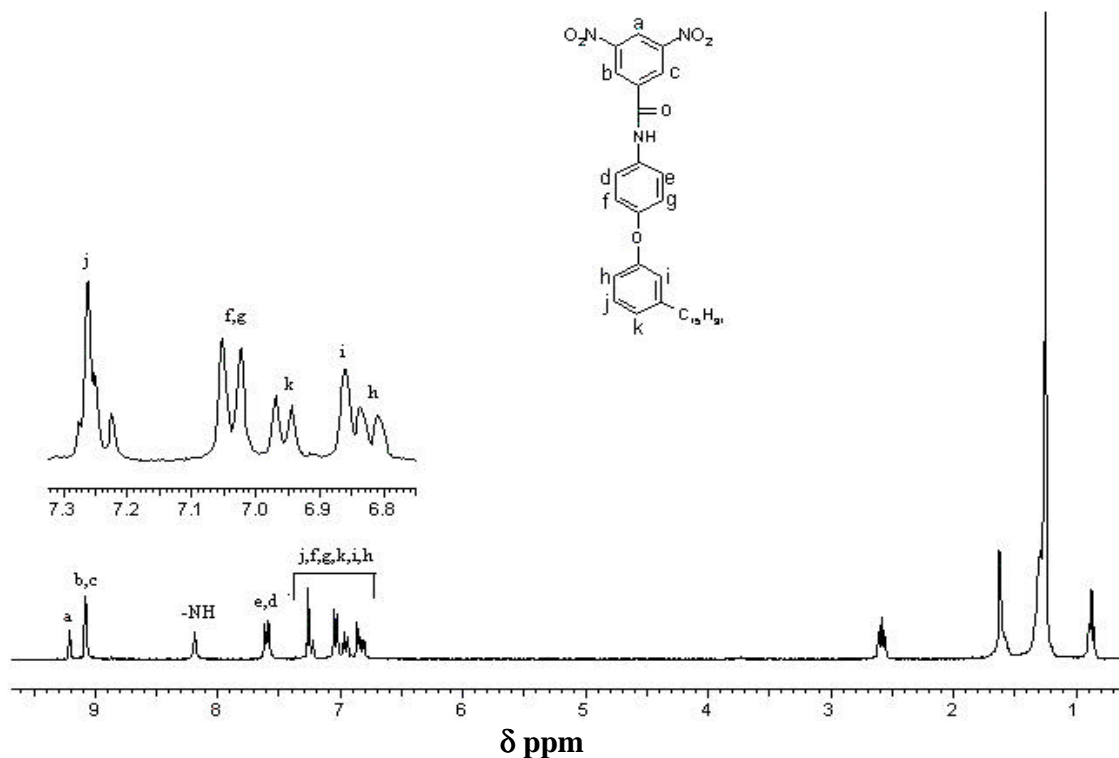
Figure 2.20. ¹H NMR spectrum of 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3c) in CDCl₃

The new absorptions at 3408-3467 cm^{-1} (-N-H stretching vibration of amine), 1592 cm^{-1} (-N-H deformation of amine) and 1356 cm^{-1} (-C-N stretching of amine) due to amine groups and the absence of absorption at 1539 and 1342 cm^{-1} due to nitro group in the FT-IR spectrum of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (3d) (Figure 2.21) confirmed that the reduction was complete. The characteristic bands of amide linkage were at 3308 cm^{-1} (-N-H stretching), 1522 cm^{-1} (-N-H deformation of amide) and 1646 cm^{-1} (-C=O). The ether group (-C-O-C-) showed absorption at 1241 cm^{-1}. The ¹H NMR spectrum of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (3d) (Figure 2.22) showed signals at 0.88, 1.09 – 1.70 and 2.56 δ ppm due to pentadecyl group. The broad singlet at 2.97-3.92 was due to the four protons of –NH₂ groups. The singlets observed at 6.07 and 6.5 δ ppm were due to one proton in between the –NH₂ groups and two protons ortho to –NH₂ groups. The protons ortho to ether group showed signals at 6.72-6.86 and 6.94-7.01 δ ppm respectively. The protons ortho to –N-H group showed a doublet at 7.47-7.62 δ ppm and the proton of –N-H group showed a singlet at 7.98 δ ppm. The proton ortho to pentadecyl group which is

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coupled with another proton showed a doublet at 6.87-6.92 δ ppm and the proton meta to pentadecyl group showed a triplet at 7.15-7.24 δ ppm.
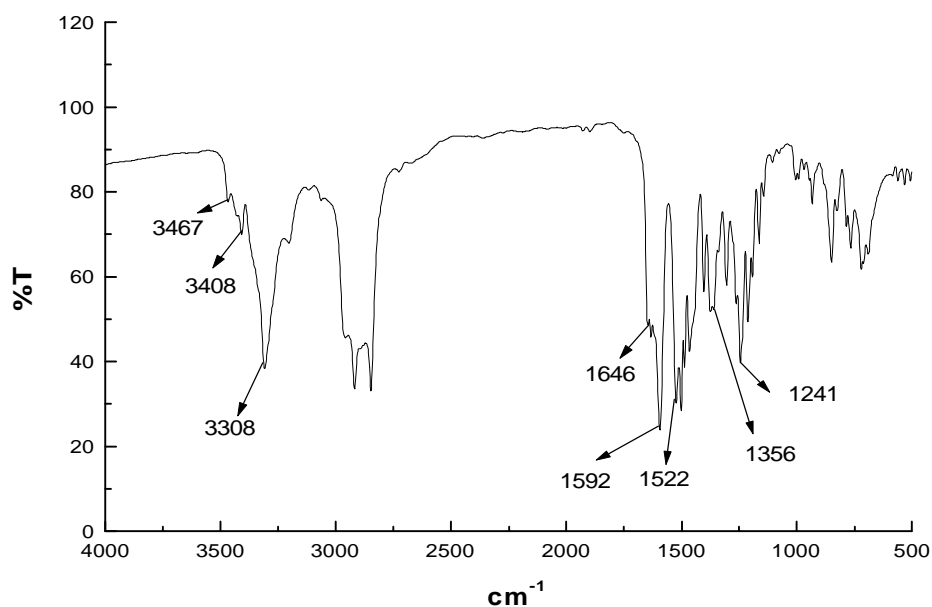
Figure 2.21. FT-IR spectrum of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3d) (nujol)
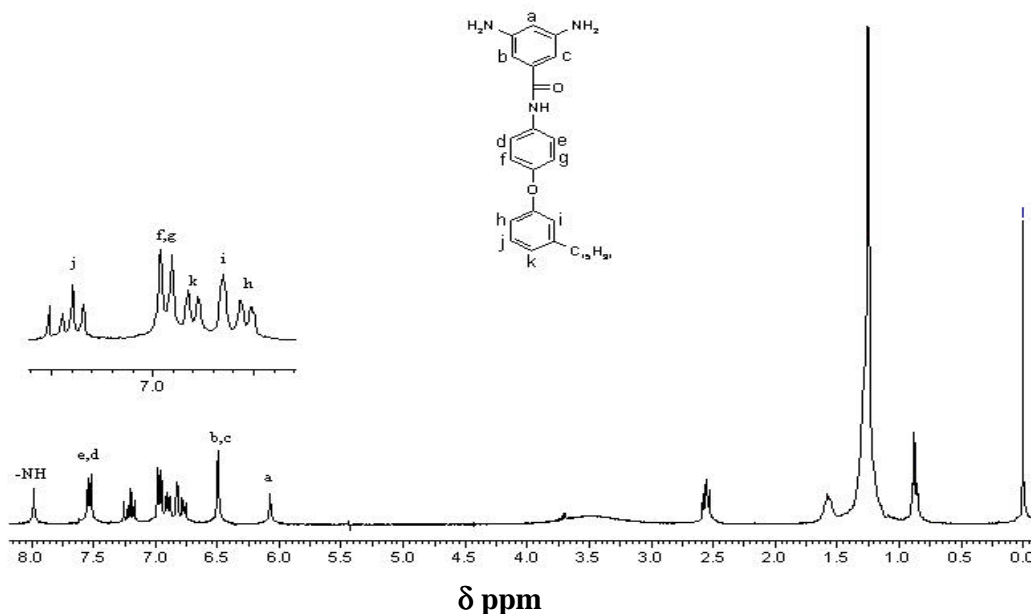
Figure 2.22. ¹H NMR spectrum of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3d) in CDCl₃

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The mass spectrum (Appendix I, Figure A.6) showed a molecular ion peak at m/z 530. Assignment of ^{13}C is shown in Figure 2.23 and the δ values agreed well with proposed structure of diamine. These results clearly confirmed that the structure of the synthesized diamine agreed well with the proposed structure.
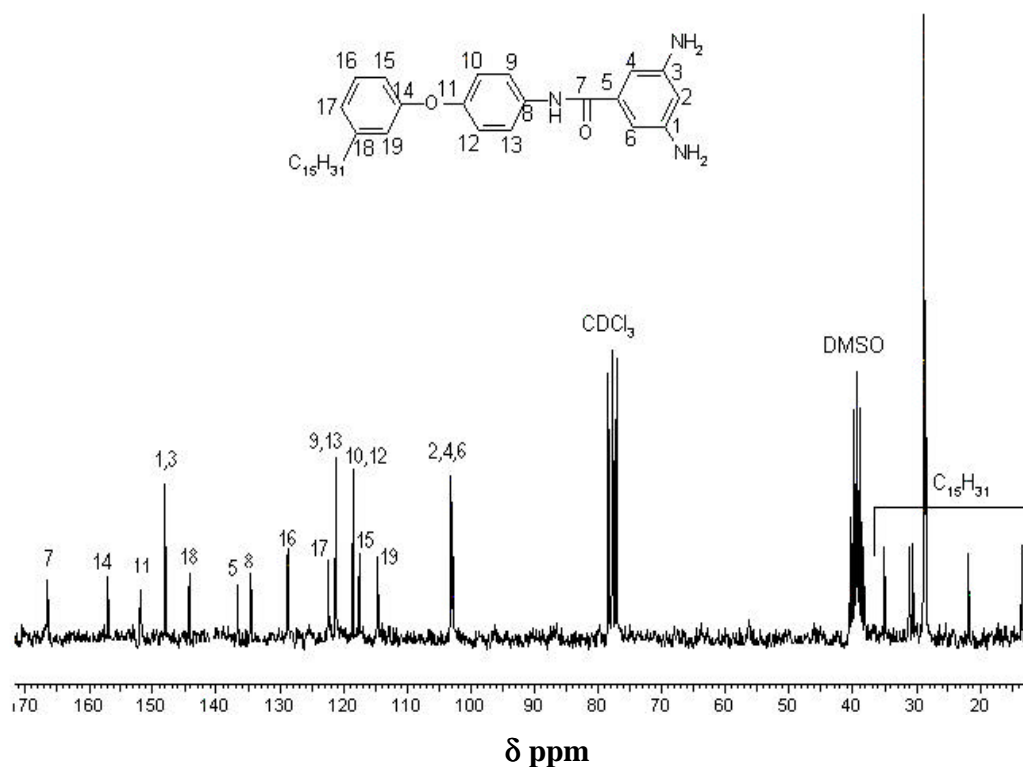
Figure 2.23. ^{13}C NMR spectrum of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3d) in CDCl$_3$ and DMSO-d$_6$ mixture

2.3.4 Synthesis of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride

This dianhydride was synthesized from o-xylene via a four step reaction as shown in Scheme 2.4. In the first step o-xylene was brominated in dark in presence of Fe catalyst to give a mixture of 3-bromo and 4-bromo-o-xylene (4a). It was observed that the ratio of 4-bromo-o-xylene in the mixture could be increased by carefully controlling the temperature of the reaction. The product obtained in this study was a 80:20 mixture of 4-bromo-xylene and 3-bromo-o-xylene, where as the bromo-o-xylene commercially available is a 70:30 mixture of 4 and 3-bromo-o-xylenes. 4a was then treated with lithium in ether *via* halogen-metal interchange to form 4 and 3-lithio-o-xylene. This lithiated product formed in situ was then

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treated with dichlorodimethylsilane to give a mixture of bis (3,4-dimethylphenyl)dimethyl silane (4b) and bis(2,3-(dimethylphenyl)dimethylsilane. Then bis (3,4-dimethylphenyl)dimethyl silane (4b) was separated from this mixture by recrystallization from benzene (a dilute solution was preferred). Aqueous $KMnO_4$-pyridine oxidation of 4b gave after neutralization the tetracarboxylic acid (4c), which was then dehydrated in refluxing acetic anhydride to bis (3,4-dicarboxyphenyl)dimethylsilane dianhydride (4d). In the oxidation step, excess $KMnO_4$ was added to ensure complete oxidation of the methyl groups (upto the point where the colour of $KMnO_4$ did not fade on refluxing). By this method the yield and purity of tetracarboxylic acid was improved. The chemical structures of all the synthesized compounds were confirmed by means of elemental analysis, FT-IR and ^{1}H NMR spectra, and the results were in good agreement with the expected structures.

FT-IR spectrum of 4-bromo-o-xylene (4a) (Figure 2.24) showed a band corresponding to –C-Br stretching frequency at 1085 cm^{-1}.
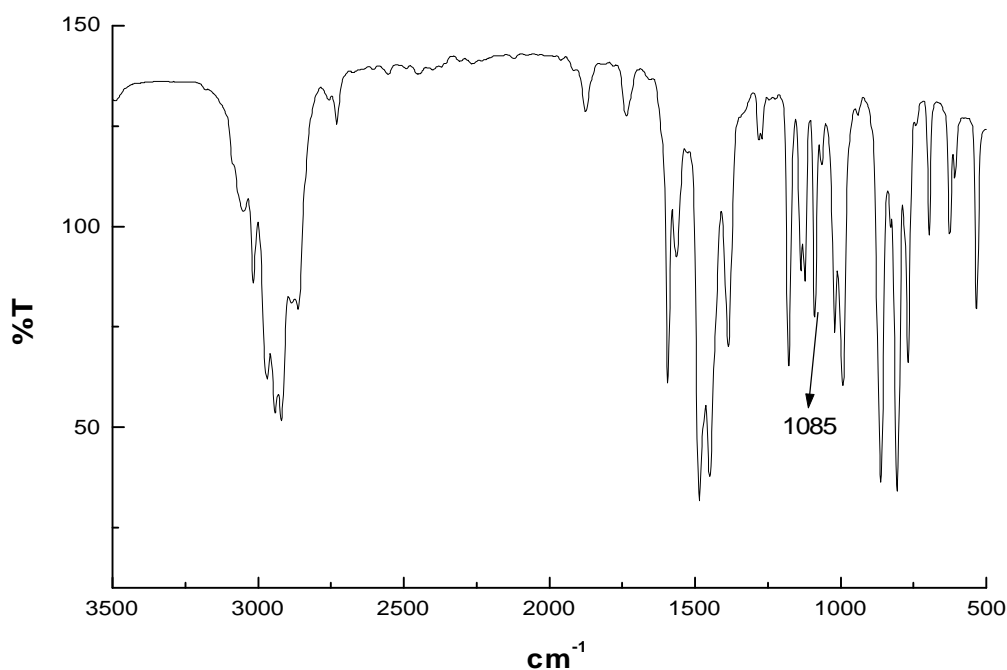
Figure 2.24. FT-IR spectrum of 4-bromo-o-xylene (4a) (Neat)

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^{1}H NMR spectrum (Figure 2.25) showed two doublets at 2.25-2.50 δ ppm due to the methyl groups of 3 and 4-bromo-o-xylene. Aromatic region showed peaks in the region 6.95-7.1 δ ppm and 7.25-7.4 δ ppm corresponding to the aromatic protons of 4-bromo-o-xylene. The peaks in the region 7.1-7.2 δ ppm and 7.4-7.5 δ ppm were due to aromatic protons of 3-bromo-o-xylene. The peak corresponding to the methyl group of o-xylene at 2 δ ppm was not found indicating complete bromination.
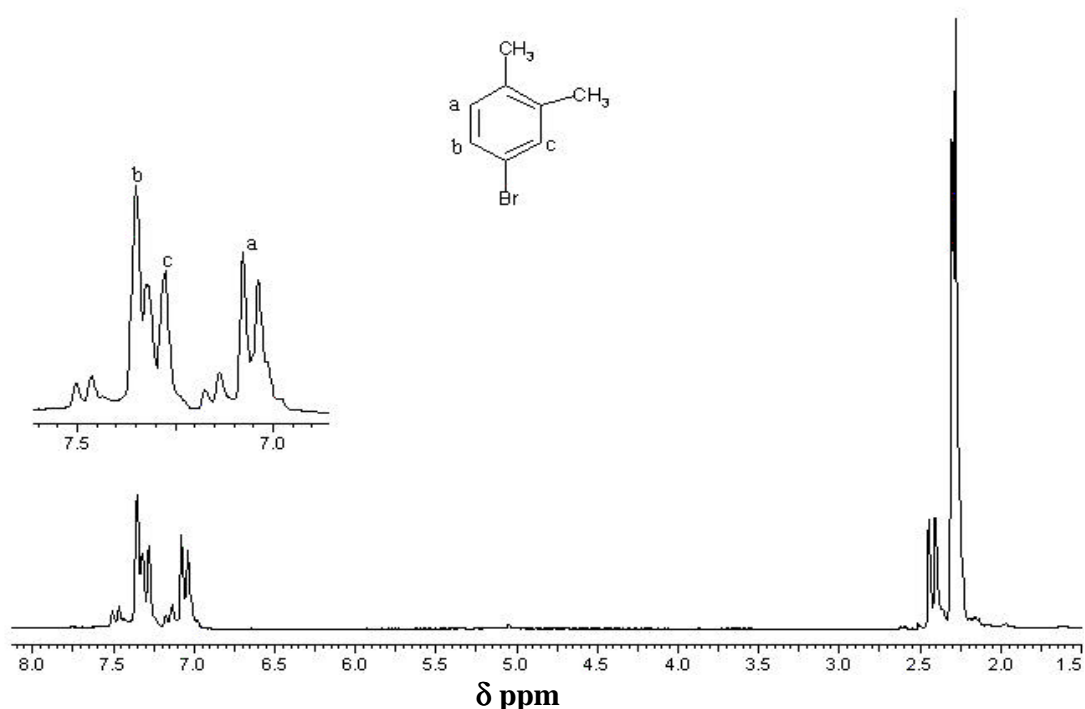
Figure 2.25. ^{1}H NMR of 4-bromo-o-xylene (4a) in CDCl$_3$

FT-IR spectrum of bis(3,4-dimethylphenyl)dimethylsilane (4b) (Figure 2.26) showed absorptions corresponding to silyl –CH$_3$ at 1247 and 797 cm^{-1}. ^{1}H NMR spectrum (Figure 2.27) showed signals in the region 0.6-0.85 δ ppm and 2.3-2.65 δ ppm due to silyl and aryl –CH$_3$. The aromatic protons in the region 7.25-7.6 δ ppm also showed the expected multiplicities and integration confirming the structure of the product.

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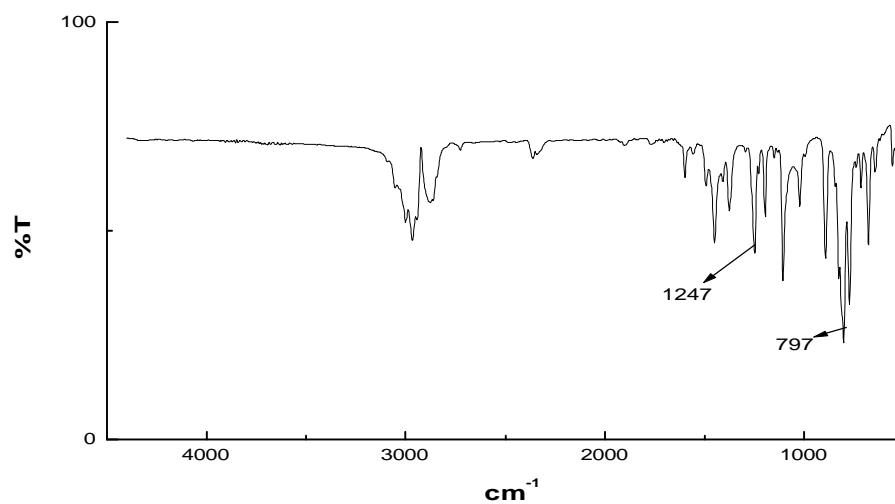
Figure 2.26. FT-IR spectrum of bis(3,4-dimethylphenyl)dimethylsilane (4b) (KBr)

δ ppm
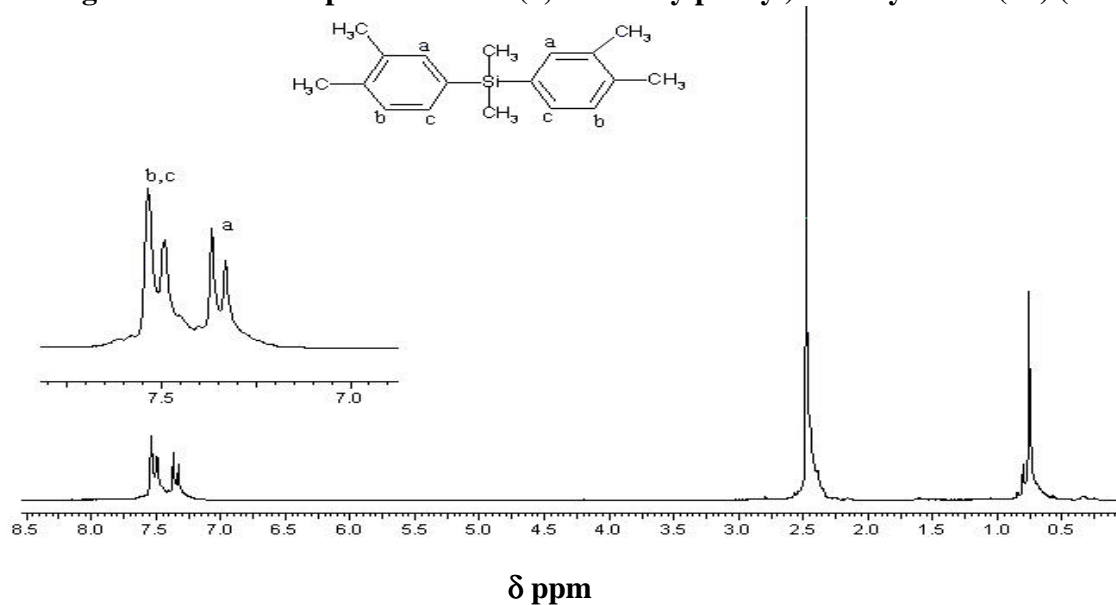
Figure 2.27. ^{1}H NMR spectrum of bis(3,4-dimethylphenyl)dimethylsilane (4b) in CDCl$_3$

FT-IR spectrum of bis(3,4-dicarboxyphenyl)dimethylsilane (4c) (Figure 2.28) showed a broad absorption in the range 3173-2154 cm^{-1}corresponding to the hydrogen bonded hydroxyl group. The absorptions due to >C=O group were seen as a doublet at 1747 and 1698 cm^{-1} due to intermolecular hydrogen bonding and intramolecular hydrogen bonding.
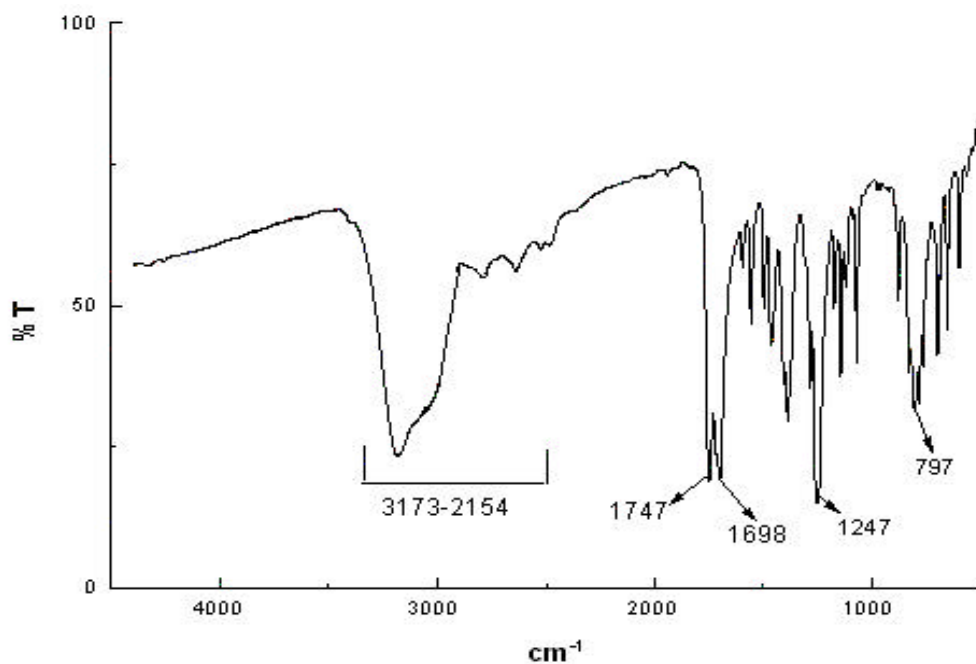
Figure 2.28. FT-IR spectrum of bis(3,4-dicarboxyphenyl)dimethylsilane (4c) (KBr)

δ ppm
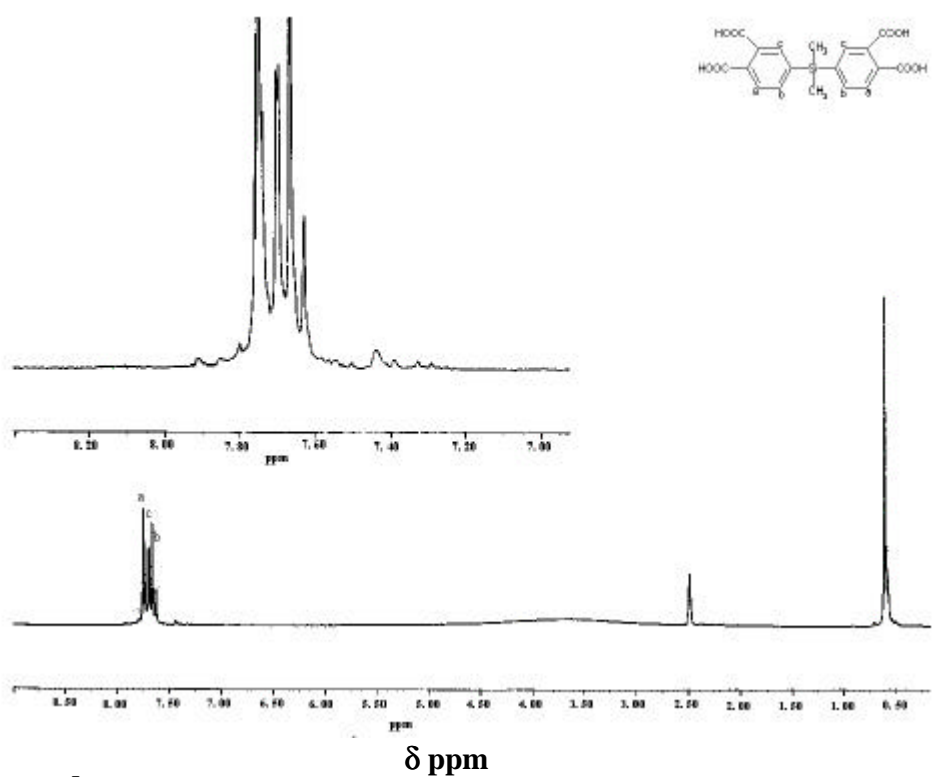
Figure 2.29. ^{1}H NMR spectrum of bis (3,4-dicarboxyphenyl)dimethylsilane (4c) in DMSO-d$_6$

The absorptions due to silyl -CH$_3$ was found at 1247 and 797 cm^{-1}. The absorption corresponding to –CH$_3$ was absent. ^{1}H NMR spectrum (Figure 2.29) showed peaks corresponding to silyl –CH$_3$ at 0.6 δ ppm. The signal in the region 2.3-2.65 δ ppm due to aryl -CH$_3$ of tetramethyl compound was absent indicating complete oxidation. The acid protons were not observed due to exchange. Aromatic protons at 7.6-7.8 δ ppm also showed the expected multiplicity and integration.

FT-IR spectrum of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (4d) (Figure 2.30) showed absorptions at 1246, 810 cm^{-1} due to silyl –CH$_3$ and a doublet at 1772-1854 cm^{-1} due to anhydride carbonyl. ^{1}H NMR spectrum (Figure 2.31) showed a multiplet corresponding to silyl –CH$_3$ at 0.8 δ ppm and the aromatic protons showed peaks in the region 8.0 - 8.2 δ ppm with expected multiplicities and integration. These results confirmed that the dianhydride prepared was consistent with the proposed structure.
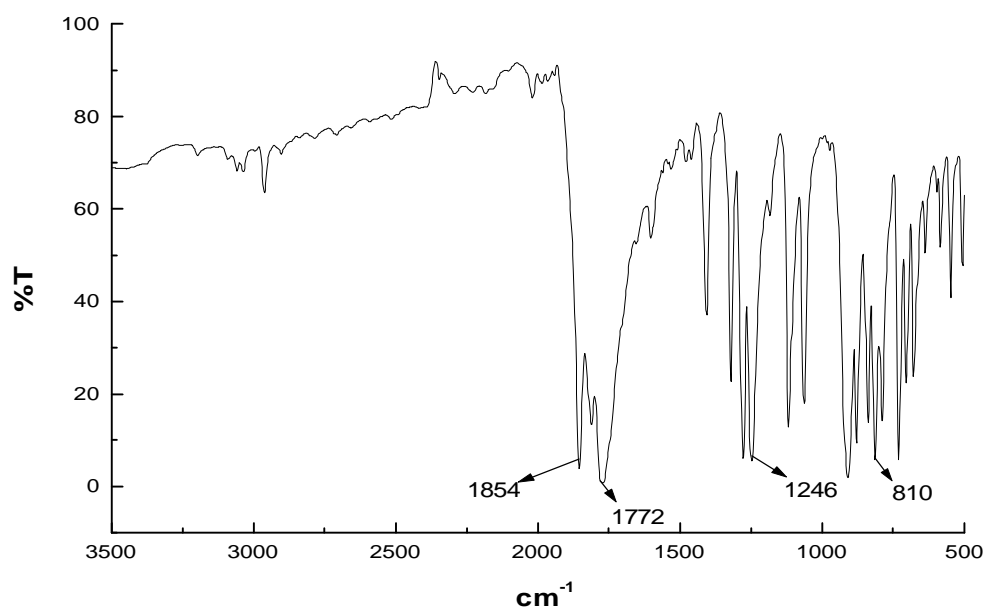
Figure 2.30. FT-IR spectrum of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (4d) (KBr)
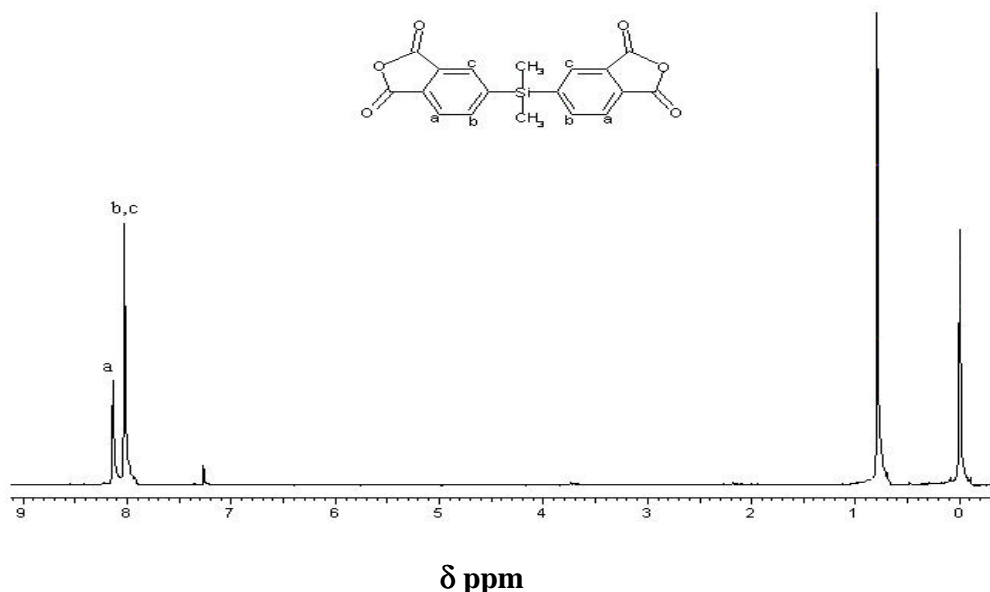
δ ppm
Figure 2. 31. ^{1}H NMR spectrum of bis (3,4-dicarboxyphenyl)dimethylsilane
dianhydride (4d) in CDCl$_3$

2.3.5 Synthesis and Characterization of bis(4-chlorocarbonylphenyl) dimethylsilane

The synthetic route of bis (4-chlorocarbonylphenyl)dimethylsilane is showed in Scheme 2.5. This was synthesized from bromotoluene according to the procedure described by Ghatge and Jadhav[17]. Reaction of bromotoluene with dichlorodimethylsilane in presence of lithium in dry ether yielded bis(4-methylphenyl)dimethylsilane (5a). Aqueous KMnO$_4$-pyridine oxidation of 5a gave after neutralization the dicarboxylic acid (5b), which was then treated with thionyl chloride to give bis(4-chlorocarbonylphenyl)dimethylsilane (5c). In the oxidation step excess KMnO4 was added to ensure complete oxidation of the methyl groups (upto the point were the colour of KMnO$_4$ did not fade on refluxing). This helped in improving the yield and purity of diacid, which in turn helped in improving the purity of diacid chloride. The chemical structures of all the synthesized compounds were confirmed by means of elemental analysis, FT-IR and ^{1}H NMR spectra, and the results were in good agreement with the expected structures.

The FT-IR spectrum of bis(4-methylphenyl)dimethylsilane (5a) (Figure 2.32) showed absorptions corresponding to silyl –CH$_3$ at 1250 and 840 cm^{-1}. ^{1}H NMR spectrum (Figure 2.33) showed signals corresponding to silyl –CH$_3$ at 0.6 δ ppm and that due to aryl –CH$_3$ at

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2.20 δ ppm. Aromatic region showed protons ortho to Si at 6.7-7.10 δ ppm and protons ortho to –CH₃ at 7.1- 7.40 δ ppm.

FT-IR spectrum of (4-carboxyphenyl)dimethylsilane (5b) (Figure 2.34) showed new absorptions in the region 2524-3017 due to hydrogen bonded –OH of carboxyl group and at 1692 cm^{-1} due to >C=O of carboxyl group along with the absorptions at 1254, 830 cm^{-1} due to silyl –CH₃. ^{1}H NMR spectrum (Figure 2.35) showed signals corresponding to silyl –CH₃ at 0.6 δ ppm and the signal due to aryl –CH₃ at 2.20 δ ppm disappeared, indicating the complete oxidation of -CH₃ groups of 5a. Two doublets found in the aromatic region at 7.60-7.75 δ ppm and 8.05-8.25 δ ppm were due to four protons ortho to silane and four protons ortho to –COOH.

In the FT-IR spectrum of (4-chlorocarbonylphenyl)dimethylsilane(5c) (Figure 2.36) the absorption in the region 2524-3017 cm^{-1} due to –COOH group of 5b disappeared and a new doublet appeared at 1774-1732 cm^{-1} due to carbonyl group of acid chloride. The absorption due to silyl –CH₃ appeared at 1212 and 832 cm^{-1}. The ^{1}H NMR spectrum (Figure 2.37) showed signals at 0.6 δ ppm due to silyl –CH₃. Aromatic protons in the region 7.62-7.77 δ ppm and 8.03-8.23 ppm corresponded to the protons ortho to silyl group and those ortho to –COCl group. These results along with the elemental analysis values confirmed the structure of the product.
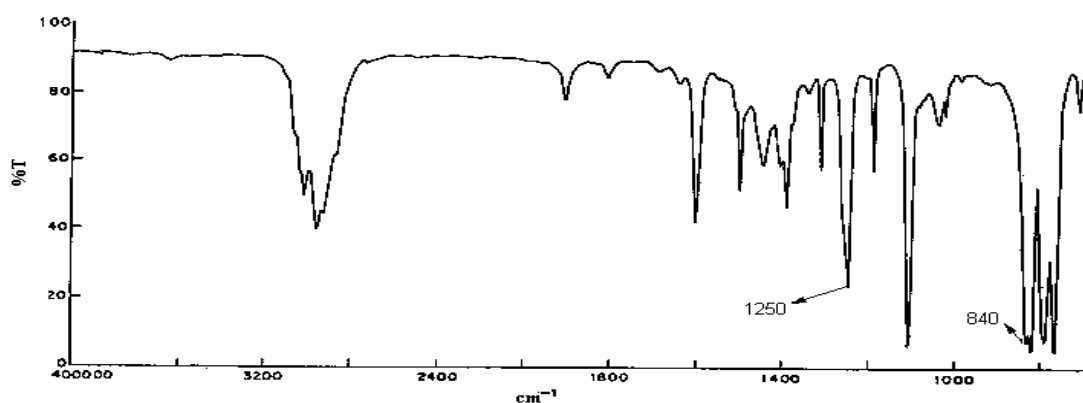
Figure 2.32. FT-IR spectrum of bis(4-methylphenyl)dimethylsilane (5a) (Neat)

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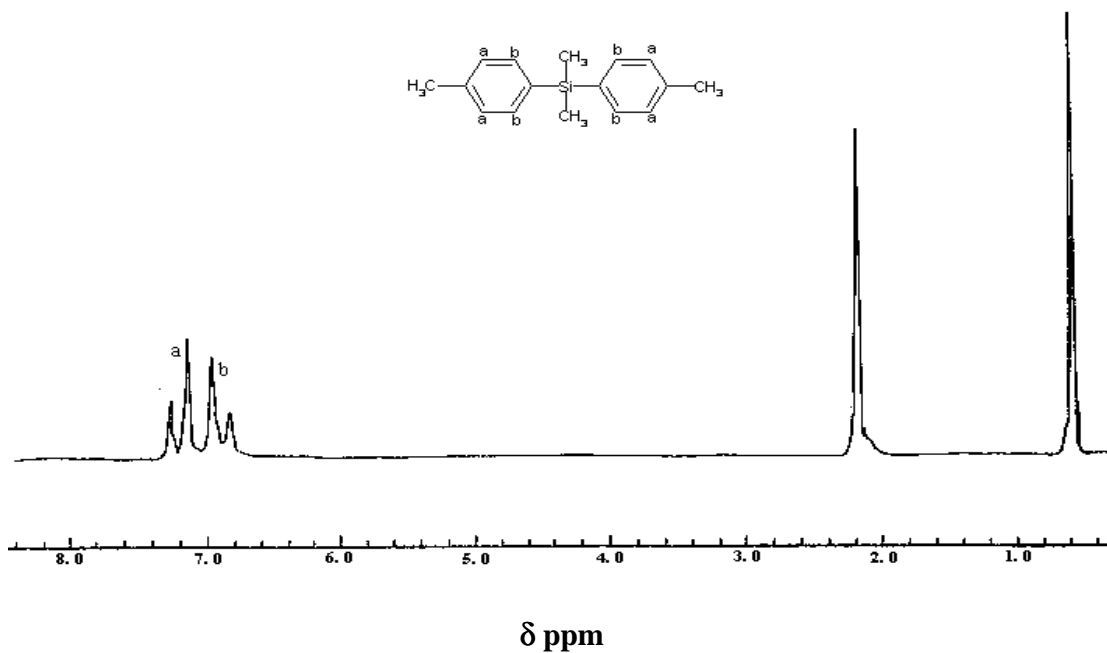
Figure 2.33. ^{1}H NMR spectrum of bis(4-methylphenyl)dimethylsilane (5a) in CDCl$_3$
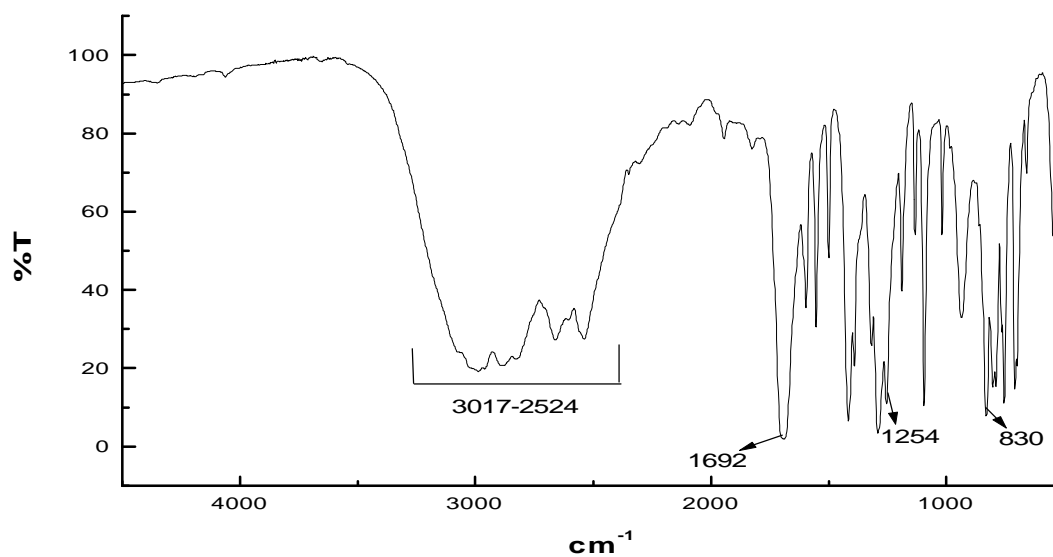
Figure 2.34. FT-IR spectrum of bis(4-carboxyphenyl)dimethylsilane (5b) (KBr)
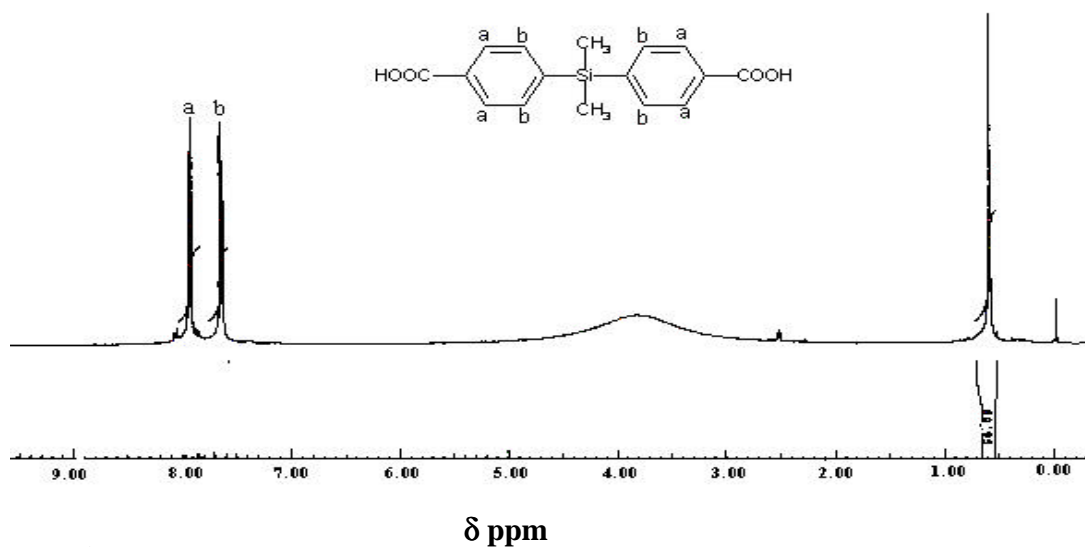
Figure 2.35. ^{1}H NMR spectrum of bis(4-carboxyphenyl)dimethylsilane (5b) in DMSO-d$_6$
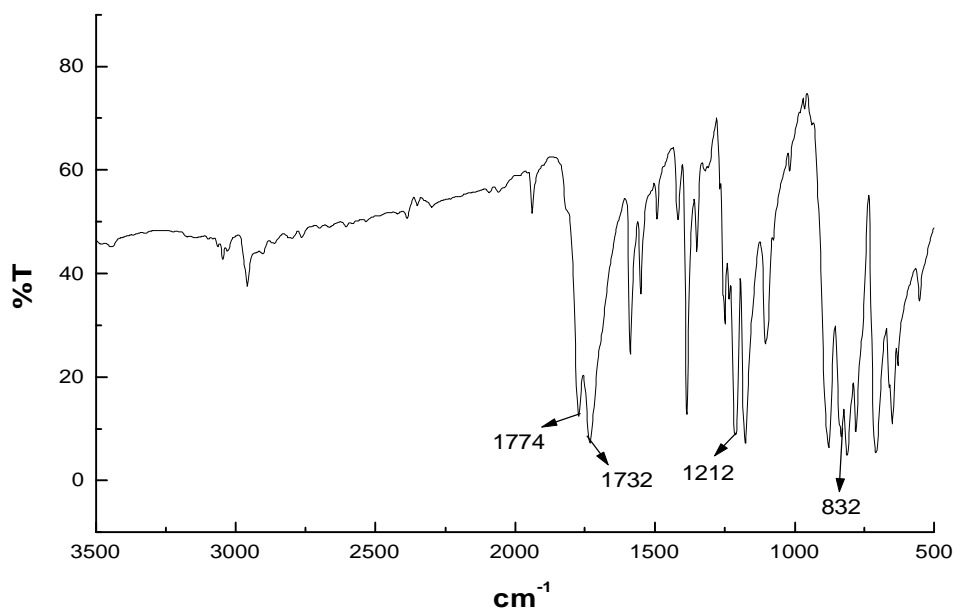
Figure 2.36. FT-IR spectrum of bis(4-chlorocarbonylphenyl)dimethylsilane (5c) (KBr)

128
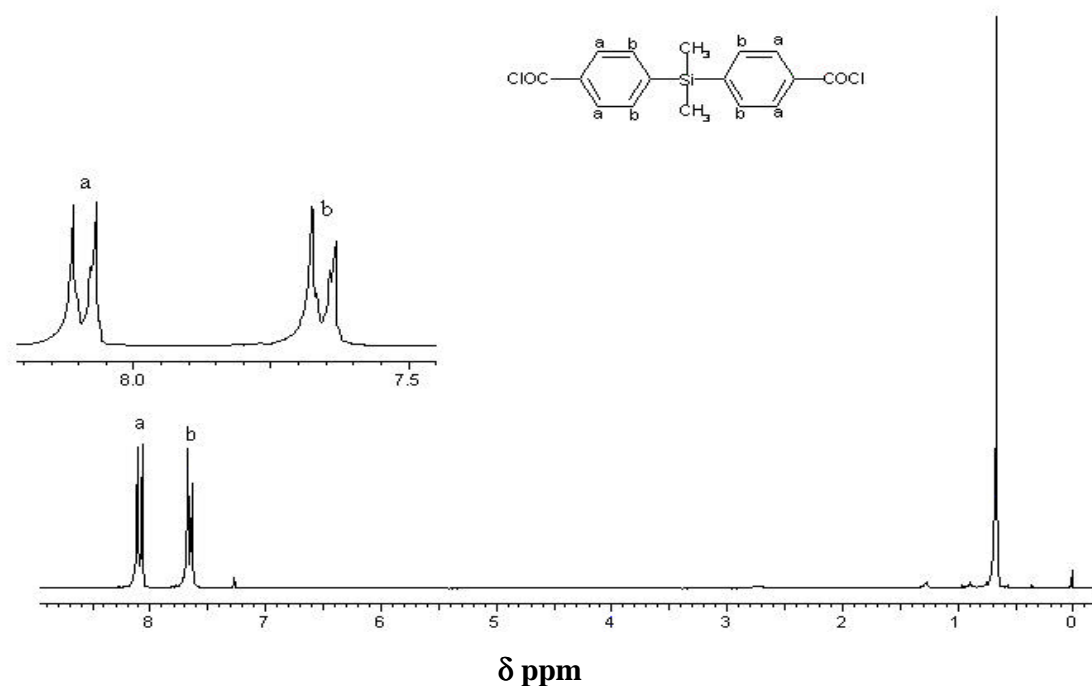
Figure 2.37. ¹H NMR spectrum of bis(4-chlorocarbonylphenyl)dimethylsilane (5c) in CDCl₃

2.4 Conclusions

- Three new diamines namely, 1-(3-pentadecylphenoxy)-2,4-diaminobenzene, 3-pentadecylphenyl-3,5-diaminobenzoate and 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide were successfully synthesized by simple condensation reactions in high purity and high yields, by using a naturally available phenol like 3-pentadecylphenol, which is a major constituent of the agricultural by product and renewable resource, Cashew Nut Shell Liquid.

- A silicon containing dianhydride bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and a silicon containing diacid chloride, bis(4-chlorocarbonylphenyl)dimethylsilane was also synthesized in good yields and purity.

- The possibility of using a renewable resource like Cashew Nut shell Liquid as a raw material for the synthesis of some important monomers like diamines, which in turn useful for the synthesis of futuristic products like polyamides and polyimides is explored.

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Chapter 3

Synthesis, Characterization and Application of Polyamides from Cardanol

3.1 Introduction

Aromatic polyamides (aramids) are thermally stable polymers with an attractive combination of excellent chemical, physical and mechanical properties.[1] However in many cases they are insoluble or do not melt below the decomposition temperature because of their high crystallinity and therefore, processing in melt or solution becomes impossible. Thus, considerable research have been carried out to develop aramids that have better processability while retaining their thermal and mechanical properties. Different strategies adopted for the synthesis of soluble/processable polyamides have been discussed in detail in Chapter 1, Section 1.2.2.

Typical approaches[2] like introduction of flexible bridging linkages, bulky substituents, non coplanar conformation, m,m' linkages and bulky pendant groups into the polymer backbone have been used to enhance the solubility and processability of polyamides. It was observed that incorporation of flexible units such as aryl ether, hexafluoroisopropylidene, sulfonyl, isopropylidene, oxyethylene, methylene and carbonyl enhances the solubility of the resulting polyamides.[3] Pendant groups were also introduced into the main chain as an effective means of enhancing solubility with retention of thermal stability.[4,5] The presence of bulky substituents like t-butyl group in the polymer main chain markedly improved the solubility, yet maintaining the thermal stability.[6] Methyl group substituents have also been used to improve the solubility of polyamides by disrupting the regularity of packing along the main chain in several substituted phenylene diamines and diacids. The study of Takatsuka et al.[7] and Chaudhuri et al.[8] showed that for methyl substituted polyamides the solubility increases with increase in methylation and those polyamides with unsymmetrical methyl substitution showed higher solubility. Vernekar et al.[9] reported the synthesis of some polyamides containing pendant pentadecyl groups along with flexible groups like sulfone ether in the main chain having enhanced solubility. Choi et al.[10] synthesized polyamides from isophthalic and terephthalic acids with bulky silyl substituents. The resulting polymers showed higher solubilities and glass transition temperatures than the corresponding polyamides synthesized from unsubstituted isophthalic and terephthalic acids. de Abajo et al.[11] synthesized 5-substituted isophthalic acid with bulky aromatic substituents and showed

that incorporation of pendant phenyl groups improves solubility without affecting the thermal stability. Polyamides containing pendant ether,[12] ester[13] and amide[14] groups have also been reported in the literature. Polyterephthalamides[12c] containing pendant biphenyloxy and naphthoxy pendant groups synthesized from m-phenylene diamines having these substituents were found to have higher thermal stability and solubility than those without these substituents, whereas polyisophthalamides[12c] synthesized from a diacid chloride having pendant phenoxy group and m-phenylene or p-phenylene diamine did not show much improvement in solubility. This indicates that the pendant substituent on a diacid or diacid chloride moiety has only little or no effect on the solubility properties of the corresponding polyamides from rigid diamines. Polyterephthalamides with ester pendant groups showed higher solubility as compared to those having pendant ether groups and this may be attributed to the greater disruption of chain packing by ester groups which are bulkier than ether groups.[13a] Polyisophthalamides with pendant amide groups also showed good solubility in some high boiling polar aprotic solvents as compared to the unmodified ones, which were soluble only in concentrated sulphuric acid.[14b] It was also evident from these studies that polyamides synthesized from isophthalic acid having m,m' linkages showed better solubility than those synthesized from terephthalic acid having p,p' linkages. Incorporation of aromatic silane moieties in the polymer backbone can also improve the solubility of polyamides.[15] Vernekar et al.[16] synthesized silicon containing polyamides with improved solubility from diacid chlorides containing dimethyl silyl and diphenyl silyl bridging groups. Soluble polyamides containing siloxane[17] moiety and non coplanar biphenylene[18] moieties are also known in literature. In many cases it is necessary to have a combined action of above factors to improve the solubility and processability of the resulting polymers.

It is evident from the above discussion that incorporation of pendant groups like alkyl, phenyl, ether, ester and amide improves the solubility of polyamides without sacrificing their excellent thermo-mechanical properties. It is also shown that the polyamides synthesized from silicon containing diacid chloride, bis (4-chlorocarbonylphenyl) dimethyl silane[19] have comparatively higher solubility than those synthesized from terephthaloyl chloride and isophthaloyl chloride. Polyamides synthesized from diamines having m,m' linkages showed more solubility than those having p,p' linkages. It is expected that a combination of these

structural modifications will give rise to polyamides with a favorable balance of properties. Thus the objective of the present work was to synthesize polyamides from m-phenylene diamines incorporating pendant connecting groups like ether, ester and amide along with pendant pentadecyl phenyl and pentadecyldiphenylether groups. The synthesis of polymers from renewable natural resources has achieved considerable attention recently and therefore a naturally occurring *meta* substituted long chain phenol, cardanol, a byproduct of cashew industry, is made use of for the synthesis of these diamines (Chapter 2, Section 2.2.3) and corresponding polyamides. Yet another objective was to synthesize polyamides containing silicon by condensing these diamines with bis (4-chlorocarbonylphenyl)dimethylsilane (DMSC), since it is known that incorporation of silicon enhances the solubility of polyamides drastically.

In this chapter the synthesis of polyamides from three new diamines namely (1) 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN), (2) 3 -pentadecylphenyl-3,5-diaminobenzoate (PPDBT) and (3) 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (PPPB) is discussed. Polyamides were synthesized by the low temperature interfacial polycondensation of these diamines with diacid chlorides namely, bis (4-chloro carbonylphenyl) dimethyl silane (DMSC), terephthaloyl chloride (TPCl) and isophthaloyl chloride (IPCl). The effect of different pendant groups on the solubility, crystallinity, thermal stability and gas permeability properties of these polyamides was also investigated. The synthesized polyamides were characterized by IR spectroscopy, ^{1}H NMR spectroscopy, solubility studies, inherent viscosity measurements, X-ray diffraction studies, thermogravimetric analysis and differential scanning calorimetry.

3.2 Experimental

3.2.1 Materials

Dichloromethane (S.D. Fine Chem., India) was dried over P_2O_5 and distilled. n-Hexane (S.D. Fine Chem., India) was first dried over $CaCl_2$ and then distilled from sodium in presence of benzophenone. Thionyl chloride (Spectrochem, India) was distilled prior to use and sodium carbonate (S.D. Fine Chem., India) was used as received.

The diamines and bis(4-chlorocarbonylphenyl)dimethylsilane (DMSC) were synthesized as given in Chapter 2, Sections 2.2.3 and 2.2.5. Terephthaloyl (TPCl) and isophthaloyl (IPCl) chlorides were synthesized from the corresponding diacids by refluxing them with thionyl chloride and by recrystallizing the resulting crude product from dry n-hexane.

3.2.2 Analytical methods

The FT-IR spectra were recorded on a Perkin-Elmer 599B spectrometer and ^{1}H NMR spectra were recorded on Bruker NMR spectrometer at 200 and 500 MHz at room temperature with tetramethylsilane as an internal standard. The X-ray diffractograms of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a heating rate of 2°/min. Thermogravimetric analysis (TGA)) were performed on Perkin-Elmer TGA-7 analyzer at a heating rate of 10°C/min in nitrogen atmosphere. The glass transition temperatures were determined on Perkin-Elmer DSC-7 analyzer or Mettler Toledo FP85 TA cell at a heating rate of 10°C/min in nitrogen atmosphere. Solubility of polyamides were determined at 5% concentration in various solvents at room temperature. Inherent viscosities of all polymers were determined with solutions of 0.5 g/dL concentration at 30.0 ± 0.1^{o}C using an Ubbelohde viscometer. The viscosity was calculated using the equation, $\eta_{inh} = 2.303/c \times \log t/t_0$, where t and t_0 are flow times for polymer solution and solvent respectively and c is the concentration of the polymer solution.

3.2.2.1 Gas permeability measurements

➢ Measurements

The gas permeability of some of the polyamide films was determined by the standard method for determining the gas permeability characteristics of plastic film and sheeting (ASTM method D 1434, (variable volume method)). The gas permeabilities were measured at 30 ± 0.1^{0}C on polyamide films of 13 cm^2 size. The upstream gas pressure (pressure on the high pressure side of membrane, P_1) was measured with a transducer, which can measure a pressure of 0-1000 psi. The upstream side was maintained at constant pressure and the permeate side at atmospheric pressure. On the permeate side of the diffusion cell, a calibrated borosilicate glass capillary (internal diameter = 4×10^{-3} mm) containing a colored methyl isobutyl ketone (MIBK) slug, having a length of 3 cm was connected. The rate of

displacement of mercury slug at a given constant pressure and the capillary cross section area yielded the flow rate of the gas, N [cc (STP)/sec].

The reproducibility of each gas permeability measurement was confirmed by taking five measurements of the same film. Measurements were also done for a duplicate film prepared under the same conditions and an average value was taken.

Four gases namely, N_2, O_2, H_2 (M/s Indian Oxygen Ltd., India) and CO_2 (Hydrogas, Bombay, India) were used for the permeation study.

➢ **Preparation of membranes**

0.1 g polymer was dissolved in chloroform (2 ml) or a solvent mixture of chloroform (2 ml) and m-cresol (2 drops). The clear solution was then filtered through a G0 sintered funnel (to remove dust particles), into a flat bottom Anumbra petri dish of 5 cm diameter and was covered with a double layer of aluminium foil. Care was taken to avoid air bubble formation. This was then kept in a dust free chamber at ambient temperature for 24 h to ensure slow evaporation of solvent to obtain a defect free film. By this method a good transparent film was obtained. This film was dried at 50-60^{0}C for 24 h under continuous vacuum and then carefully peeled from the petri dish. It was then further dried at 50°C for 48 h under continuous vacuum. The thickness of the films were in the range 50 $\pm$2 μm.

3.2.3 Synthesis of polyamides

Polyamides were synthesized from diamines 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) (Scheme 3.1), 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT) (Scheme 3.2) and 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (PPPB) (Scheme 3.3) by condensing them with diacid chlorides namely, (1) terephthaloyl chloride, (2) isophthaloyl chloride and (3) bis(4-chlorocarbonylphenyl)dimethylsilane (DMSC) by low temperature interfacial polycondensation technique. A typical procedure for low temperature interfacial polycondensation is described below.

➢ **Synthesis of polyamide from 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) and bis(4-chlorocarbonylphenyl)dimethylsilane (DMSC) – (PA-1c)**

To a 100 mL high speed reactor was added 0.5 g (0.001 mole) PPDBN and 0.129 g (0.001 mole) sodium carbonate in 15 mL water and the solution was stirred for 10 minutes at

room temperature and then cooled to 10°C. To this solution was added 0.4106 g (0.001 mole) DMSC dissolved in 15 mL dichloromethane, in one lot, with vigorous stirring. The stirring was then continued for another 0.5 hrs at this temperature and then for 0.5 hrs at room temperature. The contents of the reaction flask were then poured into 400 mL methanol. The precipitated polymer was separated by filtration, washed with distilled water, methanol and then dried under vacuum at 70°C for 24 hrs. The polymer was then purified by dissolving in chloroform and reprecipitating with methanol to give PA-1c. The yield of the polymer was about 98%. Other polyamides were also synthesized by a similar procedure and their yields and viscosity values are given in Table 3.1.

Table 3.1. Synthesis of polyamides from diamines PPDBN, PPDBT and PPPB

Polymer Code	Diacid Chloride	Diamine	Yield %	η_{inh}, dL/g
PA-1a	TPCl	PPDBN	99.2	$-^{q}$
PA-1b	IPCl	PPDBN	99.0	$-^{q}$
PA-1c	DMSC	PPDBN	98.0	0.45^{m}
PA-2a	TPCl	PPDBT	99.0	0.6^{n}
PA-2b	IPCl	PPDBT	98.5	0.55^{n}
PA-2c	DMSC	PPDBT	98.0	0.5^{n}
PA-3a	TPCl	PPPB	97.5	$-^{p}$
PA-3b	IPCl	PPPB	98.0	0.56^{n}
PA-3c	DMSC	PPPB	99.3	0.65^{n}

m = Viscosity determined in $CHCl_3$
n = Viscosity determined in NMP
p = not soluble
q = low solubility in common organic solvents

Scheme 3.1. Synthesis of polyamides from PPDBN

Where Ar =

PA-1a

PA-1b

PA-1c

Where Ar =
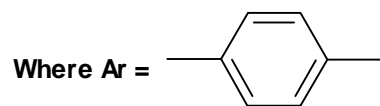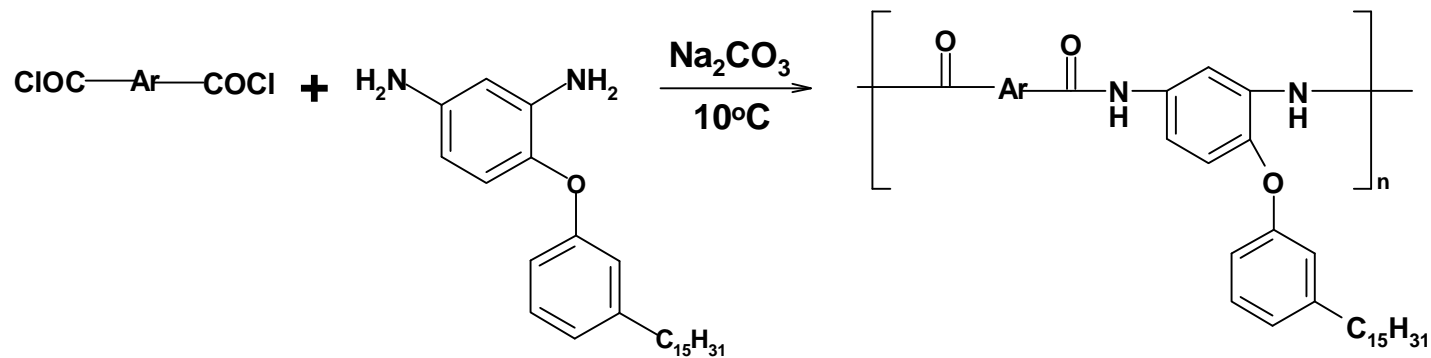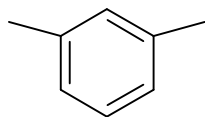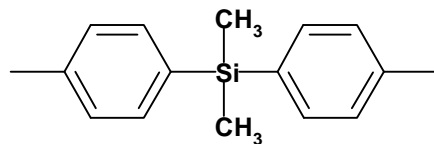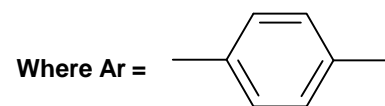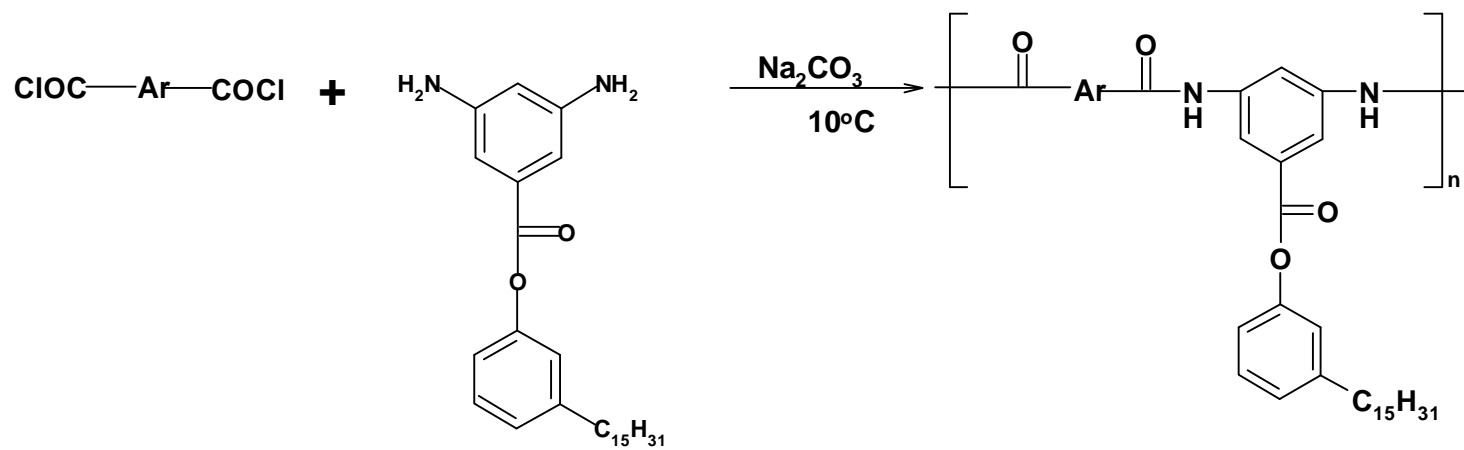
PA-2a
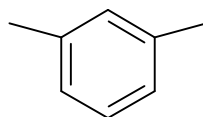
PA-2b
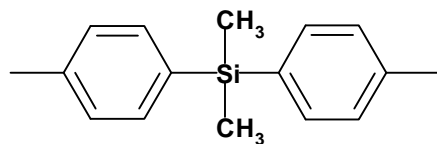
PA-2c

Scheme 3.2. Synthesis of polyamides from PPDBT

Where Ar =
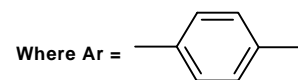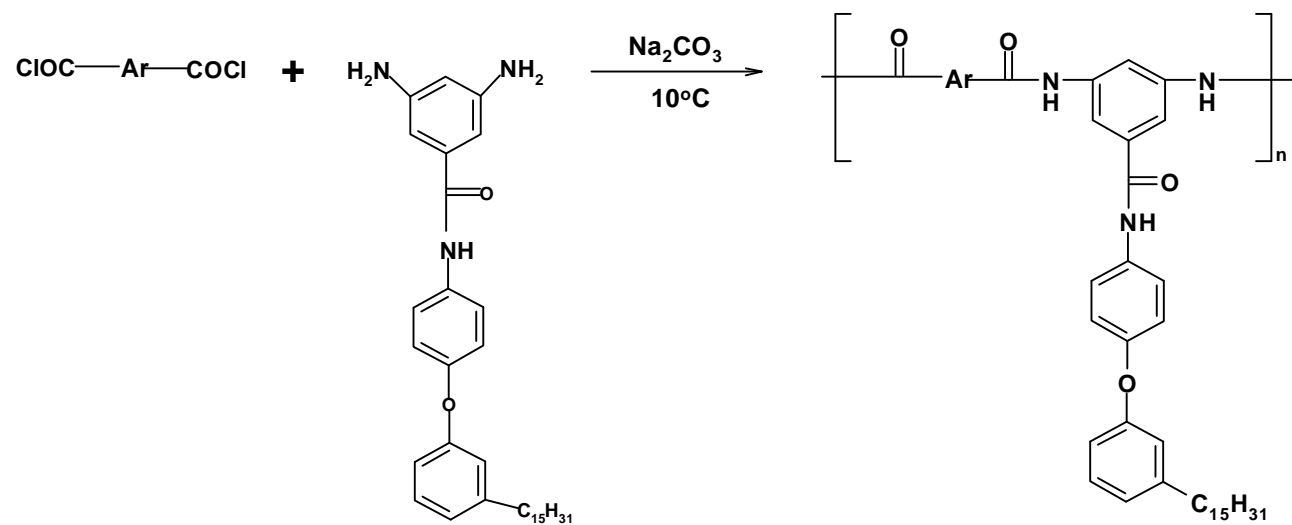
PA-3a
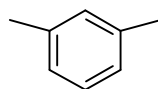
PA-3b
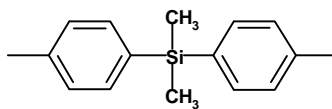
PA-3c

Scheme 3.3. Synthesis of polyamides from PPPB

3.3 Results and discussion

3.3.1 Synthesis and structural characterization of polyamides

Literature reports the synthesis of polyamides *via* different synthetic routes as discussed in Chapter 1, Section 1.2.1. Among them the widely used methods include (1) high temperature solution polycondensation, (2) low temperature solution polycondensation and (3) interfacial polycondensation. It was found that the first two methods were not useful for this study since only low molecular weight polyamides were obtained. It is known that in interfacial polymerization the monomer diffusing to the interface reacts only with the end of the polymer chain resulting in high molecular weight polymer.[20] Also since the temperatures needed are low, the side reactions are minimized. Thus a new class of modified polyamides were synthesized in this study by low temperature interfacial polycondensation of the diamines like PPDBN, PPDBT and PPPB with three diacid chlorides like TPCl, IPCl and DMSC (Schemes 3.1, 3.2 and 3.3).

The polyamides were obtained in 97.5-99.3 % yields and their inherent viscosity (η_{inh}) values ranged from 0.45 to 0.65 dL/g (Table 3.1). Most of the polyamides except PA-3a could be solution casted into flexible, and tough films, indicating the formation of high molecular weight polymer. The viscosity of polyamides PA-1a and PA-1b could not be determined due to their low solubility in common organic solvents. The polyamides synthesized from PPPB diamine were found to have the maximum viscosity.

The polymers thus obtained were characterized by FT-IR and ^{1}H NMR spectroscopy. FT-IR spectra of all polyamides exhibited characteristic absorption bands in the region 3300-3330 cm^{-1} (-N-H stretching), 1655-1665 cm^{-1} (amide I band, -C=O stretching), 1520-1545 cm^{-1} (amide II band, interaction between -N-H deformation and –C-N stretching, strong band) and 1280-1285 cm^{-1} (interaction between -N-H deformation and –C-N stretching, weak band). The FT-IR spectrum of polyamides derived from PPDBN (PA-1a-c) and PPPB (PA-3a-c) showed an additional absorption at 1248 and 1250 cm^{-1} respectively due to –C-O-C- linkage and the FT-IR spectrum of polyamides synthesized from PPDBT (PA-2a-c) showed additional absorptions at 1740, 1218 and 1192 cm^{-1} due to ester group. In the case of polyamides synthesized from PPPB, the

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absorption corresponding to the amide linkage in the side chain and main chain overlapped at 1650-1670 cm^{-1}. The FTIR spectra of polyamides synthesized from the diacid chloride DMSC (PA-1c, 2c and 3c) showed absorptions at 1208-1214 cm^{-1} and 832-836 cm^{-1} due to silyl –CH$_3$ groups. The representative IR spectra of polyamides synthesized from PPDBN (PA-1c), PPDBT (PA-2c) and PPPB (PA-3c) are shown in Figures 3.1, 3.2 and 3.3 respectively.
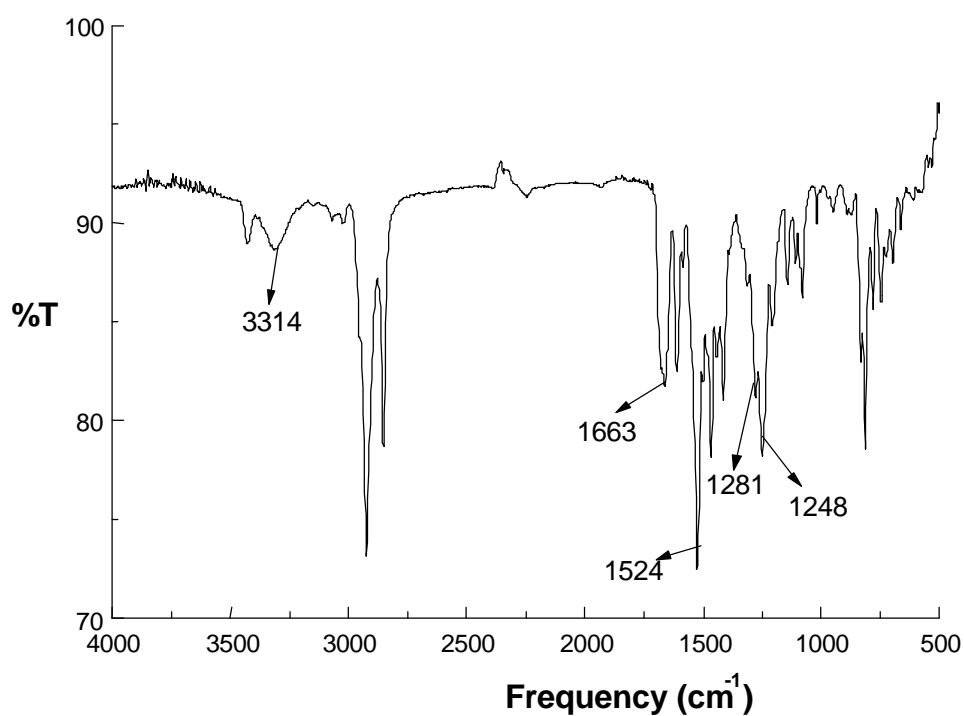
Figure 3.1. FT-IR spectrum of Polyamide PA-1c (film)
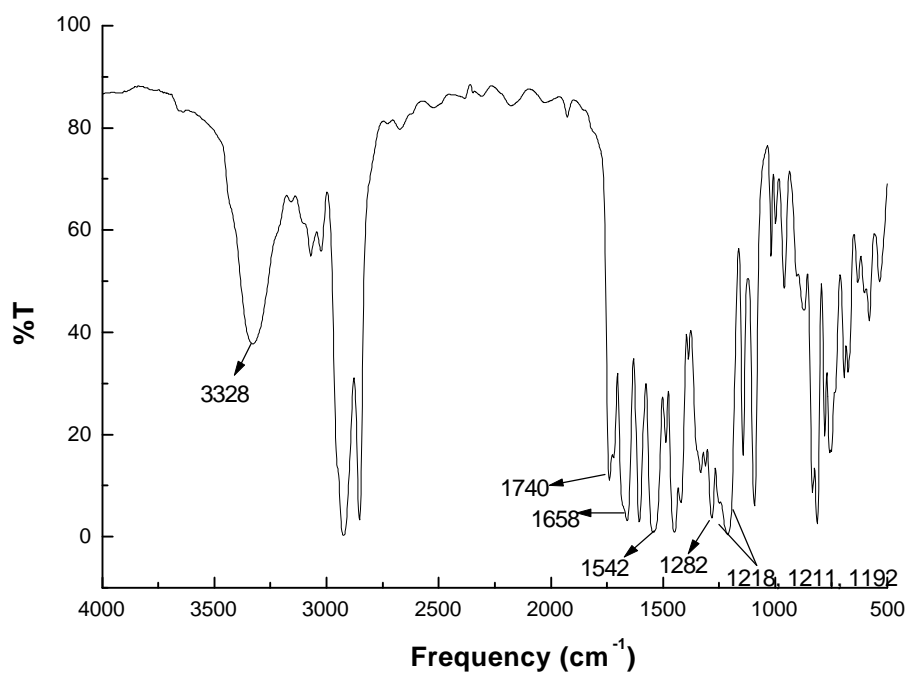
Figure 3.2. FT-IR spectrum of Polyamide PA-2c (film)
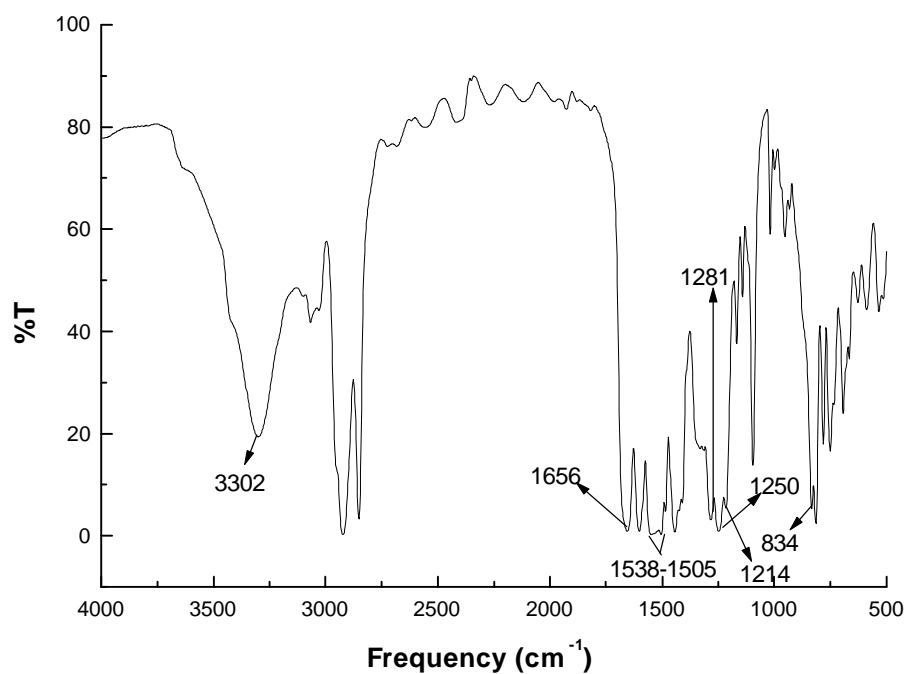
Figure 3.3. FT-IR spectrum of Polyamide PA-3c (film)

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Among the polyamides synthesized from PPDBN only the ^{1}H NMR spectrum of polyamide PA-1c was taken due to the lack of solubility of others. The ^{1}H NMR spectra of PA-1c (Figure 3.4) showed peaks at 0.5 ä ppm due to silyl –CH$_3$ and in the region 0.85-2.5 ä ppm due to pentadecyl group. The aromatic region showed broad signals in the region 6.7-8.5 ä ppm due to the aromatic protons of both diamine and DMSC. The signal at 11.5 ä ppm was due to the proton of amide –NH group. The resolution of aromatic protons was not good in this case eventhough the spectrum was recorded on a 500 MHz NMR instrument. Polyamides synthesized from PPDBT also showed signals in the region 0.85-2.5 ä ppm corresponding to pentadecyl group. The signals in the region 7.1-7.6 ä ppm and 8.65-9.4 ä ppm were due to the protons of amine moiety and the singlet at 11.5 ä ppm was due to the –NH proton of amide linkage. The polyamide PA-2c synthesized from DMSC and PPDBT showed a doublet at 7.65-7.8 ä ppm due to the four protons ortho to silyl group and a doublet at 8.2-8.4 ä ppm due to the four protons ortho to carbonyl group of acid chloride. The protons of silyl –CH$_3$ showed a singlet at 0.5 ä ppm. A representative spectrum of polyamide PA-2c is shown in Figure 3.5. The ^{1}H NMR spectra of polyamides from PPPB showed peaks in the region 0.75-2.5 ä ppm due to pentadecyl group. The signals at 6.9-7.6 ä ppm, 8-8.1 ä ppm and 8.65-9.2 ä ppm were due to the protons of amine moiety. Two singlets in the region 11.1-11.25 ä ppm were due to the –NH protons of the main chain and side chain. In the case of polyamides synthesized from DMSC the four protons ortho to carbonyl group and the four protons ortho to siliyl group showed signals at 7.6-7.75 ä ppm and 8.1-8.3 ä ppm respectively and the silyl –CH$_3$ showed a signal at 0.5 ä ppm. A representative spectrum of PA-3c is shown in Figure 3.6.
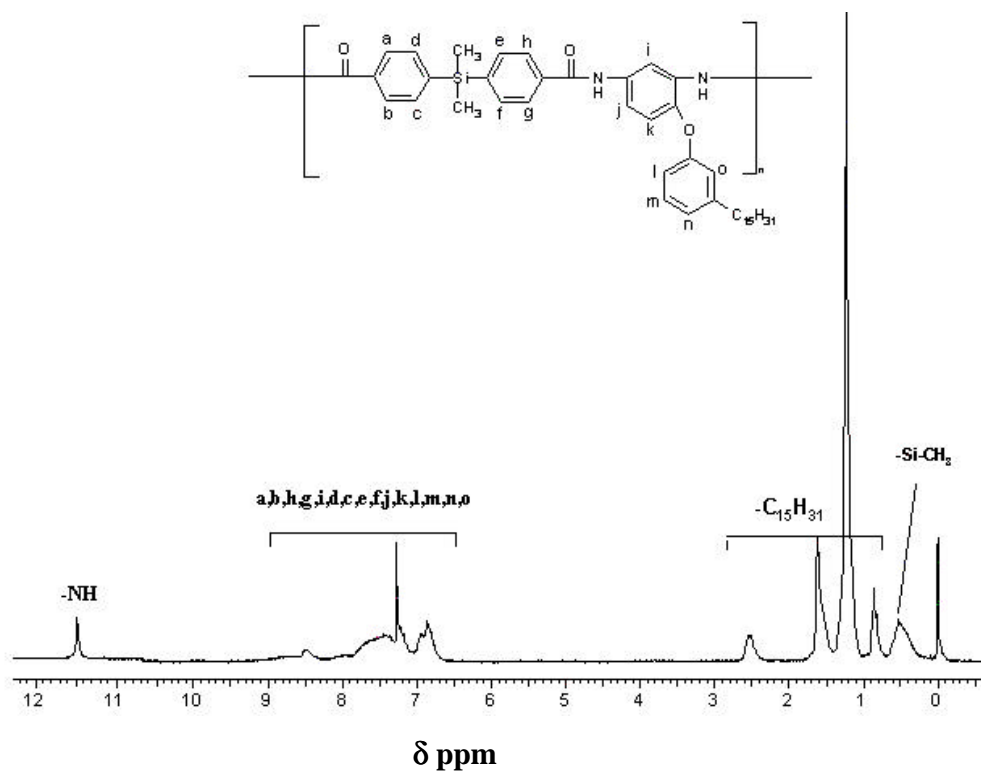
δ ppm
Figure 3.4. ¹H NMR spectrum of polyamide PA-1c
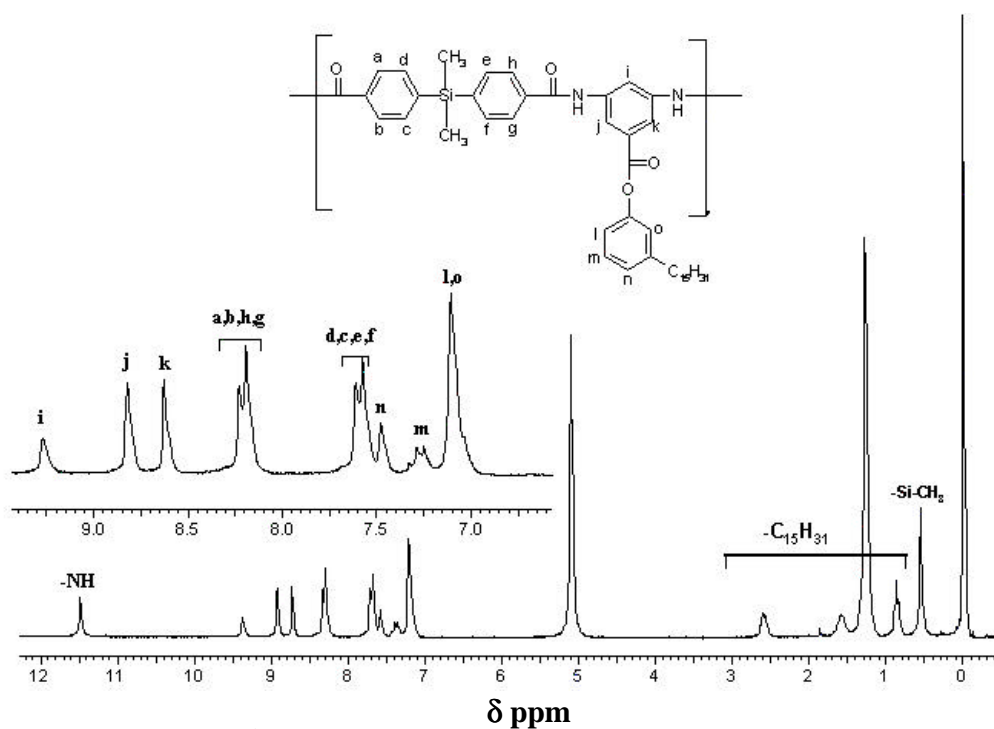
δ ppm
Figure 3.5. ¹H NMR spectrum of polyamide PA-2c in pyridine-d₅
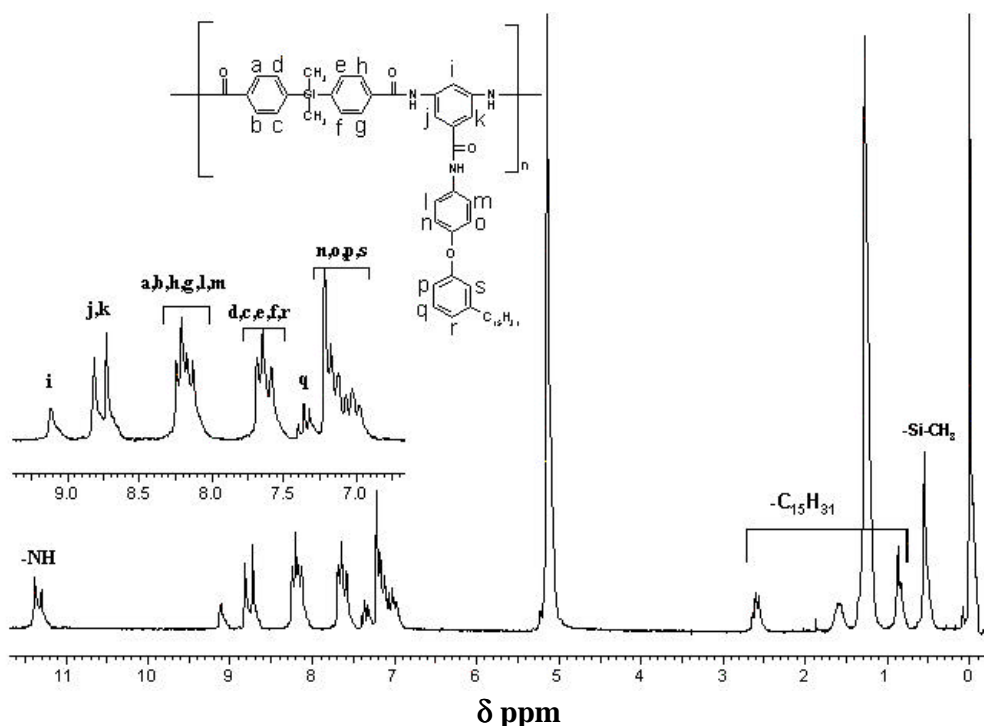
Figure 3.6. ^{1}H NMR spectrum of polyamide PA-3c in pyridine-d$_5$

3.3.2 Properties of polyamides

The properties of polyamides were evaluated by solubility measurements, X-ray diffraction, DSC and TGA.

3.3.2.1 Crystallinity

The crystallinity in polyamides results in their insolubility and is dependent on the rigidity of both diamine and diacid chloride used in their synthesis. It is known that less symmetrical monomers[21] and those having pendant groups[22] reduce the crystallinity in polyamides and improves their solubility. The degree of crystallinity in polyamides can be obtained from their wide angle X-ray diffraction (WAXD) measurements. Eventhough in the case of amorphous polymers the information from wide angle X-ray diffractograms is less precise than that of crystalline polymers, this information is often used to characterize amorphous structures. The d-spacing obtained from the X-ray diffractograms is a measure of the interchain packing in the polymers. Amorphous polymers show amorphous halos due to coherent intersegmental and intrasegmental diffraction of X-rays.[23] If the intersegmental scattering dominates the intrasegmental scattering the WAXD spectra can provide some information on the chain packing in amorphous

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polymers, whereas in the reverse case the d-spacing cannot be taken as a measure of interchain packing.

In the present study the crystallinity of polyamides were evaluated by wide-angle X-ray diffraction measurements of powder (for polymers PA-3a and PA-3b) or film samples (PA-1a-1c, PA-2a-2c and PA-3c). All polyamides from diamine PPDBN showed amorphous patterns (Figure 3.7). This may be due to the flexible pendant pentadecylphenoxy group, which increases the disorder in chains, thereby causing less chain packing. Among the polyamides synthesized from diamine PPDBT (Figure 3.8), all except the one containing rigid p-phenylene linkage (PA-2a) showed amorphous nature. In the case of PA-2a the pendant pentadecylbenzoate group failed to disrupt the chain packing completely and therefore this polyamide showed a sharp reflection peak around $2\theta = 17.7^{o}$ and two small peaks at $2\theta = 18.9^{o}$ and 19.4^{o} indicating a moderate degree of crystallinity. Most of the polyamides synthesized from diamine PPPB (Figure 3.9) showed some crystalline characteristics. PA-3a and PA-3b showed a reflection peak at $2\theta = 17^{o}$. This may be due to the hydrogen-bonding interaction of the main chain with the side chain containing amide linkages, which in turn results in an ordered arrangement of polymer chains leading to semicrystalline nature. In this series the polyamide synthesized from silicon containing acid chloride (PA-3c) showed amorphous patterns due to the flexibility induced in the polymer main chains as a result of incorporation of –Si-C-linkage, which in turn results in reduced chain packing.
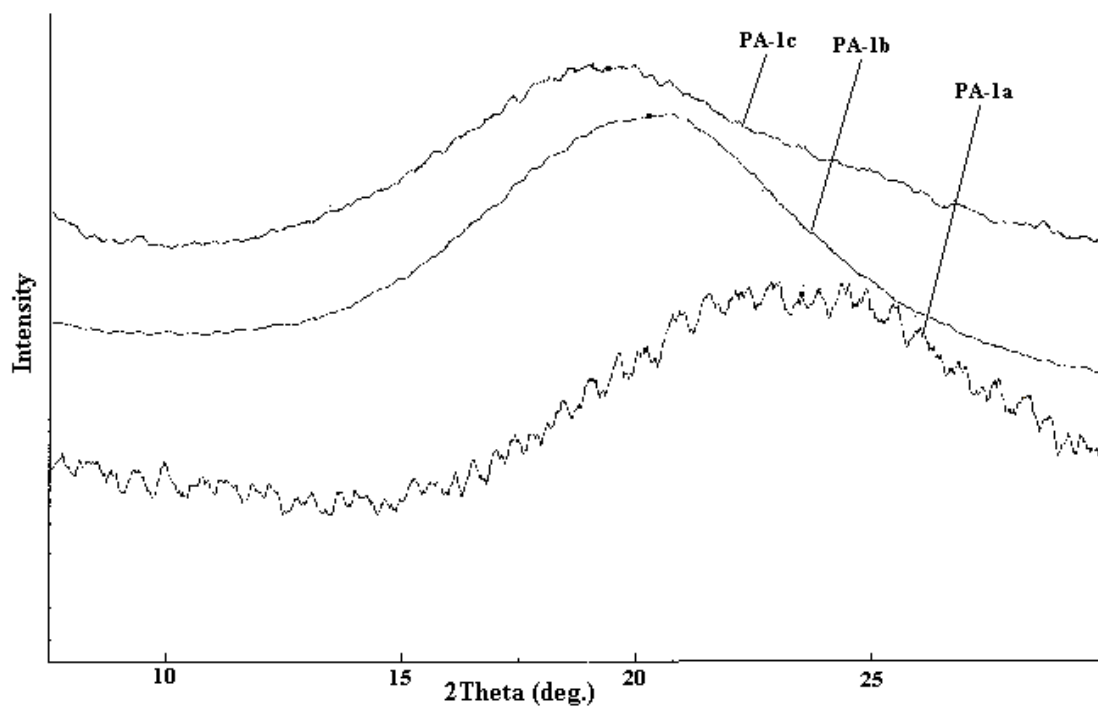
Figure 3.7. Wide-angle X-ray diffractograms of polyamides from PPDBN
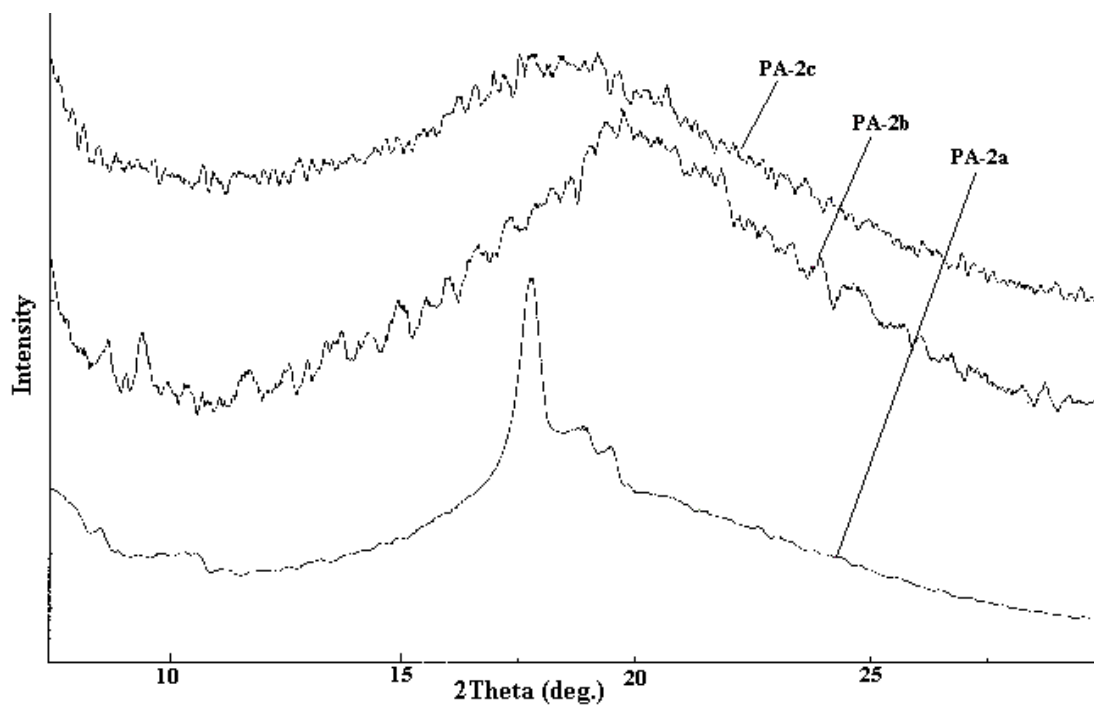
Figure 3.8. Wide-angle X-ray diffractograms of polyamides from PPDBT

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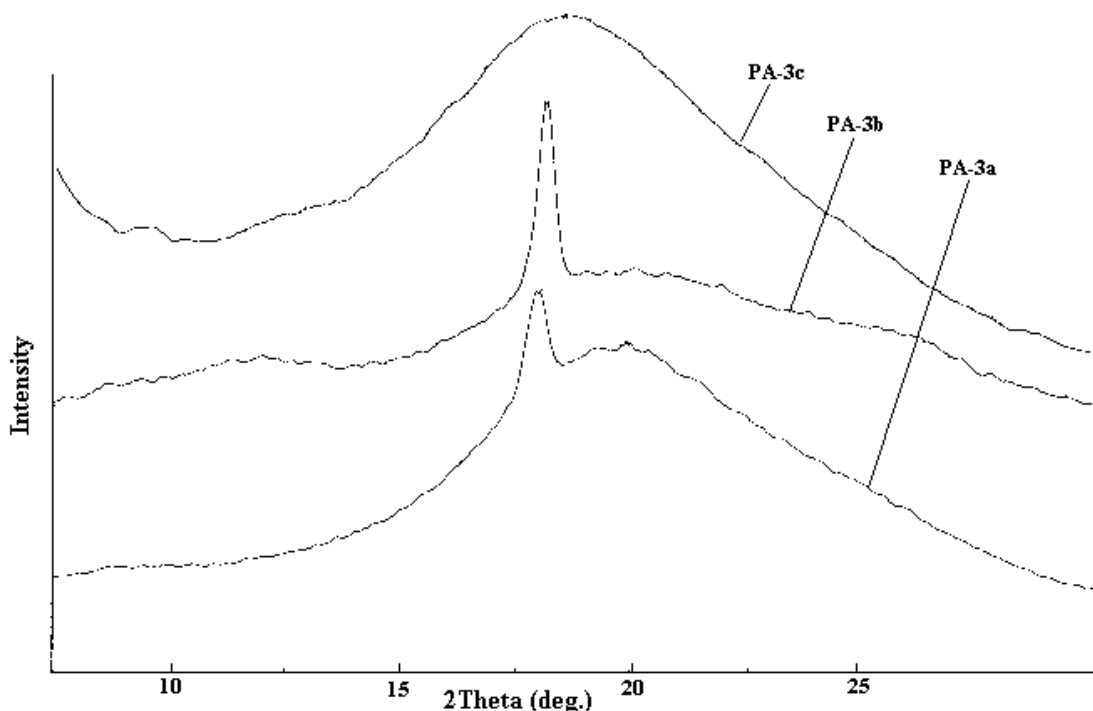
Figure 3.9. Wide-angle X-ray diffractograms of polyamides from PPPB

3.3.2.2 Solubility measurements

The solubility of the polyamides was studied qualitatively in various solvents and the results are shown in Table 3.2. Most of the polyamides were soluble in solvents like DMAc, DMF, NMP, m-cresol, pyridine and even in low boiling solvents like THF. Eventhough it was expected that the polyamides from PPDBN should have high solubility, they showed poorer solubility compared to those synthesized from PPDBT, which were soluble in a variety of solvents. The polymers synthesized from PPPB also had higher solubility than the corresponding polymers from PPDBN. Meledez et al.[12b] have also observed a similar behavior in the case of polyisophthalamides having pendant phenoxy groups. They reported that the solubility of polyamides with m-phenylene units in the main chain was not affected by the presence of pendant bulky groups and explained this on the basis of development of a certain degree of order that allowed a dense packing of the polymer chains. In the present study also, the lack of solubility of polyamides from PPDBN having a pendant pentadecylphenoxy group may be due to the development of a certain degree of order in these polyamides. The d-spacing values of these polyamides obtained from their X-ray diffractograms further support this

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observation. Eventhough the XRD curves (Figure 3.7) of polyamides from PPDBN showed only amorphous peaks as compared to those synthesized from other diamines, the d-spacing values (d_{sp}) were low as compared to others. The polyamides PA-1a (TPCl-PPDBN) and PA-1b (IPCl-PPDBN) showed a low d_{sp} value of 3.78 and 4.38 respectively, indicating a high degree of chain packing and hence the low solubility. PA-1a was soluble only in a mixture of chlorobenzene and m-cresol and PA-1b was soluble only in mixtures of m-cresol with chlorobenzene or tetrachloroethane. The polyamide PA-1c (DMSC-PPDBN) showed good solubility even in low boiling solvents like chloroform. Polyamides based on PPDBT showed good solubility in many organic solvents. It was observed that some of these polymers (PA-2c (IPCl-PPDBT) and PA-3c (DMSC-PPDBT)) could be made soluble in chloroform by adding just two drops of m-cresol. The polymer PA-3a was not soluble in any common solvents. This may be attributed to its semicrystalline nature as evident from the XRD curves (Figure 3.9). This crystalline nature may be due to the rigid p-phenylene linkages and also due to side chain packing as a result of hydrogen bonding. The structural rigidity is again confirmed by its high T_g value. All the polyamides synthesized from PPDBT showed high solubility in a variety of solvents as compared to polymers in the other two series. Polymers synthesized from PPDBT and PPPB showed low solubility in m-cresol/chlorobenzene mixture and m-cresol/tetrachloroethane mixture. In all the three series the polyamides synthesized from silicon containing acid chloride DMSC (PA-1c, PA-2c and PA-3c) showed the highest solubility. In general all polyamides based on silicon containing diacid chloride and also those based on diamine PPDBT showed high solubility in many organic solvents. It is reported in literature that polyamides synthesized from unsubstituted m-phenylene diamines are not soluble in any common organic solvents[12,13] and therefore it is evident from the present study that the incorporation of different pendant groups like pentadecylphenoxy, pentadecylbenzoate and pentadecylphenoxybenzamide along with silicon helps in the improvement of solubility of the resulting polyamides.

Table 3.2. Solubility properties of polyamides

Polymer Code	Solvents								
	NMP	**DMAc**	**DMF**	**m-cresol**	**Pyridine**	**THF**	**CHCL$_3$**	**m-cresol: Cl-benzene (1 : 0.76)**	**m-cresol: Tetrachloroethane (1:1)**
PA-1a	+ −	+ −	+ −	+ −	+ −	+ −	S	+[n]	+ −
PA-1b	+ −	+ −	+ −	+ −	+ −	+ −	S	+[n]	+
PA-1c	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
PA-2a	+ +	+ +	+ +	+ +	+ +	+[m]	+ −	+	+
PA-2b	+ +	+ +	+ +	+ +	+ +	+ +	+ −	+	+
PA-2c	+ +	+ +	+ −[a]	+ +	+ +	+ +	+ −	+ +	+ +
PA-3a	− −	− −	− −	− −	− −	− −	− −	− −	− −
PA-3b	+ +	+ +	+ +	+ +	+ +	+ +	− −	+	+
PA-3c	+ +	+ +	+ +	+ +	+ +	+ +	+ −	+ +	+ +

+ + Soluble at room temperature, + Soluble on heating, + − Partly soluble even on heating, S Swells, − − Insoluble even on heating
m = Soluble initially but became turbid on standing
n = formed a viscous clear gel, which on filtration gave a homogeneous solution but left some insoluble material
NMP – N-methyl pyrrolidone, DMF – N,N-dimethyl formamide, DMAc – N,N-dimethyl acetamide, THF – tetrahydrofuran,
CHCl$_3$ – chloroform

3.3.2.3 Thermal properties of polymers

The thermal stability and glass transition temperatures (T_g) of the polyamides were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) respectively. Both these measurements were carried out in nitrogen at a heating rate of 10^oC/min. The thermal decomposition patterns for polyamides synthesized from diamines PPDBN (PA-1a-c), PPDBT (PA-2a-c) and PPPB (PA-3a-c) are shown in Figures 3.10, 3.11 and 3.12 and the DSC thermograms are shown in Figure 3.13. The initial decomposition temperature (IDT), the decomposition temperature at 10% weight loss (T_{10}) and the maximum decomposition temperature (T_{max}) in nitrogen, for all the polymers are listed in Table 3.3. An examination of data showed that the introduction of pendant pentadecyl groups did not affect the thermal properties of the polyamides significantly and the polyamides in this study were stable upto 337-434°C. This is contradictory to the widely accepted fact that the alkyl group reduces the thermal stability significantly. Literature reports some polyamides having highly phenylated main chains and side chains[24] having thermal stabilities in the range 389-452°C in nitrogen and having viscosities in the range 1.26-1.72 dL/g. The thermal stability of polyamides in this study was also comparable with these polymers even though they had pendant alkyl groups and the slight decrease in the thermal stability may be because of the flexible connecting groups. Further the comparison of IDT and T_{10} values of polyamides in the present study with some of the reported polyamides having pendant phenoxy,[12a] benzoate[13a] and benzamide groups[14b] showed that there is no significant decrease in the thermal stability in the case of polyamides from PPDBN, whereas the thermal stability of polyamides based on PPDBT and PPPB decreased to some extent. The low thermal stability of the polyamides from PPDBT and PPPB may be due to the ester and amide connecting groups, which have comparatively low thermal stability than ether groups. In the case of polyamides based on PPDBT and PPPB with initial decomposition temperatures lower than 400°C, a two-step decomposition pattern was observed.

Polyamides synthesized from PPDBN (PA-1a-c, Table 3.3) showed IDT, T_{10} and T_{max} in the range 410-434°C, 422-439°C and 464-479°C respectively. In this series the polyamides synthesized from DMSC and PPDBN (PA-1c) had the maximum thermal stability with IDT, T_{10} and T_{max} at 434, 439 and 479°C respectively. The IDT, T_{10} and

T_{max} of other two polyamides (PA-1a (TPCl-PPDBN) and PA-1b (IPCl-PPDBN)) were almost same.

Among the three series, the polyamides synthesized from PPDBT (PA-2a-c, Table 3.3) showed the lowest thermal stability. This may be due to the pendant ester linkage, which has got less thermal stability. This is again evident from the fact that this series of polyamides showed a two-stage decomposition pattern with IDT, T_{10} and T_{max} in the range 337-359°C, 340-365°C and 411-416°C respectively for the first decomposition and in the range 492-522°C, 497-536°C and 505-568°C respectively for the second decomposition. Here the first decomposition may be due to the detachment of ester linkage. In this series eventhough the polyamide PA-2b (IPCL-PPDBT) showed the maximum IDT and T_{10} values and PA-2a (TPCL-PPDBT) the minimum, the T_{max} values of all the three polyamides were very close.

The IDT, T_{10} and T_{max} values of polyamides synthesized from PPPB (PA-3a-c, Table 3.3) were in the range 395-431°C, 401-437°C and 457-484°C respectively and these values were comparable with that of polyamides synthesized from PPDBN. In this series also polyamide PA-3c synthesized from DMSC showed the maximum thermal stability, with IDT, T_{10} and T_{max} values at 431, 437 and 484°C respectively and the polyamides synthesized from IPCl (PA-3b) showed the least thermal stability with IDT, T_{10} and T_{max} values at 395, 404 and 457°C respectively. In the case of PA-3b (IPCl-PPPB) a two stage decomposition was observed resulting in lower thermal stability. The thermal stability of PA-3a synthesized from TPCl was in between that of PA-3b and PA-3c.

Table 3.3. Thermal properties of polyamides

Polymer Code	Diacid Chloride	Diamine	IDT, °C		T$_{10}$, °C		T$_{max}$, °C		T$_g$, °C
			1	**2**	**1**	**2**	**1**	**2**	
PA-1a	TPCl	PPDBN	410	_	422		468	_	164
PA-1b	IPCl	PPDBN	410	_	422		464	_	150
PA-1c	DMSC	PPDBN	434	_	439		479	_	111
PA-2a	TPCl	PPDBT	337	522	340	536	411	568	232
PA-2b	IPCl	PPDBT	359	492	365	497	415	505	221
PA-2c	DMSC	PPDBT	347	518	354	533	416	557	186
PA-3a	TPCl	PPPB	411	_	417	_	476	_	279
PA-3b	IPCl	PPPB	395	555	401	567	457	592	262
PA-3c	DMSC	PPPB	431	_	437		484	_	225
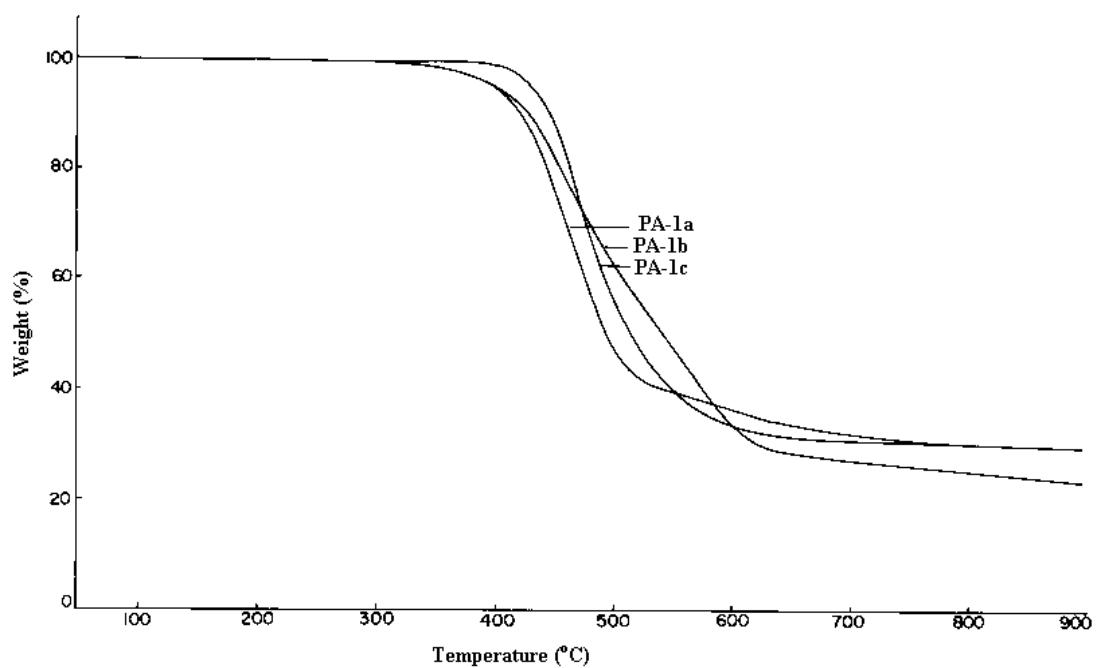
Figure 3.10. TG curves of polyamides from PPDBN in nitrogen.
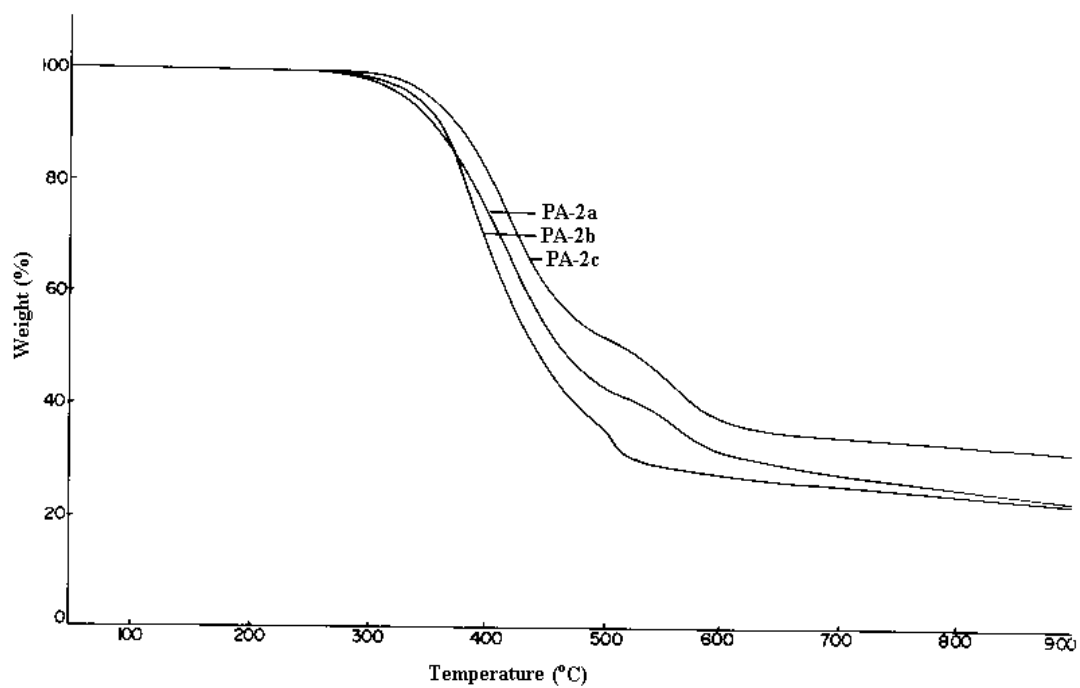
Figure 3.11. TG curves of polyamides from PPDBT in nitrogen

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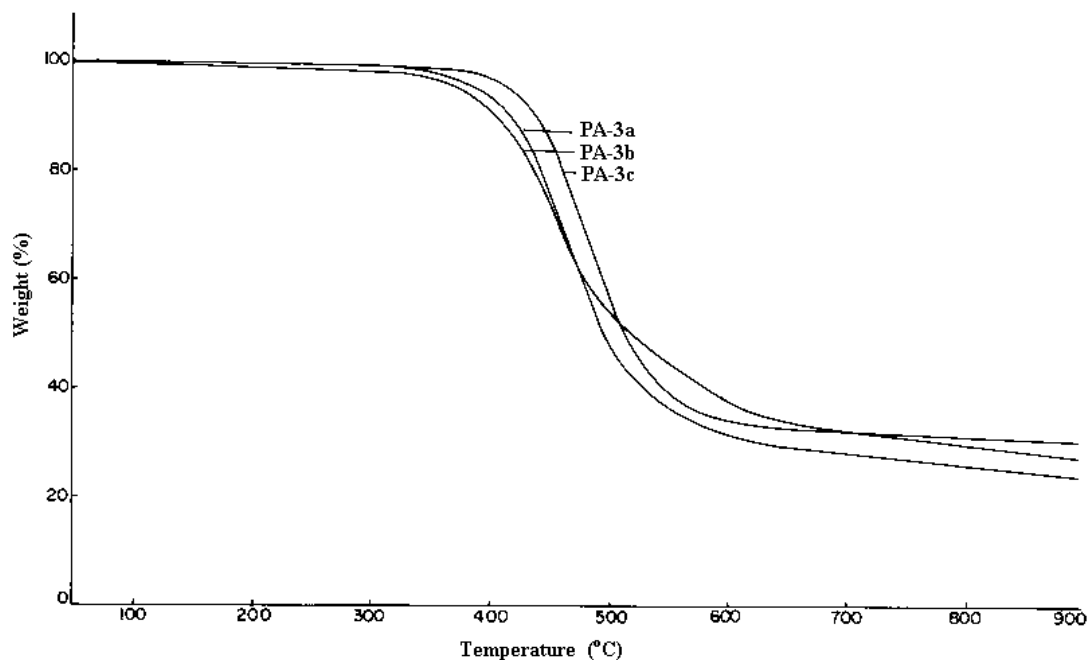
Figure 3.12. TG curves of polyamides from PPPB

The DSC curves, which were recorded at the second heating of polymers, at a heating rate of 10°C/min are given in Figure 3.13. The glass transition temperatures (T_g) of the polymers synthesized from diamines PPDBN (PA-1a-c), PPDBT (PA-2a-c) and PPPB (PA-3a-c) were in the order PA-1a-c < PA-2a-c < PA-3a-c. The T_g values for polyamides PA-1a-c, PA-2a-c and PA-3a-c were in the range 111-164°C, 186-232°C and 225-279°C respectively. The T_g's were dependent on the stiffness of the polymer backbone which in turn was dependant on the nature of diacid chloride and diamine. The polyamides synthesized from rigid diacid chloride TPCl (PA-1a, 2a and 3a) showed the maximum T_g in all the series. The polyamides synthesized from DMSC (PA-1c, 2c, 3c) showed the least T_g in all the series due to the flexibility introduced in the main chain of these polyamides as a result of –Si-C-linkage. The highest T_g values were shown by polymers containing PPPB diamine. This may be due to the hydrogen bonding interaction between the main chain and side chain amide groups which results in the close packing of the polymer chains leading to high rigidity.

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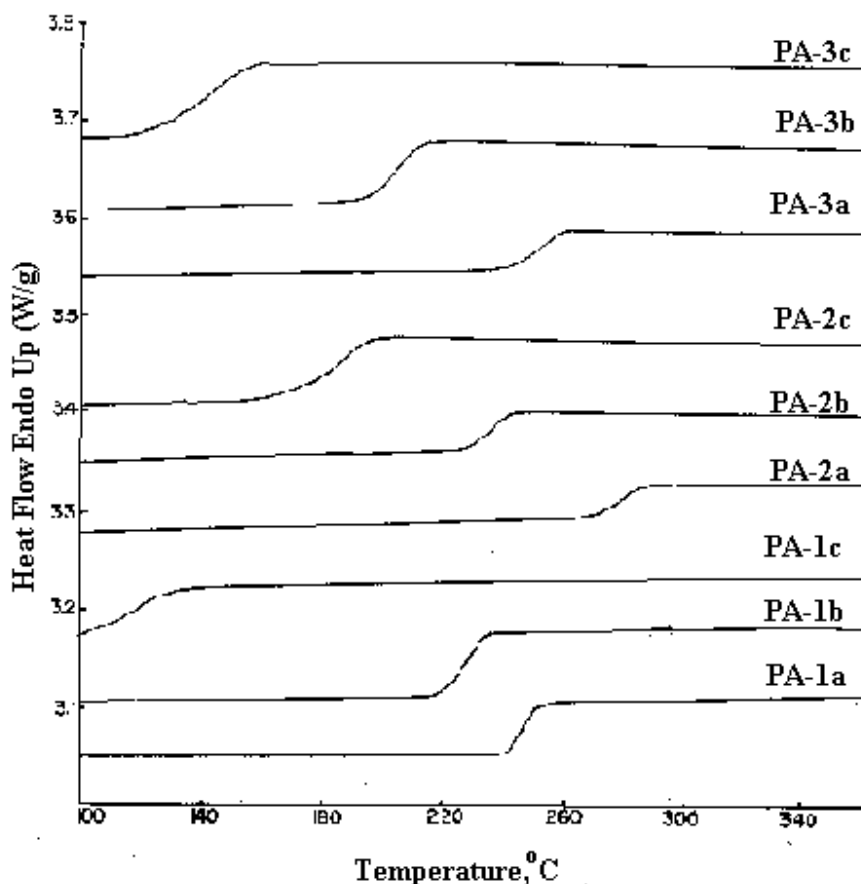
Figure 3.13. DSC thermograms of polyamides from PPDBN, PPDBT and PPPB

3.3.3 Possible application of polyamides

3.3.3.1 Gas separation membranes

Polyamides have wide applications in different fields. However, application of polyamides as membranes for gas separation has not been studied systematically. Though they have high thermal stability, high selectivity and high T_g desired for gas separation membranes, their permeabilities are generally low due to low free volume. Many strategies have been proposed for the improvement in permeability without affecting the permselectivity of the polymer gas separation membranes. Among these the most promising seems to be the proposal by Koros.[25] According to him the polymers with main chain consisting of alternating bulky rigid structural elements and flexible segments should give a combination of high selectivity and high permeability. In this regard, the silicon containing polyamides with

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different bulky pendant groups of this study seems to be promising candidates since they have a combination of rigid phenylene diamine units, flexible silane linkages and bulky pendant groups. It is expected that the bulky pendant groups along with flexible silane linkages will improve the permeability of the polyamides whereas the rigid phenylene diamine units will hinder the free rotation of main chain leading to high selectivity. Therefore to explore the possible application of silicon containing polyamides synthesized from cardanol as gas separation membranes some permeability measurements were done.

The gas permeability measurements were made as described earlier and the permeability coefficient (P) was calculated from the measured flow rate of gas N, using the equation,

$$P = \frac{l}{P_1 - P_2} \ x \ \frac{N}{A} \tag{3.1}$$

Where, P is the gas permeability in barrer (1 barrer = 10^{-10} cm^3 (STP).cm/cm^2 .s.cm Hg), l the thickness of the film in cm, P_1 and P_2 the pressures on the high pressure and low pressure side of the membrane in cm Hg, N the flow rate of gas in cm^3 (STP)/s and A the effective membrane area in cm^2.

The permeability coefficients of four gases O_2, N_2, H_2, CO_2 calculated using the above equation at 30 ± 0.1^oC are given in Table 3.4.

The ideal separation factor of gas A relative to gas B ($\alpha_{A/B}$) ca be expressed as

$\alpha_{A/B} = P_A/P_B$

where P_A and P_B are the permeability coefficients of the gases A and B. From the permeability coefficients obtained by the Equation 3.1, the ideal separation factor for different pairs of gases were calculated and the data is given in Table 3.4.

Table 3.4. Permeability, selectivity data and d-spacing values of silicon containing polyamides

Polymer Code	Dianhydride	Diamine	d-spacing A^o	Permeability Coefficients, barrers				Selectivity				
				P_{O2}	P_{N2}	P_{H2}	P_{CO2}	P_{O2}/P_{N2} α_1	P_{CO2}/P_{N2} α_2	P_{H2}/P_{N2} α_3	P_{H2}/P_{CO2} α_4	P_{H2}/P_{O2} α_5
PA-1c	DMSC	PPDBN	4.58	10.48	6.4	33	31.36	1.63	4.90	5.15	1.05	3.14
PA-2c	DMSC	PPDBT	4.8	8.3	2.54	28.2	34.0	3.26	13.38	11.10	0.82	3.39
PA-3c	DMSC	PPPB	4.79	26	26	45	25	1	0.96	1.7	1.80	1.73

An analysis of the data showed a general trend of permeability increase correlated with selectivity decrease for these polymers (PA-1c, 2c, and 3c). In the case of polymers PA-1c (DMSC-PPDBN) and PA-3c (DMSC-PPPB), the permeability of hydrogen showed the highest, followed by those of the progressively larger penetrants. But in the case of polyamide PA-2c (DMSC-PPDBT) the permeability of CO_2 was higher than that of H_2. Polyamide PA-1c (DMSC-PPDBN) showed high selectivity for the pair of gases H_2/N_2 whereas PA-2c (DMSC-PPDBT) showed maximum selectivity for the pair of gases CO_2/N_2. The polyamide PA-3c (DMSC-PPPB) was found to be highly selective towards the pair of gases H_2/CO_2.

This difference may be attributed to the effect of different pendant substituents, which affects the free volume of the resulting polymers and solubility of different gases in these polymers in different ways.

The permeabilities of PA-3c (DMSC-PPPB) were higher and selectivities lower than that of PA-1c (DMSC-PPDBN) and PA-2c (DMSC-PPDBT). This high permeability and low selectivity in the former case may be due the longer bulky pendant group, which restricts the chain segmental packing and increases the free volume. The mobility of side chain also may be higher in this case because of the two connecting groups and this in turn can lead to high permeability. It is known that the gas permeation through a polymer membrane is mainly determined by the free volume and local mobilities of the chain segments of the polymer and/or substituents.[26] An increase in the free volume or increase in the local mobility of the chain segments of the polymer and/or the substituents will lead to an increase in the gas permeability and decrease in the selectivity.[27] The d-spacing values obtained from X-ray diffractograms are an indication of the disruption of chain packing and give an idea about the effect of different substituents on the permeability and selectivity of polymers. But the d-spacing values obtained for the polymers in this study does not go hand in hand with the permeability data. The d-spacing values were in the order PA-2c > PA-3c > PA-1c. According to this data the polyamide PA-2c having the highest d-value should have the maximum permeability and the least selectivity. Even though the permeability of CO_2 was higher in the case of PA-2c, the permeabilities of other gases were low. This high permeability of CO_2 may be due to the high solubility of CO_2 in this polyamide as a result of interaction with the pendant ester groups. In this case the permeability may be mainly dependent on solubility

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rather than diffusivity. This polyamide showed a higher selectivity that cannot be explained from the d-values. Some literature reports show that such high permeability associated with high selectivity is due to a combination of high free volume and low chain segmental mobility.[28] XRD spectra of amorphous polymers show amorphous halo due to coherent intersegmental and intrasegmental diffraction of X-rays.[23] In the case of polyamides synthesized from PPDBT the intrasegmental scattering may be dominant and therefore the the d_{sp} values will correspond to the packing of pendant groups and not to the packing of main chain. This may be a possible reason for their low permeability and high selectivity as compared to the other polyamides PA-1c and PA-3c, eventhough their d_{sp} values are higher. The packing of side chains may lead to restricted chain mobility and thus result in high selectivity and low permeability.

3.4 Conclusions

1. New series of polyamides having pendant pentadecylphenoxy, pentadecylbenzoate and pentadecylphenoxybenzamide groups were synthesized from substituted m-phenylene diamines namely (1) 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) (2) 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT) and (3) 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (PPPB) by low temperature interfacial polycondensation.

2. Most of these polymers were soluble in a wide range of solvents like NMP, DMAc, DMF, m-cresol, pyridine and THF as compared to those synthesized from unsubstituted m-phenylene diamines indicating that the incorporation of bulky pendant groups lead to a significant improvement in solubility. The nature of pendant groups also affected the solubility and the polymers having pendant pentadecylbenzoate group displayed the maximum solubility. The polyamides synthesized from silicon containing diacid chloride also showed high solubility.

3. Incorporation of pendant alkyl group did not affect the thermal stability of these polymers significantly and hence they exhibited reasonably good thermal stability. The pendant pentadecylphenoxy groups lowered the glass transition temperatures (T_g) considerably, but the pendant pentadecylphenoxybenzamide and pentadecylbenzoate groups did not

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have much effect on the T_g. The incorporation of silicon also lowered the glass transition temperature of the resulting polyamides.

4. The silicon containing polyamides in each series (PA-1c, PA-2c and PA-3c) showed good permeability towards gases N_2, O_2, H_2 and CO_2. The systematic variations in chemical structure were found to lead to significant changes in permeabilities and selectivities, providing a wide range of gas separation properties. The polyamide PA-3c (DMSC-PPPB) with long flexible substitution showed high permeability and low selectivity. The polyamide PA-2c (DMSC-PPDBT) with low intersegmental package and high intrasegmental packing showed the highest selectivity, but the permeability slightly decreased. The polyamide PA-1c showed intermediate permeabilities and selectivities

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Chapter 4

Part – A

Synthesis and Characterization of Polyimides from Cardanol

4(a).1 Introduction

Aromatic polyimides constitute a major class of thermally stable high performance polymers. Polyimides have achieved wide acceptance in the modern industry because of their excellent thermal and oxidative ability, resistance to practically all kinds of radiation and organic chemicals and good dielectric properties.[1] These polymers make approximately 40% of the commercially available heat-resistant, nonmetallic materials, where prolonged use at temperatures up to 300°C is required.[2] Some of their important application areas include alignment layers for liquid crystal display devices, gas separation membranes and interlayer dielectrics for semiconductor devices (eg., wire coating materials or as substrates for flexible printed circuits). However most of these polymers are difficult to process because of their high softening temperatures and limited solubility in common organic solvents, which restricts their further applications.[3] Since conventional polyimides are insoluble, they are usually processed as the corresponding soluble poly (amic acid) precursors and then either thermally or chemically imidized. However there are some problems owing to the unstability of poly (amic acid)s and liberation of water of imidization process. Therefore solvent soluble polyimides having good processability are desired.

Attempts to understand the structure-property relationship in polyimides by systematically changing the diamine and dianhydride moiety have been numerous and as a result of these studies several criteria have been proposed to obtain polyimides with improved solubility.[4,5] These include (1) introduction of aliphatic or other kinds of flexible linkages that reduce chain stiffness, (2) introduction of bulky side substituents, which help in the separation of the polymer chains and hinder molecular packing and crystallization, (3) use of enlarged monomers containing angular bonds, which suppress coplanar structures, (4) use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers, which lower regularity and molecular ordering and (5) copolymerization of two or more diamines or dianhydrides. Examples involving these modifications are discussed in detail in Chapter 1.

The incorporation of ether groups or other flexible linkages into the main chain generally leads to an improvement in solubility whereas the glass transition temperatures (T_g)

and thermal stability are lowered significantly.[6] On the other hand, introduction of bulky groups[7] into the polymer main chain or the attachment of bulky pendant groups like phenyl[8] along the backbone helps in retaining the thermal properties, while providing a good solubility due to decrease in packing density and crystallinity. Pendant ether and thio groups are also known to improve the solubility.[9] Flexible p-sulfone ether diamines[10] having pendant alkyl groups are known to improve the solubility while decreasing the T_g where as pendant alkyl groups on rigid diamines like m-phenylene diamine[11] improves the solubility without affecting the thermal properties. Incorporation of m,m' linkages[12] and silicon also improves the solubility of polyimides.[13] It was expected that a combination of these structural modifications will minimize the trade off between the processability and properties of aromatic polyimides.

Thus the objective of the present work was to synthesize polyimides containing pendant connecting groups like ether, ester and amide along with pentadecylphenyl and pentadecyldiphenyl ether groups in the polyimide side chain from m-phenylene diamines incorporating these substituents. Another objective was to synthesize polyimides containing silicon from a silicon containing dianhydride bis(3,4-dimethylphenyl)dimethylsilane dianhydride and these diamines. As a part of the ongoing program concerning the utilization of cashew nut shell liquid for the synthesis of novel polymers, we attempted the synthesis of these diamines and the corresponding polyimides from cardanol. These polyimides with bulky pendant groups were expected to have specialty application in different fields.

This chapter deals with the synthesis of polyimides from diamines namely, (1) 4-(3-pentadecylphenoxy)benzene-1,3-diamine   (PPDBN)   (2)   3-pentadecylphenyl-3,5-diaminobenzoate(PPDBT)   and   (3)   3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (PPPB). These diamines were condensed with dianhydrides namely, pyromellitic dianhydride,   3,3',4,4'-bipenyltetracarboxylicacid   dianhydride,   3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 3,3',4,4'-oxydiphthalic dianhydride, 4,4'-bis(hexafluoroisopropylidenebis(phthalicanhydride)   and   bis(3,4-dicarboxy phenyl)dimethylsilane dianhydride by a one step high temperature solution polycondensation method in m-cresol at 200°C. The effect of variation of dianhydrides on the different

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properties like crystallinity, solubility, glass transition temperature and thermal stability is discussed.

Copolymerization with some conventional diamine like 4,4'-oxydianiline (ODA) was also done by varying the amine composition to find out the effect of varying ratios of alkyl group on the properties of these ODA containing polyimides which are commercially important. For this purpose copolyimides were synthesized from 4-(3-pentadecylphenoxy)benzene-1,3- diamine (PPDBN) and ODA by condensing them with dianhydrides like 6-FDA, SiDA and ODPA. For the comparison of properties under identical conditions several homopolyimides based on ODA with dianhydrides like 6-FDA, ODPA and SiDA were also synthesized. Copolyimides containing silicon were also synthesized from diamine PPDBN by condensing it with a mixture of dianhydrides, one of them being SiDA to study the effect of incorporation of silicon on the solubility and other properties like thermal stability and gas permeability. All homo polyimides and copolyimides were characterized by IR and ^{1}H NMR spectroscopy, solubility properties, inherent viscosity, X-ray diffraction studies, thermogravimetric analysis and differential scanning calorimetry. The optical transparency of some the polyimide films were also determined by measuring the percentage transmittance.

Since alkyl group containing polyimides are known to have application as alignment layers for liquid crystal display devices,[14] as gas separation membranes[15] and as electrical insulators with low dielectric characteristics,[16] the application of these new class of polyimides and copolyimides in these areas have also been investigated by measuring the pretilt angle, permeability properties (permeation of gases like O_2, N_2, H_2 and CO_2) and dielectric constants.

4(a).2 Experimental

4(a).2.1 Materials

The diamines were synthesized as given in Chapter 2, Section 2.2.3. The dianhydrides, pyromellitic dianhydride (PMDA (Aldrich, USA)), 3,3',4,4'-bipenyl tetracarboxylicacid dianhydride (BPDA (Aldrich, USA)), 3,3',4,4'-benzophenonetetracarboxylicacid dianhydride

(BTDA (Aldrich, USA)), 3,3',4,4'-oxydiphthalicdianhydride(ODPA (Aldrich, USA)) and 4,4'-bis(hexafluoro isopropylidenebis(phthalic anhydride) (6-FDA (Aldrich, USA)) were sublimed before use. Bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SiDA) was synthesized as given in Chapter 2, Section 2.2.4. m-cresol (S.D. Fine Chem., India) was stirred with CaH_2 for 24 h and then vacuum distilled.

4(a).2.2 Analytical methods

The FT-IR spectra were recorded on a Perkin-Elmer 599B spectrometer on solution cast films. ^{1}H NMR spectra were recorded on a Bruker NMR spectrometer at 200 and 500 MHz at room temperature with tetramethylsilane as an internal standard. The X-ray diffractograms of polymers were obtained on a Rigaku Dmax 2500 X-ray diffractometer at a heating rate of 2°/min. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 analyzer at a heating rate of 10^oC/min in nitrogen atmosphere and differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-7 analyzer at a heating rate of 10^oC/min in nitrogen atmosphere. The UV-visible spectra were recorded on a HP 8452A diode array spectrophotometer. Solubility of homopolyimides and copolyimides were determined at 5% concentration in various solvents at room temperature or on heating. Inherent viscosities of polymers were determined with solutions of 0.5 g/dL, 0.1 g/dL or 0.2 g/dL concentration at 30.0 ± 0.1^oC using an Ubbelohde viscometer. The viscosity was calculated using the equation,

η_{inh} = 2.303/c x log t/t$_0$, where t and t$_0$ are flow times for polymer solution and solvent respectively and c is the concentration of the polymer solution.

The model structure for polymer fragments was obtained by means of Hyperchem program, Version 5.0.[17] The transmission electron microscopy measurements were carried out on a Jeol Model 1200EX instrument operated at an accelerating voltage of 120 kV.

4(a).2.3 Synthesis of polyimides

Homo and copolyimides were synthesized from diamines by condensing them with different dianhydrides by a one step solution method.

4(a).2.3.1 Synthesis of homopolyimides

Homopolyimides were synthesized from diamines 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) (Scheme 4(a).1), 3-pentadecyl phenyl-3,5-diaminobenzoate (PPDBT) (Scheme 4(a).2) and 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (PPPB) (Scheme 4(a).3) by condensing them with dianhydrides namely, pyromellitic dianhydride (PMDA), 3,3',4,4'-bipenyl tetracarboxylicacid dianhydride(BPDA), 3,3',4,4'-benzophenonetetracarboxylicacid dianhydride(BTDA,), 3,3',4,4'-oxydiphthalicacid dianhydride (ODPA), 4,4'-bis(hexafluoroisopropylidenebis(phthalic anhydride) (6-FDA) and bis (3,4-dicarboxyphenyl)dimethylsilane dianhydride(SiDA) by a one step high temperature solution method in m-cresol.

A typical procedure for one-step high temperature polycondensation is described below.

➢ **Synthesis of homopolyimide from 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) and bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (SiDA) – (PI-1f)**

Polyimides were prepared following a general procedure from the dianhydrides and diamines in m-cresol. To a 50 mL three necked round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and a guard tube was added 0.5 g (0.0012 mole) PPDBN and 6.2 mL m-cresol. Then 0.429 g (0.0012 mole) SiDA was added to this at room temperature, with stirring under a stream of nitrogen. The reaction mixture was then stirred at room temperature for 3 h to obtain a homogeneous solution and then heated to 220^0C and maintained at this temperature for 12 h. The water formed during imidization was removed continuously with a stream of nitrogen. The resulting viscous solution (15 % (w/v)) was then cooled and poured into 300 mL methanol to precipitate the polymer. The polymer was then filtered, washed with methanol, extracted with methanol for 24 h and dried at 80^oC under vacuum for 12 h to obtain a fluffy polymer. Yield of the polymer obtained was about 98%. The polyimide structure was confirmed by FT-IR and ^{1}H NMR (for soluble polyimides) spectroscopy and completion of imidization was confirmed by FTIR spectroscopy. All other homopolyimides were also synthesized by a similar procedure. Their yields and viscosities are given in Tables 4(a).1-3.
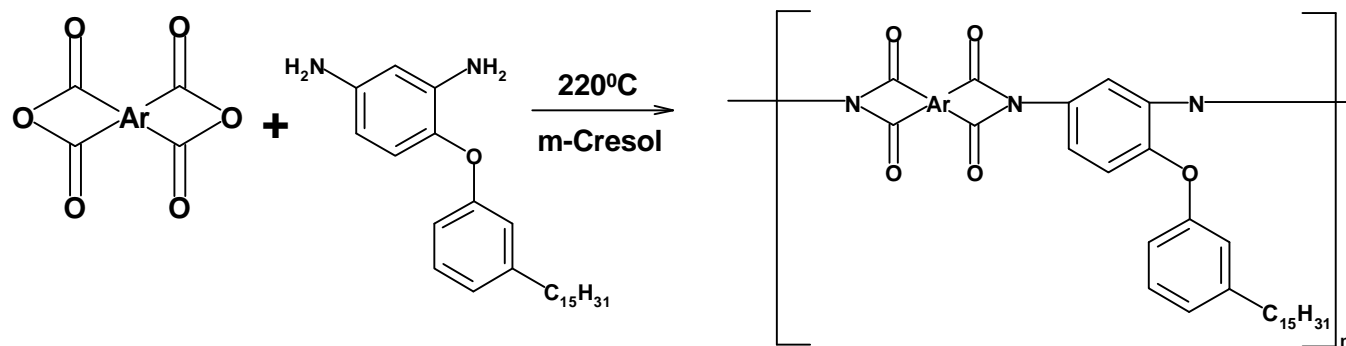
Where Ar =
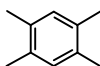
PI-1a
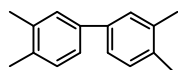
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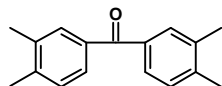
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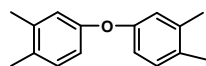
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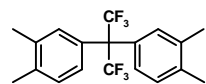
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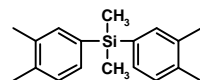
PI-1f

Scheme 4(a).1. Synthesis of polyimides from 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN)
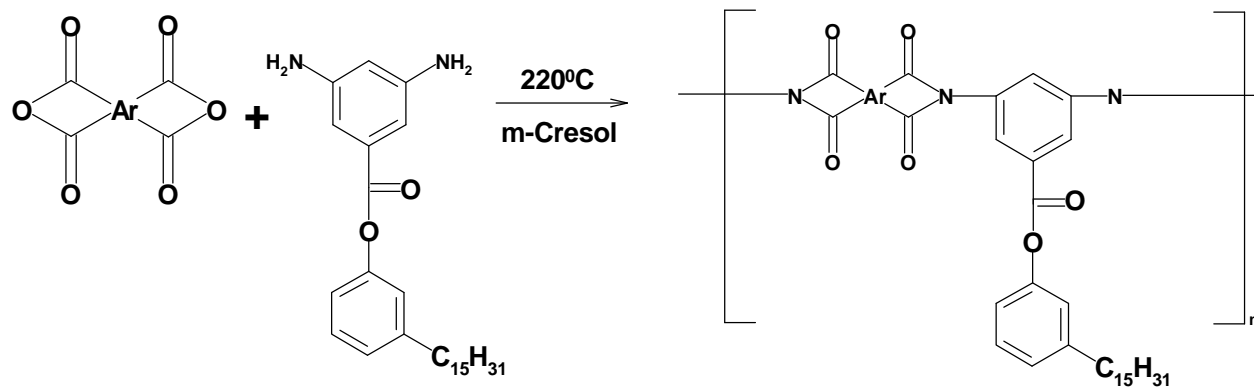
Where Ar =

PI-2a
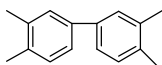
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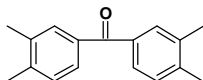
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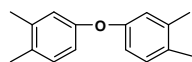
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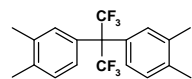
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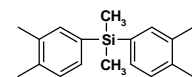
PI-2f

Scheme 4(a).2. Synthesis of polyimides from 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT)

Where Ar =

PI-3a

PI-3b

PI-3c

PI-3d

PI-3e

PI-3f
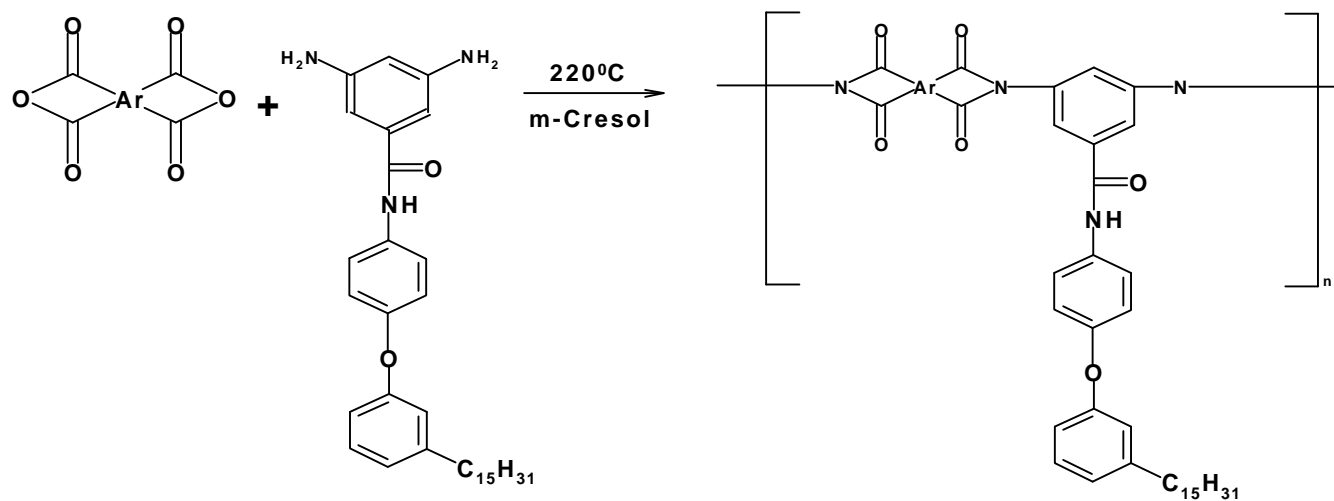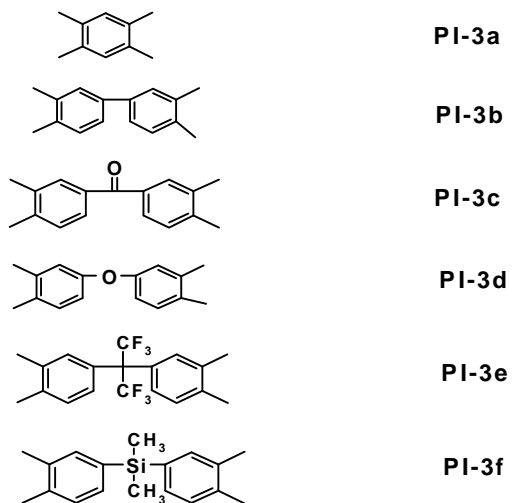
Scheme 4(a).3. Synthesis of polyimides from 3,5-diamino-N-(4-(3-pentadecylphenoxyphenyl)benzamide (PPPB)

Table 4(a).1. Synthesis of polyimides from 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN)

Polymer code	Dianhydride	Diamine	Yield, %	η_{inh}, dL/g^m
PI-1a	PMDA	PPDBN	99.1	–
PI-1b	BPDA	PPDBN	99.4	–
PI-1c	BTDA	PPDBN	98.6	–
PI-1d	ODPA	PPDBN	98.3	0.45
PI-1e	6-FDA	PPDBN	99.6	0.62
PI-1f	SiDA	PPDBN	98.1	0.42

m = 0.5 g/dL in chloroform at 30 ± 0.1^oC

Table 4(a).2. Synthesis of polyimides from 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT)

Polymer code	Dianhydride	Diamine	Yield, %	η_{inh}, dL/g^m
PI-2a	PMDA	PPDBT	97.3	–
PI-2b	BPDA	PPDBT	98.1	–
PI-2c	BTDA	PPDBT	97.4	0.25^n
PI-2d	ODPA	PPDBT	99.2	0.55^p
PI-2e	6-FDA	PPDBT	98.5	0.45
PI-2f	SiDA	PPDBT	98	0.35

m = 0.5 g/dL in chloroform at 30 ± 0.1^oC

n = 0.1 g/dL in m-cresol at 30 ± 0.1^oC, p = 0.5 g/dL in m-cresol at 30 ± 0.1^oC

Table 4(a).3. Synthesis of polyimides from 3,5-diamino-N-(4-(3-pentadecylphenoxy) phenyl)benzamide (PPPB)

Polymer code	Dianhydride	Diamine	Yield, %	η_{inh}, dL/g^m
PI-3a	PMDA	PPPB	97.5	–
PI-3b	BPDA	PPPB	98.6	–
PI-3c	BTDA	PPPB	97.0	0.23^n
PI-3d	ODPA	PPPB	99.5	0.55^p
PI-3e	6-FDA	PPPB	97.2	0.32
PI-3f	SiDA	PPPB	97.8	0.30

m = 0.5 g/dL in chloroform at 30 ± 0.1^oC

n = 0.2 g/dL in m-cresol at 30 ± 0.1^oC, p = 0.5 g/dL in m-cresol at 30 ± 0.1^oC

4(a).2.3.2 Synthesis of copolyimides

Copolyimides were also synthesized from either a mixture of diamines or a mixture of dianhydrides by a high temperature solution polycondensation method. Copolyimides containing diamines PPDBN and ODA in different ratios were synthesized by reacting them with dianhydrides like ODPA (Scheme 4(a).4), 6-FDA (Scheme 4(a).4) and SiDA (Scheme 4(a).4) and copolyimides containing 50 % SiDA and 50 % other dianhydrides like PMDA, BPDA, BTDA, ODPA and 6-FDA were synthesized by condensing them with 4-(3-pentadecyphenoxy)benzene-1,3-diamine (Scheme 4(a).5). Homopolyimides from ODA and dianhydrides like ODPA, 6-FDA and SiDA were also synthesized for comparative study.

A typical procedure for the copolymerization is as follows

➢ **Synthesis of copolyimide CPI-3c**

To a 50 mL three necked flask round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and a guard tube was added 0.3496 g (0.00085 mole) PPDBN, 0.1704 g ODA (0.00085 mole) and 7.4 mL m-cresol. Then 0.6 g (0.0017 mole) SiDA was added to this at room temperature, with stirring under a stream of nitrogen. The reaction mixture was then stirred at room temperature for 3 h to obtain a homogeneous solution and then heated to 220^{0}C and maintained at this temperature for 12 h. The water formed during imidization was removed continuously with a stream of nitrogen. The resulting viscous solution (15 % (w/v)) was then cooled and poured into 300 mL methanol to precipitate the polymer. The polymer was then filtered, washed with methanol, extracted with methanol for 24 h and dried at 80°C under vacuum for 12 h to obtain a fluffy polymer. Yield of the polymer obtained was about 98%. The copolyimide structure was confirmed by FT-IR and NMR (for soluble polyimides) spectroscopy. All other copolyimides were also synthesized by a similar procedure. The yields and viscosities of copolyimides are given in Tables 4(a).4 and 5.

Scheme 4(a).4. Copolyimides based on PPDBN and ODA with dianhydrides ODPA, 6-FDA and SiDA

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Scheme 4(a).5. Copolyimides based on PPDBN with a mixture of dianhydrides
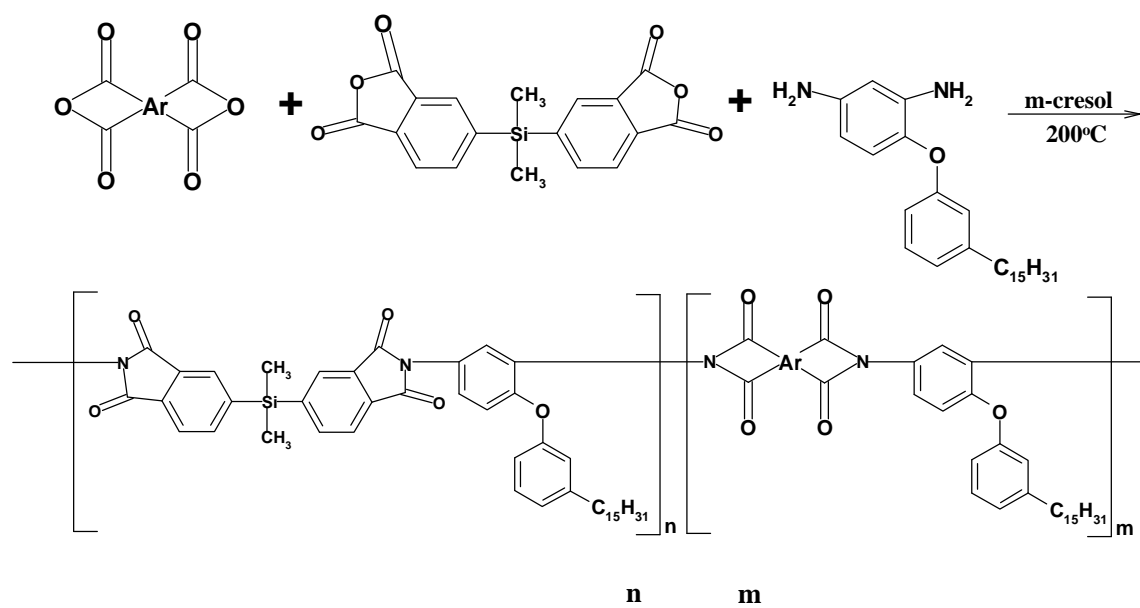
	n	m	
Where Ar =	50	50	CPI-4a
	50	50	CPI-4b
	50	50	CPI-4c
	50	50	CPI-4d
	50	50	CPI-4e

Table 4(a).4. Synthesis of homopolyimides from ODA and copolyimides containing varying ratios of ODA and PPDBN with dianhydrides ODPA, 6-FDA and SiDA

Polymer code	Dianhydride	Diamine (mole %)		Yield, %	η_{inh}, dL/g^m
		ODA	PPDBN		
PI-4a	ODPA	100	–	99.57	0.85^n
CPI-1a	ODPA	95	5	99.42	0.75^n
CPI-1b	ODPA	80	20	98.47	0.89
CPI-1c	ODPA	50	50	98.36	0.73
PI-4b	6-FDA	100	–	99.23	0.72^n
CPI-2a	6-FDA	95	5	99.33	0.74
CPI-2b	6-FDA	80	20	99.05	0.79
CPI-2c	6-FDA	50	50	98.98	0.74
PI-4c	SiDA	100	–	98.91	0.73
CPI-3a	SiDA	95	5	99.53	1.40
CPI-3b	SiDA	80	20	99.34	1.23
CPI-3c	SiDA	50	50	98.5	0.45

m = 0.5 g/dL in chloroform

n = 0.5 g/dL in m-cresol

Table 4(a).5. Synthesis of copolyimides based on PPDBN with a mixture of dianhydrides

Polymer code	Diamine	Dianhydride		Yield, %	η_{inh}, dL/g^m
		50 %	50 %		
CPI-4a	PPDBN	SiDA	PMDA	98.45	0.55
CPI-4b	PPDBN	SiDA	BPDA	99.32	0.69
CPI-4c	PPDBN	SiDA	BTDA	98.77	0.45
CPI-4d	PPDBN	SiDA	ODPA	99.56	0.46
CPI-4f	PPDBN	SiDA	6-FDA	98.89	0.44

m = 0.5 g/dL in chloroform

4(a).3   Results and discussion

4(a).3.1 Synthesis and structural characterization of homopolyimides

The two major methods used for the synthesis of polyimides are, (1) the two-step method via the poly(amic acid) intermediates and (2) the one step solution polymerization. The one-step method has got some advantages over the two step method. In this method complete imidization takes place in solution itself since the reaction is carried out at high temperature (~200^{0}C). Moreover at high temperatures, diamines and dianhydrides having low reactivity can also be reacted to give high molecular weight polyimides. In this study we could not obtain high molecular weight polyimides by two-step method and therefore all the polyimides were synthesized by the one-step method. Three substituted m-phenylene diamines namely 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN), 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT) and 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (PPPB), having pentadecylphenoxy, pentadecylbenzoate or pentadecyl phenoxybenzamide substituents and a series of dianhydrides were reacted in m-cresol at 220°C as shown in Schemes 4(a).1, 4(a).2 and 4(a).3 to obtain the respective polyimides. Depending on the rigidity of dianhydrides, the reaction mixture became either a homogeneous solution, a clear gel, or a heterogeneous slurry (due the precipitation of the polymer in the later stages of reaction).

In all the three series the polyimides from rigid dianhydrides like PMDA, BPDA and BTDA did not give a homogeneous solution. The polyimides from PMDA, PI-1a (PMDA-PPDBN), PI-2a (PMDA-PPDBT) and PI-3a (PMDA-PPPB) precipitated out of the solution after a 3 h reaction period at 220°C, where as polyimides PI-1b (BPDA-PPDBN), PI-2b (BPDA-PPDBT), PI-3b (BPDA-PPPB), PI-1c (BTDA-PPDBN), PI-2c (BTDA-PPDBT) and PI-3c (BTDA-PPPB) from dianhydrides BPDA and BTDA formed a gel.

All polyimides synthesized from flexible dianhydrides like ODPA, 6-FDA and SiDA gave soluble polyimides, which remained in solution through out the reaction period. The polyimides were either powders or had a fluffy nature. The polyimides obtained from dianhydrides PMDA (PI-1a,2a and 3a), BPDA (PI-1b,2b and 3b) and BTDA (PI-1c,2c and 3c)

were yellow coloured, but the polyimides obtained from dianhydrides ODPA (PI-1d,2d,3d), 6-FDA (PI-1e,2e,3e) and SiDA (PI-1f,2f,3f) were light colourled.

The yields were in the range 97 - 99.5% and their inherent viscosities were in the range 0.23 – 0.62 dL/g (Tables 4(a).1-3). The polyimides PI-1a-c (PPDBN-PMDA, BPDA, BTDA), PI-2a, 2b (PPDBT-PMDA, BPDA) and PI-3a, 3b (PPPB-PMDA, BPDA) could not be dissolved completely in any solvents for the viscosity measurements. They were not soluble in sulfuric acid also. The viscosity of polyimides PI-2c and 3c were determined using 0.1% and 0.2% solutions respectively, since the 0.5% solutions remained as a gel. Viscosity of all other polyimides was determined either in chloroform or m-cresol.

The polyimides thus obtained were characterized by FT-IR and ^{1}H NMR spectroscopy. In the case of all polyimides obtained from diamines PPDBN, PPDBT and PPPB the absorption bands corresponding to polyamic acid at 1650 cm^{-1} (amide I), 1534 cm^{-1} (amide II), 1712 cm^{-1} (acid –C=O) and 3250 cm^{-1} (-NH and –OH group) were absent indicating complete imidization. FT-IR spectra of all the polyimide films from diamine PPDBN showed absorption bands at 1723 and 1780 cm^{-1} (imide I), 1356 cm^{-1} (imide II), 1100 cm^{-1} (imide III) and 728 cm^{-1} which are characteristic of imide structure. The bands at 1254 cm^{-1} were due to ether group of diamine. A representative FT-IR spectrum of polyimide PI-1d is shown in Figure 4(a).1. FT-IR spectra of all the polyimide films from diamine PPDBT showed absorption bands at 1730, 1784 cm^{-1} (imide I), 1393 cm^{-1} (imide II), 1104 cm^{-1} (imide III) and 722 cm^{-1} which are characteristic of imide structure. The bands corresponding to ester group overlapped with the bands of imide ring. A representative FT-IR spectrum of polyimide PI-2e is given in Figure 4(a). 2.
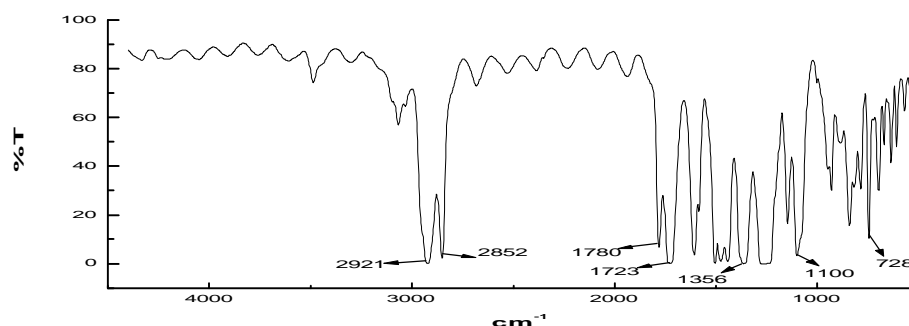
Figure 4(a).1. FT-IR spectrum of polyimide PI-1d (Film)
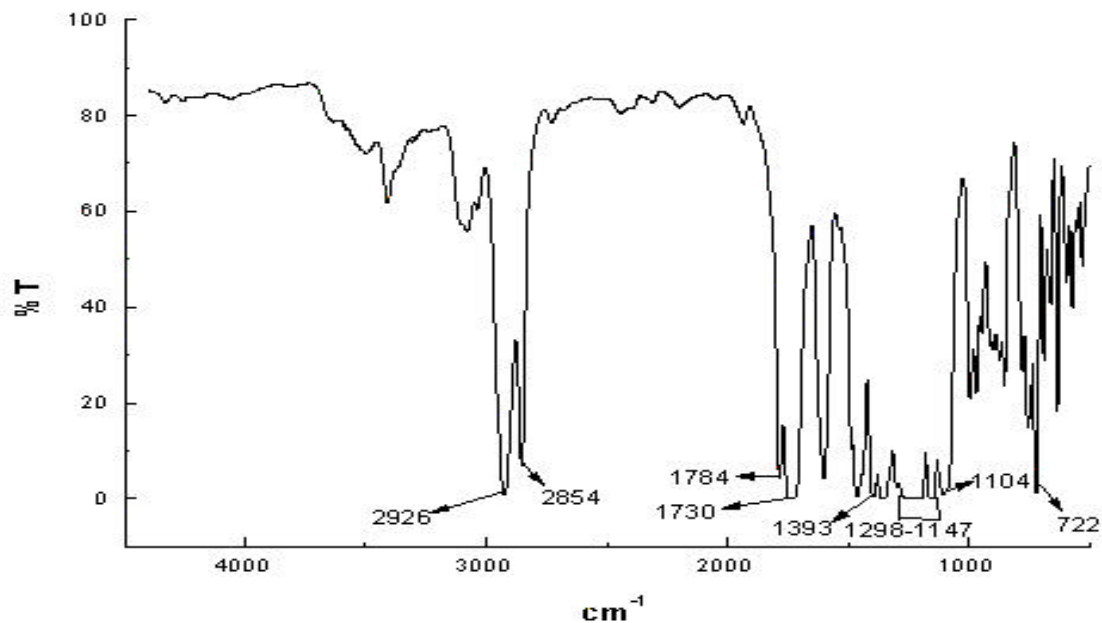
Figure 4(a).2. FT-IR spectrum of polyimide PI-2e (Film)

FTIR spectra of all the polyimide films from diamine PPPB showed absorption bands at 1730-1780 cm^{-1} (imide I), 1346 cm^{-1} (imide II), 1088 cm^{-1} (imide III) and 728 cm^{-1} which are the characteristic bands of imide structure. The bands at 3365 and 1671 cm^{-1} were due to the amide –N-H and amide carbonyl groups. A representative FT-IR spectrum of polyimide PI-3f is given in Figure 4(a).3.
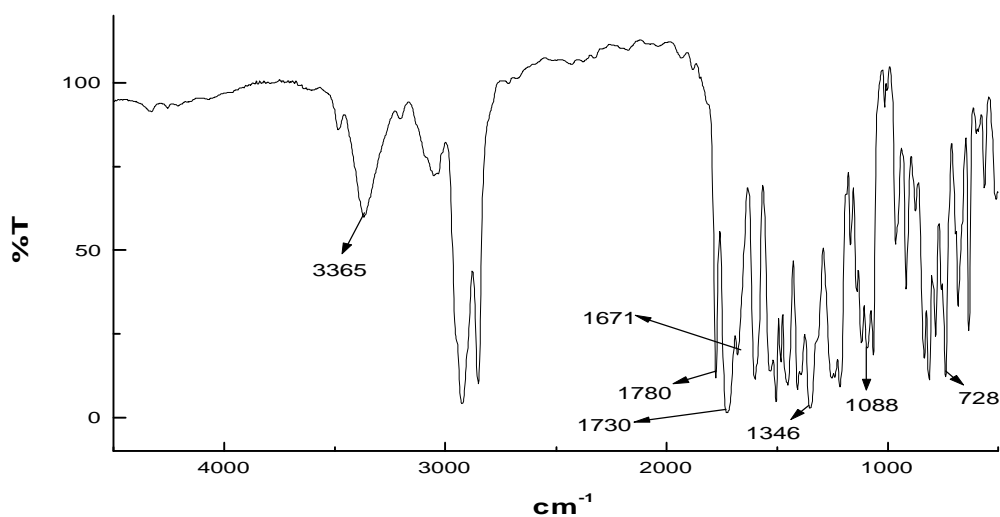
Figure 4(a).3. FT-IR spectrum of polyimide PI-3f (Film)

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^{1}H NMR spectra of polyimides from PPDBN showed signals corresponding to pentadecyl group at 0.87, 1.06-1.86 δ ppm and 2.53 δ ppm. Other protons in the region 6.8-7.3 δ ppm were due to the aromatic protons of the diamine. The aromatic protons of dianhydride showed signals in the region 7.7-8.2 δ ppm in all the cases. In the case of polyimide from SiDA (PI-1f) the silyl –CH$_3$ groups showed a singlet at 0.71 δ ppm (Figure 4(a).4). A representative spectrum of polyimide PI-1f is shown in Figure 4(a).4.
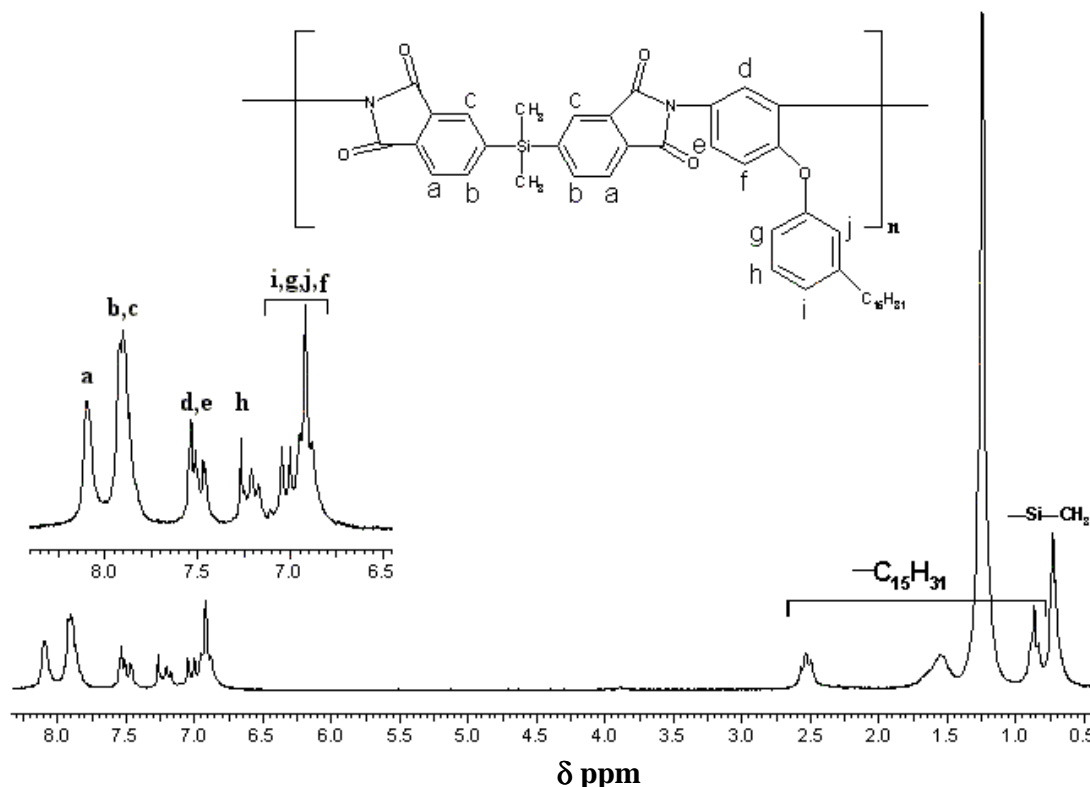
Figure 4(a).4. ^{1}H NMR spectrum of polyimide PI-1f in CDCl$_3$

^{1}H NMR spectra of polyimides from PPDBT showed signals corresponding to pentadecyl groups at 0.87, 1.07-1.84 δ ppm and 2.59 δ ppm respectively. Two protons ortho to pentadecyl group and the one at para position showed signals in the region 6.95-7.15 δ ppm. The one proton meta to pentadecyl group showed a triplet at 7.2 δ ppm. The remaining 3 protons of the diamine (protons in the m-phenylene unit) and the two protons ortho to silyl –CH$_3$ showed signals in the region 7.85-8.05 δ ppm. The four protons ortho to the carbonyl group of the dianhydride showed signals in the region 8.05-8.45 δ ppm. In the case of

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polyimides from SiDA the silyl –CH3 groups showed a singlet at 0.77 δ ppm. A representative NMR spectrum of polyimide PI-2f is shown in Figure 4(a).5.

δ ppm
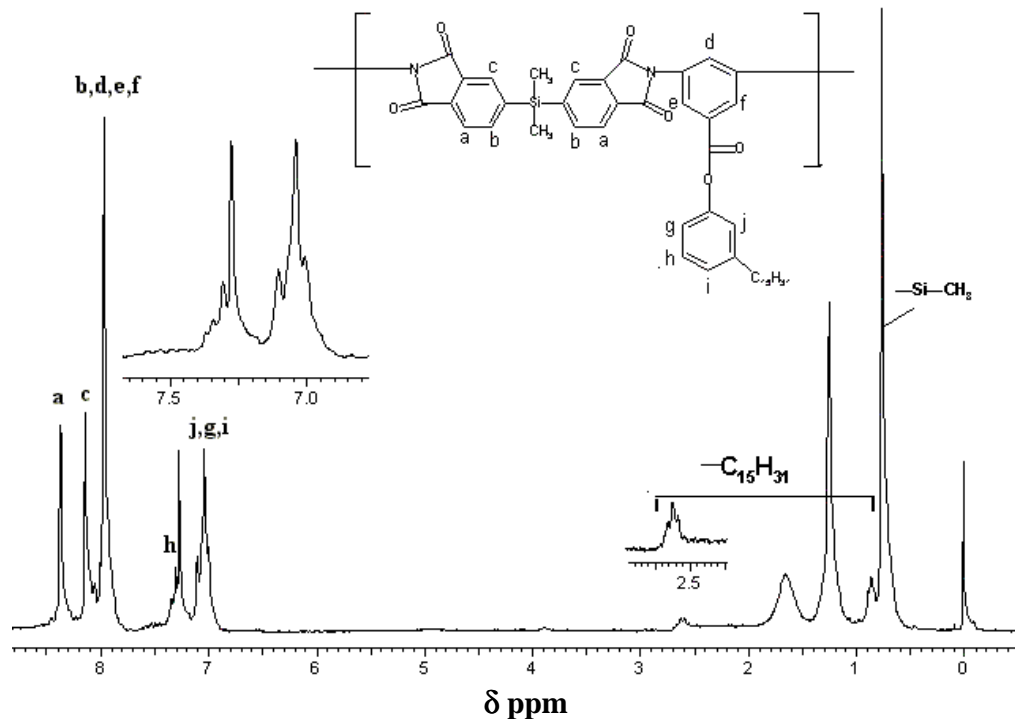
Figure 4(a).5. ^{1}H NMR spectrum of polyimide PI-2f in CDCl₃

^{1}H NMR spectra of polyimides from PPPB showed signals corresponding to pentadecyl group at 0.87, 1.02-1.98 δ ppm and 2.53 δ ppm. Other broad signals in the region 6.48-8.22 δ ppm were due to the aromatic protons of the diamine and dianhydride. A representative spectrum of polyimide PI-3f is shown in the Figure 4(a).6.
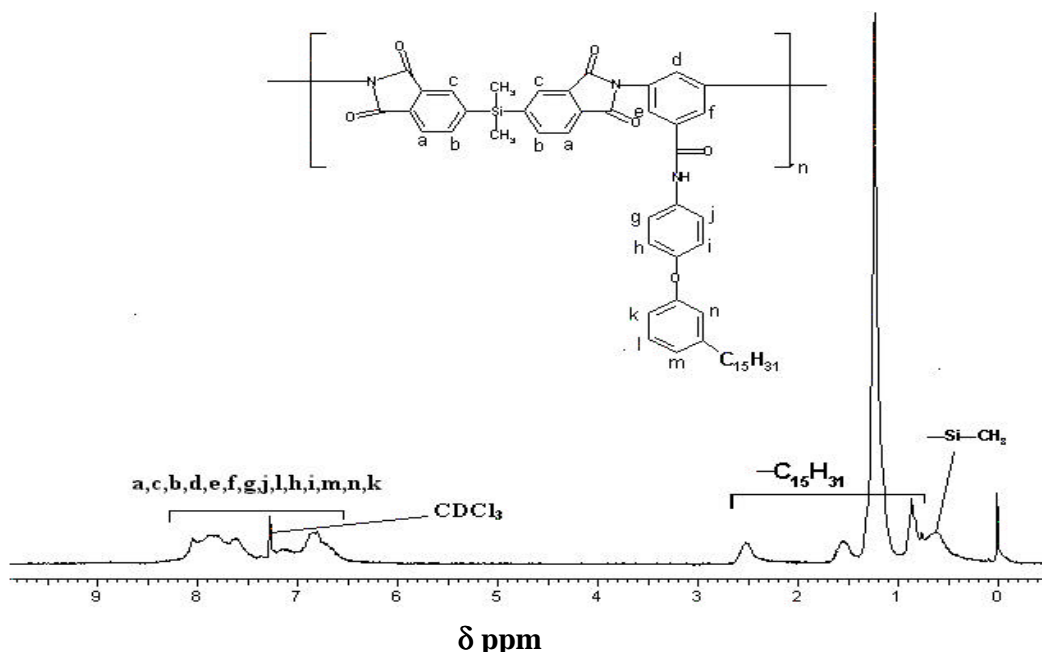
δ ppm
Figure 4(a).6. ^{1}H NMR spectrum of polyimide PI-3f in CDCl₃

4(a).3.2 Properties of polyimides

The properties of polyimides were evaluated by solubility measurements, X-ray diffraction (XRD), differntial scanning calorimetry (DSC), thermogravimetric analysis (TGA) and UV-visible spectroscopy.

4(a).3.2.1 Crystallinity of homopolyimides

Crystallinity in polymers strongly influences their solubility, thermal and mechanical properties and is dependent on the rigidity of both the monomers. Highly crystalline polymers have good thermal and mechanical properties but have low solubility. Polyimides in general are semicrystalline in nature and have limited solubility, which in turn affects their end use applications. One of the successful methods used to improve their solubility without significantly affecting the thermal and mechanical properties is the incorporation of bulky pendant groups in the polyimide backbone. These pendant groups inhibit chain packing and decrease the coplanarity of the aromatic rings, thus reducing the inter and intra chain interactions to enhance solubility. The wide angle X-ray diffraction studies give information about the inter chain and intra chain packing in polymers, which in turn is an indication of their degree of crystallinity. In the present study the crystallinity of polyimides were evaluated

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by wide angle X-ray diffraction measurements of powder (polyimides from PMDA, BPDA and BTDA in all the series) or film samples (polyimides from ODPA, 6-FDA and SiDA in all the series) in order to study the effect of incorporation of different pendant groups on the packing of polymer chains and solubility.

The XRD spectra of polyimides from diamine PPDBN is shown in Figure 4(a).7. All polyimides except PI-1a showed amorphous nature. PA-1a showed two reflection peaks indicating a semicrystalline nature.

All the polyimides based on diamine PPDBT showed more than one reflection peak indicating a semicrystalline nature. The polyimides with PMDA (PI-2a) and BPDA (PI-2b) showed sharper peaks indicating a higher degree of crystallinity than that of other polymers from BTDA (PI-2c), ODPA (PI-2d), 6-FDA (PI-2e) and SiDA (PI-2f).
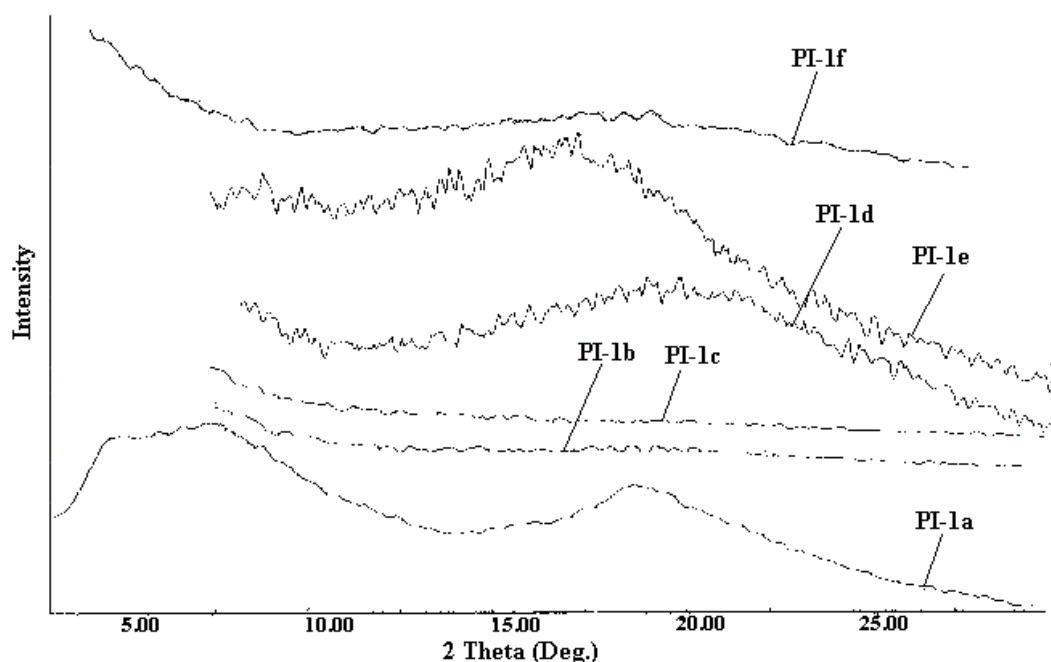
Figure 4(a).7. Wide-angle X-ray diffractograms of polyimides from PPDBN
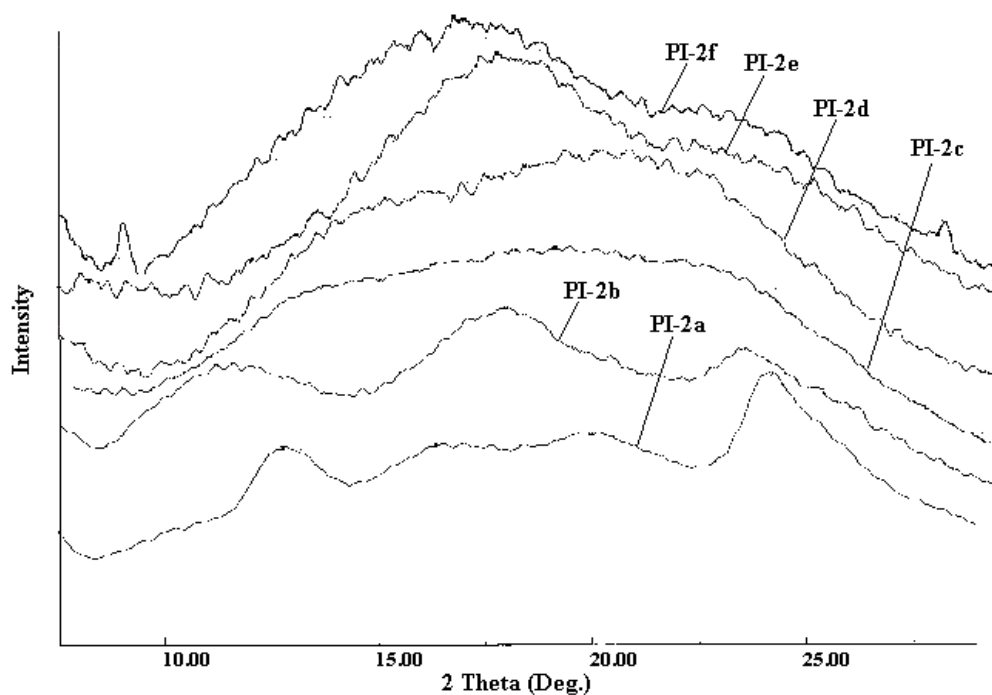
Figure 4(a).8. Wide-angle X-ray diffractograms of polyimides from PPDBT

Polyimides from diamine PPPB, with dianhydrides PMDA (PI-3a), BPDA (PI-3b) and BTDA (PI-3c) (Figure 4(a).9) showed more than one reflection peaks indicating semicrystalline nature. Other polyimides from dianhydrides ODPA (PI-3d), 6-FDA (PI-3e) and SiDA (PI-3f) showed only a broad single peak indicating the amorphous nature.

In general the polyimides from flexible dianhydrides like ODPA, 6-FDA and SiDA are amorphous in nature where as those from rigid dianhydride like PMDA are semicrystalline in nature. The polyimides from dianhydrides BPDA and BTDA were either semicrystalline or amorphous depending on the diamine part.
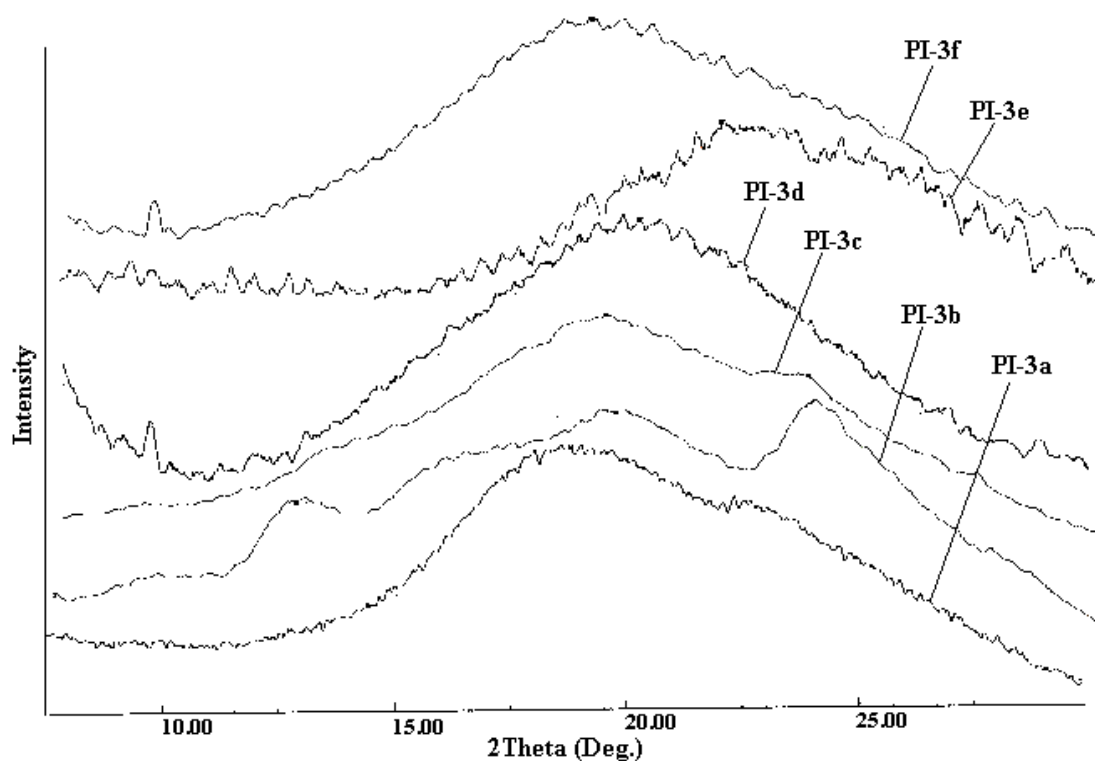
Figure 4(a).9. Wide-angle X-ray diffractograms of polyimides from PPPB

4(a).3.2.2 Solubility measurements

Solubility tests were carried out at 5% concentration in various solvents. The observed data showed that the polyimides based on diamine PPDBN with dianhydrides ODPA (PI-1d), 6-FDA (PI-1e) and SiDA (PI-1f), were soluble in a wide range of polar solvents like NMP, DMAc, DMF, pyridine, m-cresol. o-chlorophenol, nitrobenzene (Table 4(a).6). They were also soluble in low boiling solvents like chloroform and THF. This high solubility may be due to the disruption of the chain packing in these polyimides by pendant pentadecylphenoxy group and by flexible linkages like ether, hexafluoroisopropylidene and silane in the main chain. The polyimides containing rigid dianhydrides like PMDA (PI-1a), BPDA (PI-1b) and BTDA (PI-1c), were not soluble in any of the above solvents. In m-cresol PI-1a was only partially soluble even on heating and PI-1b and PI-1c formed a gel. This may be due to the development of a certain degree of order that allowed dense packing of polymer chains.

The solubility data of polyimides based on diamine PPDBT having a pentadecylbenzoate group is given in Table 4(a).7. In this case the polyimides with dianhydrides PMDA (PI-2a), BPDA (PI-2b) and BTDA (PI-2c) were not soluble in any test

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solvents at a concentration of 5 wt %. In m-cresol they formed a gel on heating. But a very dilute solution (0.1% concentration) of polyimide PI-2c could be made in m-cresol after keeping for three days. The polyimide PI-2d from the dianhydride ODPA was soluble in a limited number of solvents like m-cresol, o-chlorophenol, nitrobenzene and NMP (on heating). It was partly soluble in solvents like chloroform, DMF, DMAc and pyridine and was insoluble in THF and DMSO. The polyimides PI-2e and 2f containing dianhydrides 6-FDA and SiDA were soluble in almost all the polar solvents tested. They have high solubility even in low boiling solvents like chloroform and tetrahydrofuran. This high solubility is induced by a combination of the pendant pentadecyl group and the flexible linkages containing silicon and hexafluoroisopropylidene groups.

The solubility data of polyimides based on diamine PPPB having a pentadecylphenylbenzamide group, is given in Table 4(a).8. In this case the polyimides with dianhydrides PMDA (PI-3a), BPDA (PI-3b) and BTDA (PI-3c) were not soluble in any common solvents at a concentration of 5 wt %. In m-cresol they formed a gel on heating. But a very dilute solution (0.2% concentration) of polyimide PI-3c could be made in m-cresol after keeping for three days. The polyimide PI-3d from the diahydride ODPA was soluble in solvents like m-cresol, o-chlorophenol, nitrobenzene, DMAc, NMP, THF and pyridine and was partially soluble in chloroform and swelled in DMF. The polyimides PI-3e and 3f containing dianhydrides 6-FDA and SiDA were soluble in almost all the polar solvents tested. They exhibited high solubility even in low boiling solvents like chloroform and tetrahydrofuran. This high solubility is induced by a combination of the pendant pentadecyl group and the flexible linkages containing silicon and hexafluoroisopropylidene groups.

Among the three series, polyimides synthesized from PPDBN showed higher solubility in the case of dianhydrides like ODPA, 6-FDA and SiDA. The solubility of BTDA containing polyimides decreased with change in diamines in the order PPDBN < PPDBT < PPPB. The polyimides having flexible linkages in the main chain showed higher solubility than those having a rigid backbone. All polyimides synthesized from SiDA and 6-FDA were highly soluble in all the solvents tested. In the case of polyimides with ODPA, the solubility decreased in the order PI-1d (ODPA-PPDBN) > PI-3d (ODPA-PPPB) > PI-2d (ODPA-PPDBT). None of the polyimides were soluble in DMSO and this may be due to the presence

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of hydrophobic alkyl group. The poor solubility of polyimides from rigid dianhydrides and polyimides PI-2d (ODPA-PPDBT) and PI-3d (ODPA-PPPB) may be due to the development of some intra chain order in these polyimides. Thus this study shows the effect of different pendant substitution on the solubility of resulting polyimides.

It is known that for a polymer, computational modeling helps in getting a fundamental insight on the translation of structural properties of monomers and oligomers into observable polymer properties and therefore the polymer properties can be predicted on the basis of computed monomer and oligomer structures.[18] There are some literature reports where many researchers have attempted to explain the solubility behavior[19] and difference in T_g[20] of the polyimides based on single chain conformations. Therefore in the present study modeling studies were attempted to explain the various trends observed in solubility behavior of these polyimides based on some model structures of polyimide fragments. The modeling studies were done for oligomers having seven repeat units since it was observed that the particular conformation repeats after every seventh repeat unit. The single chain conformation of these oligomers were obtained from HyperChem version 5.0. The model structures were optimized using an MM+ force field. The single chain conformations of polyimides based on PPDBN is given in Figures 4(a).10-15.

In the case of polyimides from diamine PPDBN with rigid dianhydrides like PMDA, BPDA and BTDA the main chain showed a certain degree of intrachain order as can be seen from Figures 4(a).10-12. In this case the intimate chain stacking necessary for intermolecular interaction is disturbed since the chain cannot take up an extended conformation. However some intrachain packing is observed which may lead to certain degree of order and results in low solubility. When the flexibility in the dianhydride part increased as in the case of polyimides PI-1d (ODPA-PPDBN), PI-1e (6-FDA -PPDBT) and PI-1f (SiDA-PPPB), the polyimides showed either an extended conformation as in the case of PI-1d (ODPA-PPDBN) or coiled conformation as in the case of PI-1e (6-FDA-PPDBN) and PI-1f (SiDA-PPDBN).

Table 4(a).6. Solubility properties of polyamides from PPDBN and various anhydrides

Polymer Code	Diamine	Dianhydride	Solvents									
			NMP	DMAc	DMF	DMSO	Pyrdine	THF	CHCl$_3$	m-Cresol	o-Cl-phenol	Nitro benzene
PA-1a	PPPBN	PMDA	+ -	+ -	+ -	- -	+ -	+ -	+ -	- -	- -	- -
PA-1b	PPPBN	BPDA	+ -	+ -	+ -	- -	+ -	+ -	+ -	+ -	+ -	+ -
PA-1c	PPPBN	BTDA	+ -	+ -	+ -	- -	+ -	+ -	+ -	+ -	+ -	+ -
PA-1d	PPPBN	ODPA	++	++	++	- -	++	++	++	++	++	++
PA-1e	PPPBN	6-FDA	++	++	++	- -	++	++	++	++	++	++
PA-1f	PPPBN	SiDA	++	++	++	- -	++	++	++	++	++	++

++ Soluble at room temperature, + soluble on heating, +- partly soluble even on heating, -- insoluble even on heating
NMP: N-methylpyrrolidone, DMAc: N-N'-dimethyl acetamide, DMF: N-N'-dimethyl formamide, DMSO: dimethyl suphoxide, THF: tetrahydrofuran, CHCl$_3$: chloroform

Table 4(a).7. Solubility properties of polyimides from PPDBT and various dianhydrides

Polymer Code	Diamine	Dianhydride	Solvents									
			NMP	DMAc	DMF	DMSO	Pyrdine	THF	CHCl$_3$	m-Cresol	o-Cl-phenol	Nitro benzene
PA-2a	PPDBT	PMDA	+ -	+ -	+ -	- -	- -	- -	- -	- -	- -	- -
PA-2b	PPDBT	BPDA	+ -	+ -	+ -	- -	- -	- -	- -	+ -	+ -	+ -
PA-2c	PPDBT	BTDA	+ -	+ -	+ -	- -	- -	- -	- -	++[m]	+ -	+ -
PA-2d	PPDBT	ODPA	+	+ -	+ -	- -	+ -	- -	+ -	++	++	++
PA-2e	PPDBT	6-FDA	++	++	++	- -	++	++	++	++	++	++
PA-2f	PPDBT	SiDA	++	++	++	- -	++	++	++	++	++	++

++ Soluble at room temperature, + soluble on heating, +- partly soluble even on heating, -- insoluble even on heating
NMP: N-methylpyrrolidone, DMAc: N-N'-dimethyl acetamide, DMF: N-N'-dimethyl formamide, DMSO: dimethyl suphoxide, THF: tetrahydrofuran, CHCl$_3$: chloroform

m = soluble at a very low concentration (0.1 %) after keeping for three days at room temperature

Table 4(a).8. Solubility properties of polyimides from PPPB and various dianhydrides

Polymer Code	Diamine	Dianhydride	Solvents									
			NMP	DMAc	DMF	DMSO	Pyrdine	THF	CHCl$_3$	m-Cresol	O-Cl-phenol	Nitro benzene
PA-3a	PPPB	PMDA	+ -	+ -	+ -	- -	- -	- -	- -	+ -	+ -	+ -
PA-3b	PPPB	BPDA	+ -	+ -	+ -	- -	- -	- -	- -	+ -	+ -	+ -
PA-3c	PPPB	BTDA	+ -	+ -	+ -	- -	- -	- -	- -	++^{m}	+ -	+ -
PA-3d	PPPB	ODPA	++	++	++	- -	++	+-	++	++	++	++
PA-3e	PPPB	6-FDA	++	++	++	- -	++	++	++	++	++	++
PA-3f	PPPB	SiDA	++	++	++	- -	++	++	++	++	++	++

++ Soluble at room temperature, + soluble on heating, +- partly soluble even on heating, -- insoluble even on heating

NMP: N-methylpyrrolidone, DMAc: N-N'-dimethyl acetamide, DMF: N-N'-dimethyl formamide, DMSO: dimethyl suphoxide, THF: tetrahydrofuran, CHCl$_3$: chloroform

m = soluble at a very low concentration (0.2 %) after keeping for three days at room temperature

In the case of PI-1d (ODPA-PPDBN) even though the chain has an extended conformation the inter chain packing will be difficult due to the antiparallel orientation of alkyl groups with respect to the main chain as shown in Figure 4(a).13. The model structure of PI-1d further shows a flexible main chain and hence many conformations will be possible for this polyimide. This flexibility is expected because of the presence of ether groups in the main chain and side chain. Because of the conformational flexibility the intrachain interactions are lowered thus facilitating better penetration of solvent molecules and hence the high solubility. The polyimides PI-1e (6-FDA-PPDBN) (Figure 4(a).14) and PI-1f (SiDA-PPDBN) (Figure 4(a).15) containing flexible dimethyl silyl and hexafluoroisopropylidene linkages showed a coiled conformation with a highly flexible main chain. This might lead to a random arrangement of chains in the bulk state, with low interchain and intra chain interactions and hence the high solubility. It was expected that in the case of polyimides from diamines PPDBT and PPPB also the orientation of the single chains could possibly explain the solubility properties.

It was expected that the polyimides based on all the three diamines PPDBN, PPDBT and PPPB with ODPA should have high solubility since they have flexible groups in the main chain and also in the side chain. But in contrary to this, the polyimides from diamines PPDBT and PPPB with ODPA exhibited low solubility. Therefore an attempt was made to explain this difference in solubility behavior based on their model structures. The single chain conformations of these polyimides are given in Figures 4(a). 13,16 and 17. In the case of polyimide PI-1d the single chain showed an extended conformation in which the alkyl groups in the neighboring units orienting outward in an alternating pattern. The low solubility of PI-2d (ODPA-PPDBT) and PI-3d (ODPA-PPPB) as compared to PI-1d may be due to the restriction of side chain flexibility due to the presence of rigid ester and amide groups. Ester and amide groups always prefer to remain in a planar form and thereby reduces the conformational flexibility. In the case of polyimides PI-2d (ODPA-PPDBT) (Figure 4(a).16) and PI-3d (ODPA-PPPB) (Figure 4(a).17) the seven repeat units neatly arranged into a heptagonal structure where alkyl groups also followed a particular orientation. In these cases even though the inter chain interactions were disrupted there is some possibility of intra chain order due to the packing of alkyl groups and the main chain. In the case of PI-2d (ODPA-

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PPDBT) the alkyl groups showed a parallel orientation with respect to main chain and in the case of PI-3d (ODPA-PPPB) the alkyl groups were antiparallel to the main chain but parallel to the pendant phenyl groups. The models obtained for a single chain with 14 repeat units showed two such heptagons and therefore it can be assumed that this kind of a packing will be seen after every seventh repeat unit and will be extending all over the chain. This may be a possible reason for their reduced solubility.

The conformations obtained in this study may be only one of the possible minimum energy conformations and explains the solubility behavior of these polyimides. However to have a proper insight into the structure of these polyimides one should know exactly how these single chains arrange in an amorphous state for which detailed modeling studies are required which is beyond the scope of this work.
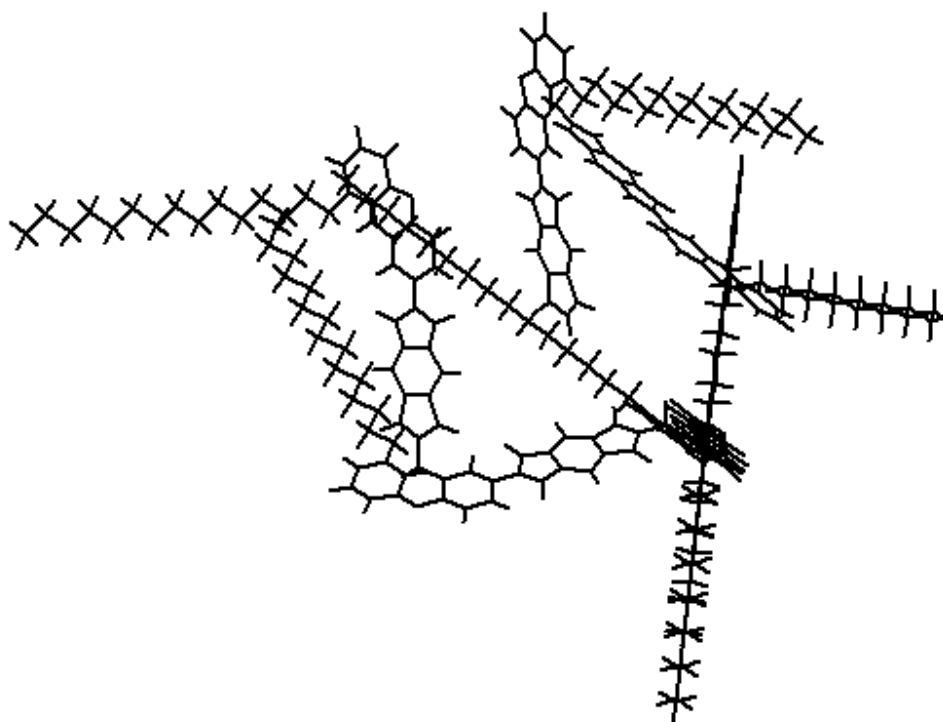
Figure 4(a). 10. Single chain conformation of polyimide PI-1a (PMDA-PPDBN)
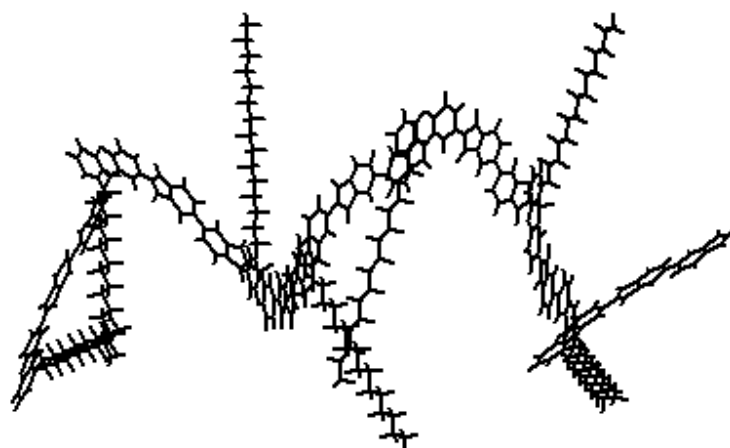
Figure 4(a). 11. Single chain conformation of polyimide PI-1b (BPDA-PPDBN)
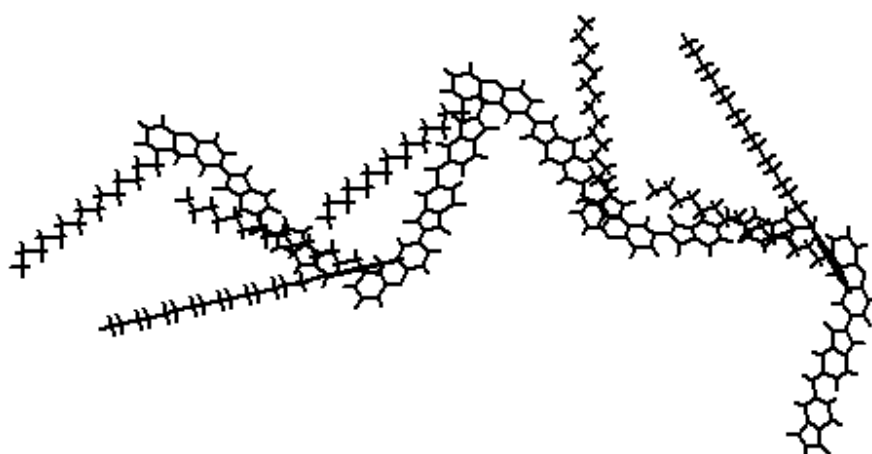
Figure 4(a). 12. Single chain conformation of polyimide PI-1c (BTDA-PPDBN)
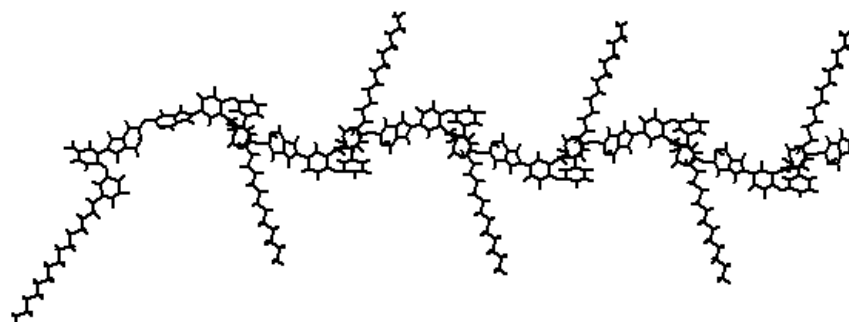
Figure 4(a). 13. Single chain conformation of polyimide PI-1d (ODPA-PPDBN)
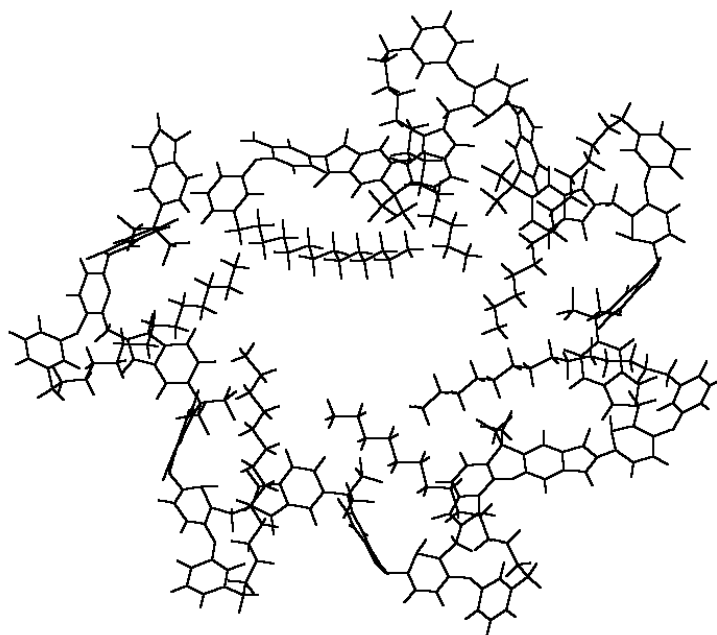
Figure 4(a). 14. Single chain conformation of polyimide PI-1e (6-FDA-PPDBN)
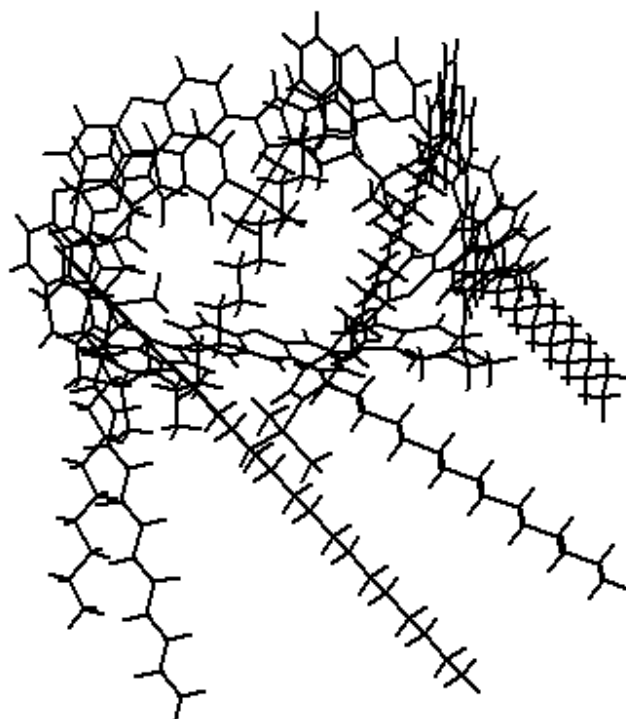
Figure 4(a). 15. Single chain conformation of polyimide PI-1f (SiDA-PPDBN)

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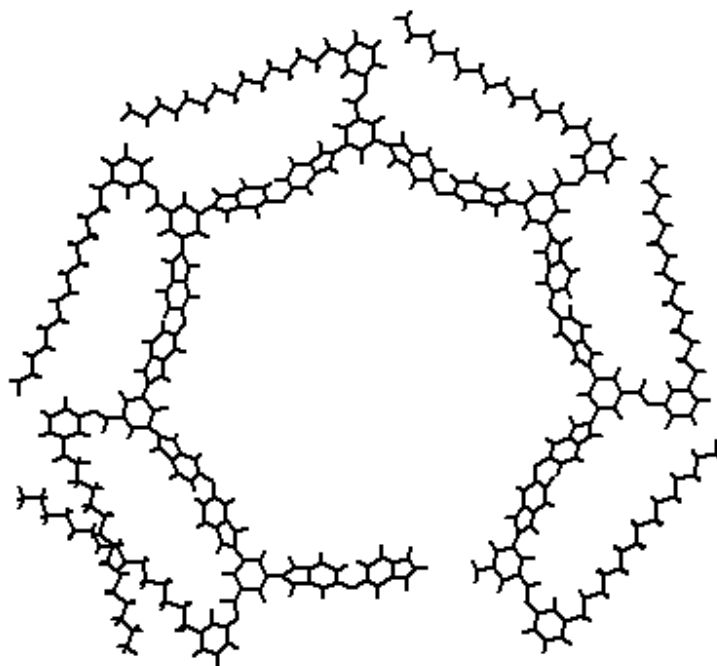
Figure 4(a). 16. Single chain conformation of polyimide PI-2d (ODPA-PPDBT)
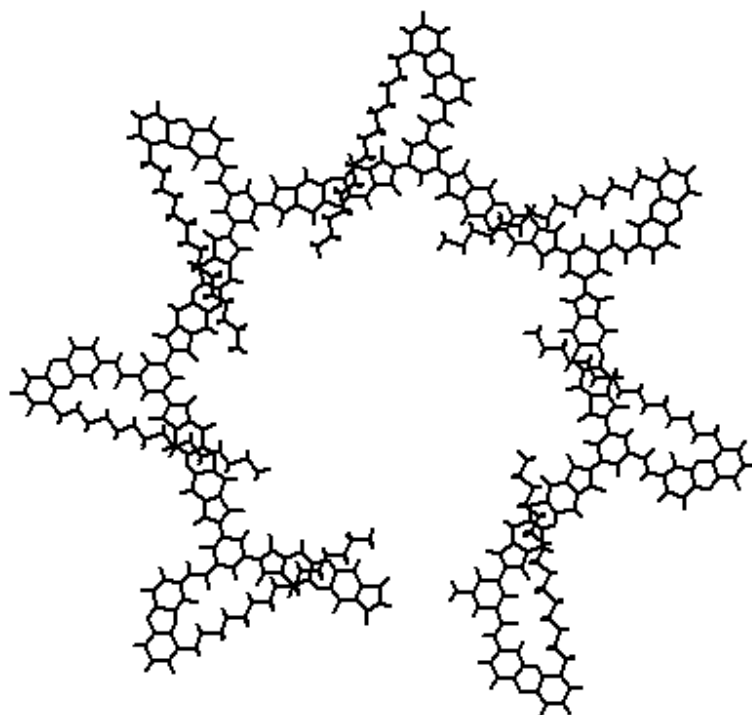
Figure 4(a). 17. Single chain conformation of polyimide PI-3d (ODPA-PPPB)

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4(a).3.2.3 Thermal properties

The thermal stability of a polymer is generally determined by initial decomposition temperature (IDT), decomposition temperature at different weight losses and maximum decomposition temperature (T_{max}). These values are determined by TGA. The higher these values the higher will be the thermal stability. Glass transition temperature determined by DSC is related to the softening point of polymer and determines its glassy nature. The thermal properties of a polymer are influenced by the structure of monomers. In the case of polyimides structure of both dianhydride and diamine influences the thermal stability.

In the present study, the thermal stability and glass transition temperatures of the polyimides were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) respectively. Both the measurements were done at a heating rate of 10^oC/min in nitrogen. The thermal decomposition patterns for the polyimides synthesized from diamine PPDBN, PPDBT and PPPB are given in Figures 4(a).18–20. The initial decomposition temperature (IDT), the decomposition temperature at 10% weight loss (T_{10}) and the maximum decomposition temperature (T_{max}) for all the polyimides are given in Table 4(a).9-11. An examination of the data showed that all the polyimides exhibit good thermal stability, being stable up to 423-506°C. This is contradictory to the widely accepted fact that the thermal stability of the polyimides is considerably reduced by the introduction of alkyl groups. In this study it was observed that alkyl group does not reduce the thermal stability of the polyimide significantly and the reduction in thermal stability is mainly because of the flexibility in the main chain. It was observed that as the main chain flexibility increases the thermal stability decreases. The thermal decomposition temperatures of all the polyimides from the three series were very close to each other and highest thermal stability was shown by polyimides PI-2a (PMDA-PPDBT) and PI-2e (6-FDA-PPDBT) even though they had an ester linkage in the side chain.

The polyimides synthesized from diamine PPDBN (PI-1a-1f, Table 4(a).9) showed IDT, T_{10} and T_{max} values in the range 447-465°C, 450-468°C and 481-504°C respectively. The initial decomposition temperatures were very close to each other and were in the order PI-1c > 1b >1a > 1e > 1d > 1f. In this series the polyimide based on SiDA showed the lowest initial decomposition temperature due to the flexible dimethyl silyl linkages. T_{10} values were in the

order PI-1c > 1b > 1d > 1e > 1a > 1f and the polyimide PI-1a from PMDA showed the minimum T_{10} temperature. The T_{max} values were in the order PI-1c > 1d = 1b > 1e > 1a > 1f and here the lowest value was shown by SiDA containing polyimide.

In the case of polyimides synthesized from diamine PPDBT, the IDT, T_{10} and T_{max} values were in the range 423–506 ^{0}C, 436–514 ^{0}C and 466–557 ^{0}C respectively. The polyimide PI-2a showed the maximum thermal stability with an IDT, T_{10} and T_{max} values of 506, 514 and 557 ^{0}C respectively (Table 4(a).10). The IDT value was minimum in the case of polyimide PI-2d containing ODPA and T_{10} and T_{max} values were the lowest in the case of PI-2f containing SiDA. The polyimide PI-2e from 6-FDA having a flexible hexafluoroisopropylidene linkage showed higher thermal stability than polyimides from rigid dianhydrides like BPDA and BTDA. All the polyimides showed good thermal stability inspite of the presence of ester linkage in the side chain.

The polyimides from PPPB showed the least thermal stability among the three series. The IDT, T_{10} and T_{max} values were in the range 434–447 ^{0}C, 443–449 ^{0}C and 483–497 ^{0}C respectively (Table 4(a).11). In this case the IDT, T_{10} and T_{max} values were very close for the six polyimides. The maximum IDT was shown by PI-3c based on dianhydride BTDA. The maximum T_{10} and T_{max} value was shown by ODPA containing polyimide PI-3d even though it had a flexible ether linkage in the main chain. In general all polyimides showed good thermal stabilities with no decomposition below 434^{0}C indicating that the pendant alkyl groups do not affect the thermal stability significantly.

The DSC thermograms, which were recorded at the second heating of polyimides, at a heating rate of 10 ^{0}C per minute are shown in Figures 4(a).21-23. The glass transition temperature of polyimides synthesized from PPDBN (Table 4(a).9) were in the order PI-1b > 1a > 1c > 1e > 1d > 1f. The maximum T_g (226^{0}C) was shown by BPDA containing polyimide and the minimum (123^{0}C) was shown by SiDA containing polyimide. The other polyimides from rigid dianhydrides like PMDA and BTDA also showed high T_g's.

Among the three series the polyimides synthesized from diamine PPDBT showed the highest T_g values in the range 174–240^{0}C (Table 4(a).10). Here also the maximum value was shown by BPDA containing polyimide and the minimum was shown by 6-FDA containing polyimide. All the polyimides synthesized from rigid dianhydrides like PMDA, BPDA and

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BTDA showed high T_g's and were above 200^0C. The polyimide PI-2d (ODPA-PPDBT) based on ODPA also showed T_g above 200^0C even though it had a flexible ether group. This may be due to the intrachain packing existing in this polyimide, which reduces the overall flexibility (single chain conformation given in Figure 4(a).16 Page No. 196)

The T_g values of polyimides synthesized from diamines PPPB were in between those synthesized from PPDBN and PPDBT (Table 4(a).11). In this series the BTDA containing polyimides showed the highest T_g value of 237^0C and the lowest T_g (189^0C) was shown by PI-3e based on dianhydride 6-FDA. The T_g values of all other polyimides were in between these values and in general polyimides synthesized from rigid dianhydrides (PMDA, BPDA and BTDA) showed high T_g values than those synthesized from flexible dianhydrides like ODPA, SiDA and 6-FDA.

Table 4(a).9. Thermal properties of polyimides from PPDBN

Polymer Code	Dianhydride	Diamine	IDT, ^{o}C	T_{10}, ^{o}C	T_{max}, ^{o}C	T_g, ^{o}C
PI-1a	PMDA	PPDBN	449.6	451	485.9	212
PI-1b	BPDA	PPDBN	456	460	493	226
PI-1c	BTDA	PPDBN	465	468	504	171
PI-1d	ODPA	PPDBN	448	457	493	146
PI-1e	6-FDA	PPDBN	449	456	487	156
PI-1f	SiDA	PPDBN	447	450	481	123

Table 4(a).10. Thermal properties of polyimides from PPDBT

Polymer Code	Dianhydride	Diamine	IDT, ^{o}C	T_{10}, ^{o}C	T_{max}, ^{o}C	T_g, ^{o}C
PI-2a	PMDA	PPDBT	506	514	557	228
PI-2b	BPDA	PPDBT	435	449	497	240.5
PI-2c	BTDA	PPDBT	468	487	529	236.9[m]
PI-2d	ODPA	PPDBT	423	443	476	216
PI-2e	6-FDA	PPDBT	483	488	534	174
PI-2f	SiDA	PPDBT	430	436	466	185

m = the sample was heated to the softening point and then quenched in liquid nitrogen before determining T_g

Table 4(a).11. Thermal properties of polyimides from PPPB

Polymer Code	Dianhydride	Diamine	IDT, $^{\circ}$C	T_{10}, $^{\circ}$C	T_{max}, $^{\circ}$C	T_g, $^{\circ}$C
PI-3a	PMDA	PPPB	437	445	489	219
PI-3b	BPDA	PPPB	434	443	487	224
PI-3c	BTDA	PPPB	447	446	489	237[m]
PI-3d	ODPA	PPPB	442	449	497	216[m]
PI-3e	6-FDA	PPPB	434	444	483	186
PI-3f	SiDA	PPPB	441	447	489	193[m]

m = the sample was first heated to the softening temperature and then quenched with liquid nitrogen before determining T_g
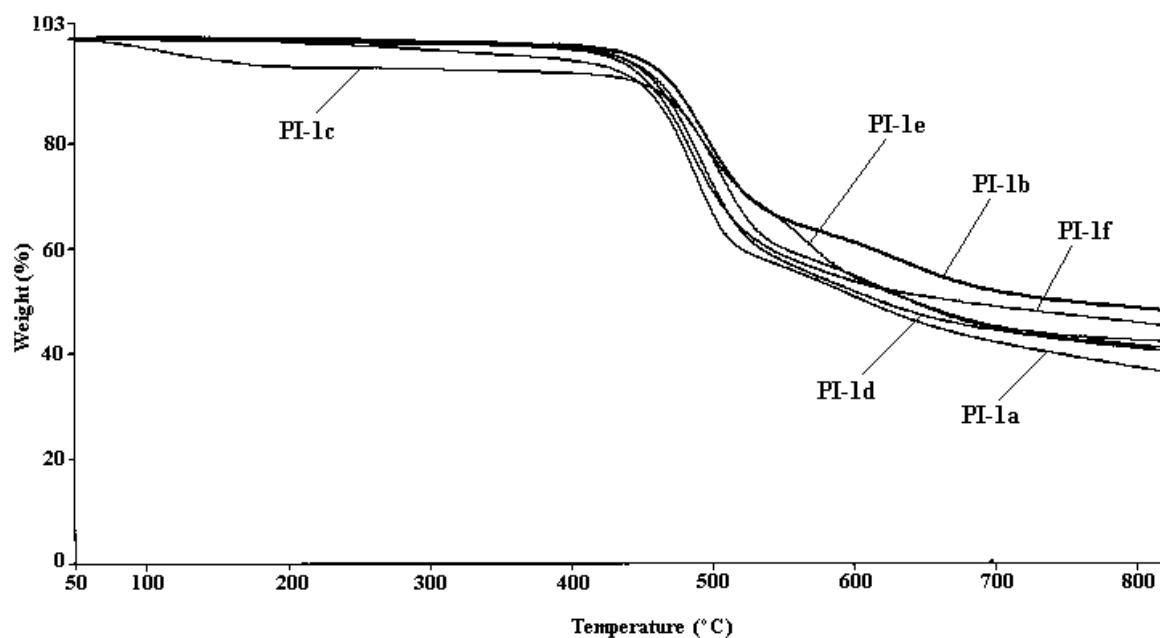
Figure 4(a).18. TG curves of homopolyimides from PPDBN
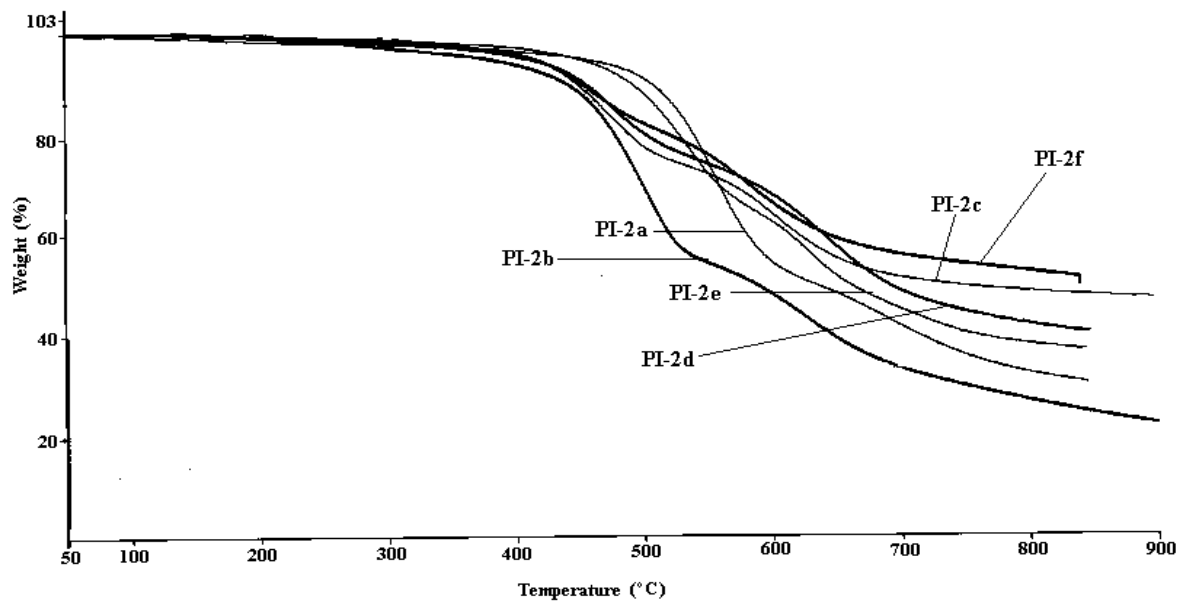
Figure 4(a).19. TG curves of homopolyimides from PPDBT
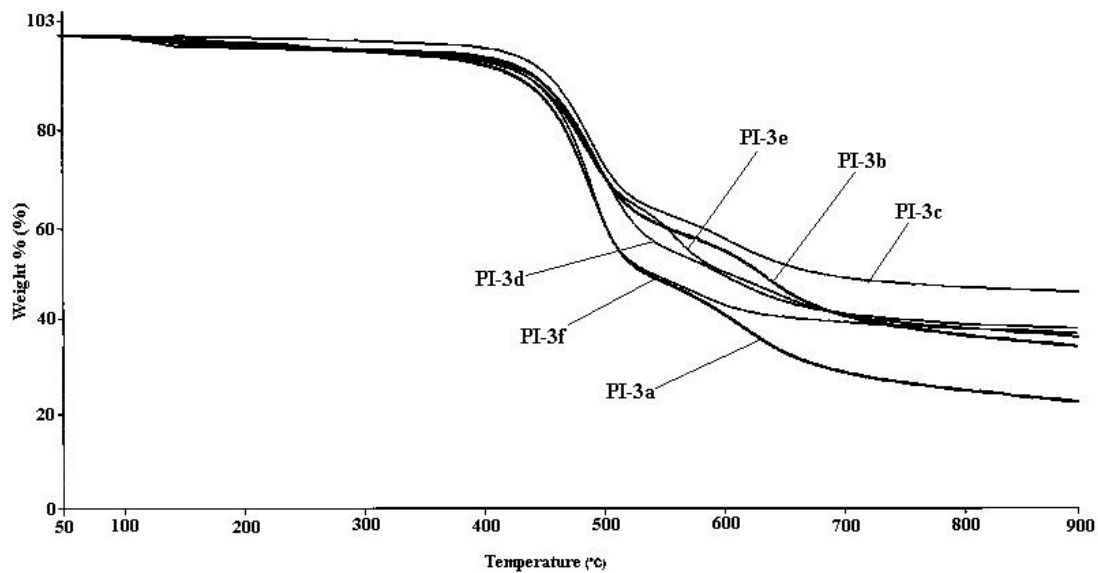
Figure 4(a).20. TG curves of homopolyimides from PPPB

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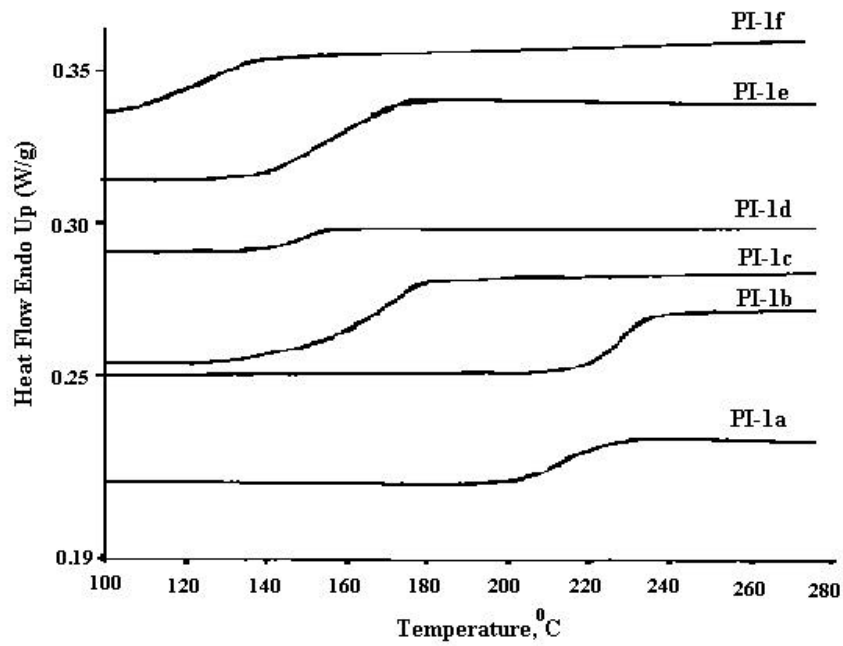
Figure 4(a).21. DSC thermograms of polyimides from PPDBN with different dianhydrides
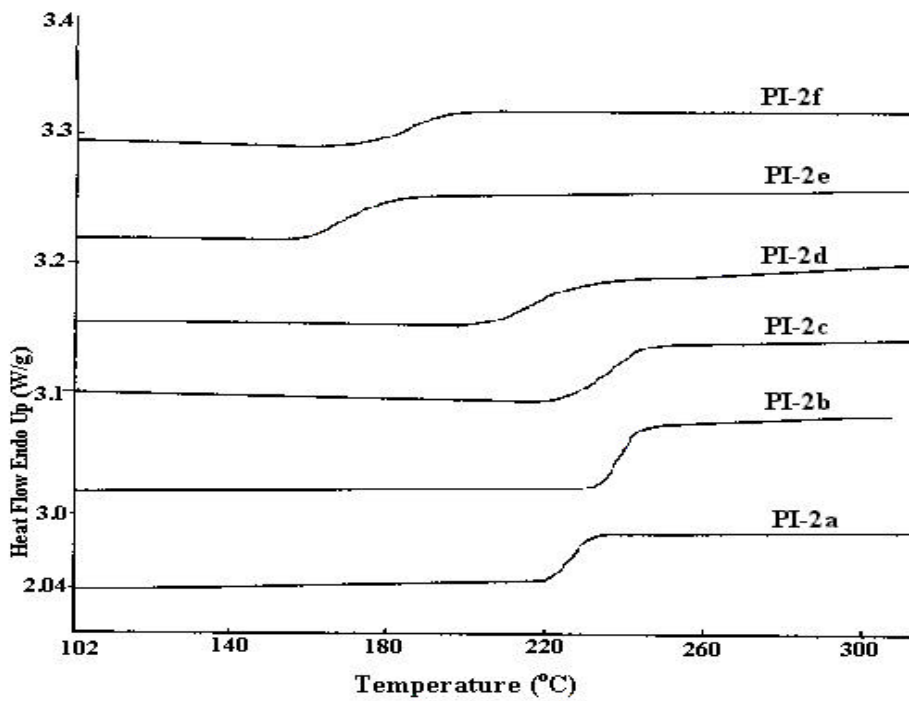
Figure 4(a).22. DSC thermograms of polyimides from PPDBT with different dianhydrides

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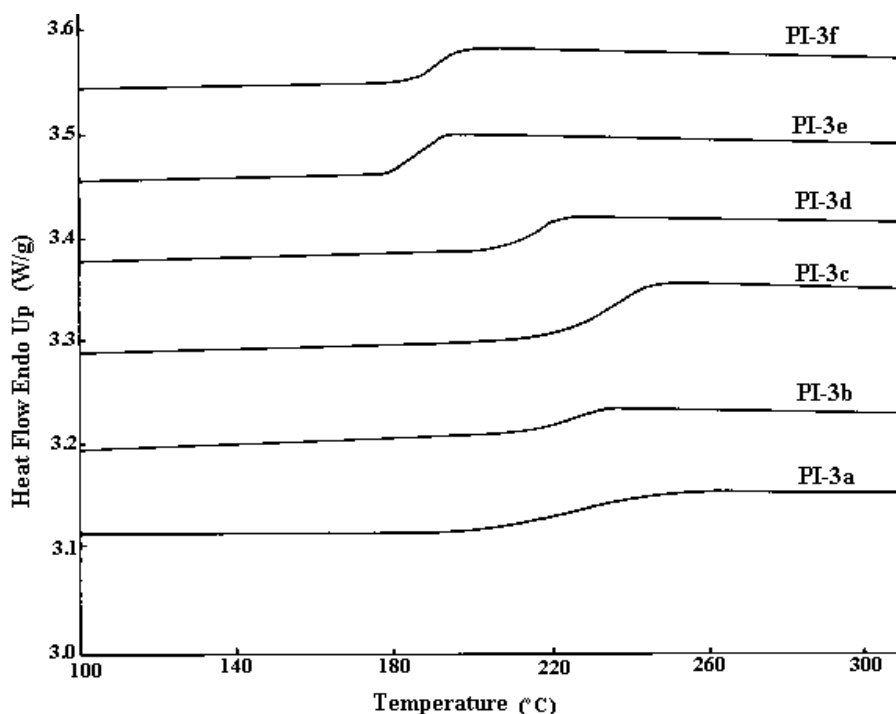
Figure 4(a).23. DSC thermograms of polyimides from PPPB with different dianhydrides

4(a).3.2.4 Optical Transparency of homopolyimides

Strong absorption of wholly aromatic polyimides in the ultraviolet to visible range, sometimes become a serious obstacle in practical uses. For example the visible absorption of polyimide films is unfavorable in some applications such as flexible solar radiation protectors, alignment layers in liquid crystal display devices, optical wave guides for communication inter connectors and optical half-wave plates for planar light wave circuits. However, most of the conventional polyimides show considerable coloration due to charge-transfer complexing between alternating electron-donor (diamine) and electron acceptor (dianhydride) moieties.[21] St. Clair et al.[22] investigated the structure-coloration relationship in a number of polyimides and have shown that the modifications that can result in a lowering of charge-transfer complexing generally lead to polyimides with a low color intensity. The fluorine containing monomers have gained particular importance in the synthesis of optically transparent polyimides since the polyimides synthesized from them are highly soluble, colorless and thermally stable.[23] Some alicyclic monomers have also been investigated for the synthesis of optically transparent polyimides.[24] But the polyimides synthesized from them face the

problem of low thermal stability. An alternative effective approach for lowering the color of polyimides has been to use diamines and dianhydrides having pendant alkyl groups that not only eliminate electronic interactions, but also tend to break up extended conjugation along the main chain.[25] In the present study the optical transparencies of the polyimide films having thickness of 50 μm were determined by transmission UV-visible spectroscopy.

Figure 4(a).24 shows the UV-visible spectra of the homopolyimides from PPDBN (PI-1d-f), PPDBT (PI-2d-f) and PPPB (PI-3d-f) with dianhydrides ODPA, 6-FDA and SiDA. The wavelengths of onset of transmission and cut-off are given in Table 4(a).12. It is considered that the shorter the wavelengths of onset and cut off transmission, the higher will be the transparency of film. In the case of all polyimides the transmission of light started below 400 nm and were found to be optically transparent. Among the three series the maximum transparency was shown by PI-2e (6-FDA-PPDBT) with an onset off transmission at 338 nm and the least by PI-2d (ODPA-PPDBT). In the case of diamines based on PPDBN and PPDBT those with dianhydride 6-FDA showed the maximum transparency and in the case of polyimides based on PPPB, the one with SiDA (PI-3f) showed the maximum transparency. The polyimides PI-1e, PI-2e having highest transparencies transmitted nearly 75 % of light. The polyimide PI-2d (ODPA-PPDBT) with least transparency transmitted only 13 % of light. All these polyimides have onset and cut off transmittance wavelength between 338–364 and 406–456 nm respectively which were better than the commercially available polyimide Kapton with onset and cut-off wavelengths at 414 and 550 nm respectively.

Table 4(a).12. Optical transparencies of homopolyimides

Polymer Code	Dianhydride	Diamine	Onset (nm)	Cut-off (nm)
PI-1d	ODPA	PPDBN	354	424
PI-1e	6-FDA	PPDBN	340	456
PI-1f	SiDA	PPDBN	350	442
PI-2d	ODPA	PPDBT	364	406
PI-2e	6-FDA	PPDBT	338	418
PI-2f	SiDA	PPDBT	342	412
PI-3d	ODPA	PPPB	358	422
PI-3e	6-FDA	PPPB	362	456
PI-3f	SiDA	PPPB	350	424
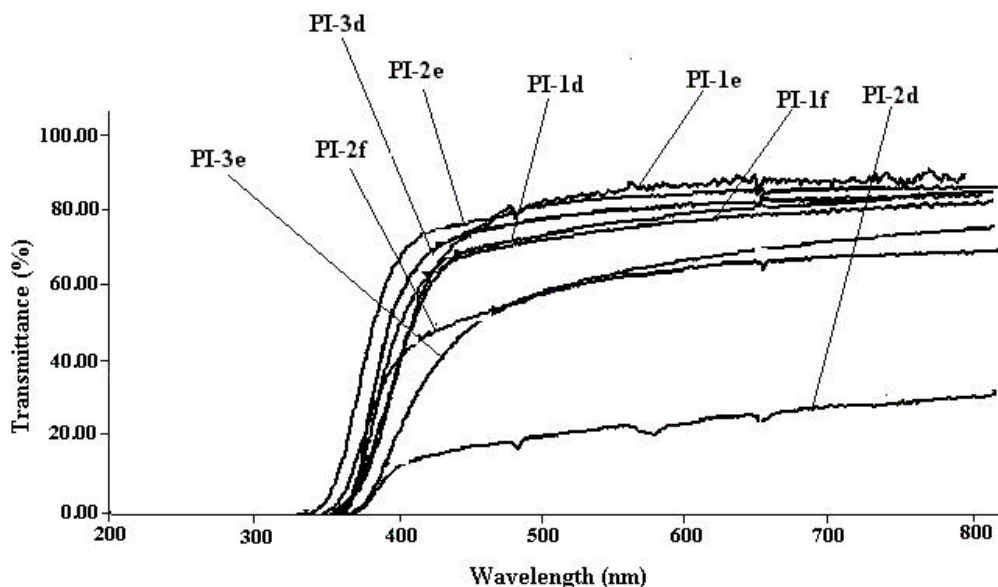
Figure 4(a).24. UV-visible spectra of homopolyimides based on diamines PPDBN, PPDBT and PPPB with dianhydrides ODPA, 6-FDA and SiDA

4(a).3.3 Synthesis and structural characterization of copolyimides

One of the approaches used in the modification of polyimides inorder to achieve a combination of desired properties such as solubility, thermal stability and mechanical properties, is to merge the properties of different polyimides into one system. Such modification in properties can be achieved through copolymerization or blending. Copolymerization is particularly attractive since tailoring the properties of the resulting polymer is possible even on molecular levels. Random copolyimides are synthesized by the reaction of a single dianhydride with two or more diamines or by the reaction of a single diamine with two or more dianhydrides.[26] Copolymerization is the most general and powerful tool used for systematically modifying the properties of commercial polymers.[27] Polyimides of the diamine oxydianiline (ODA) are commercially important because of their excellent thermal and mechanical properties. But these polymers have the problem of insolubility and it was expected that copolymerization with another diamine will improve their solubility. A systematic study is required to study the effect of incorporation of another diamine on the final properties of these polyimides. Therefore to investigate the effect of pendant pentadecylphenoxy group on the properties like thermal stability, solubility, gas permeability, dielectric constant etc. of some ODA containing polymers, several copolyimides were

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synthesized from 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) and ODA with dianhydrides like 6-FDA, ODPA and SiDA as shown in Scheme 4(a).4. These copolyimides contain ODA and PPDBN in three different ratios, 95:5, 80:20 and 50:50.

Though pendant pentadecylphenoxy group in diamine enhances the solubility of polyimides, some homopolyimides particularly those based on rigid dianhydrides such as PMDA, BTDA and BPDA with PPDBN showed low solubility. Incorporation of silicon is known to enhance the solubility of polyimides. Therefore to study the effect of incorporation of silicon on the solubility and other properties of PPDBN containing polymers several silicon containing copolyimides of PPDBN with SIDA and other dianhydrides were also synthesized. These copolyimides were synthesized as shown in Schemes 4(a).5 by a high temperature solution polymerization method.

All copolyimides having varying amine composition (CPI-1a-c, CPI-2a-c and CPI-3a-c) were obtained in good yields and also most of them had high viscosities (Table 4(a).4.). All copolyimides except CPI-3c had viscosities above 0.72 dL/g. The copolyimides synthesized from a mixture of dianhydrides were also obtained in good yields and had viscosities in the range 0.44 – 0.69 dL/g (Table 4(a).5). Homopolyimides from ODA (PI-4a-c), although reported in literature, were synthesized for comparative study under identical conditions (Table 4(a).4).

The polyimides thus obtained were characterized by FT-IR and ^{1}H NMR spectroscopy. FT-IR spectra of all copolyimides based on diamine PPDBN with varying diamine ratio and a mixture of dianhydrides showed absorption bands at 1708, 1776 cm^{-1} (imide I), 1358 cm^{-1} (imide II), 1105 cm^{-1} (imide III) and 728 cm^{-1} which are characteristic of imide structure. The band at 1235 cm^{-1} was due to ether group of diamine. Polyimides containing SiDA showed a band at 837 cm^{-1} due to Si-CH$_3$ vibrations. Another band of Si-CH$_3$ overlapped with the –C-O-C- stretching vibrations at 1235 cm^{-1}. A representative FT-IR spectrum of polyimide CPI-3c is shown in Figure 4(a).25.

The ^{1}H NMR spectrum of all the copolyimides showed signals corresponding to pentadecyl group in the region 0.8-2.6 δ ppm. In the case of copolyimides with varying diamine composition, the aromatic protons of diamines showed signals in the region 6.6-7.6 δ ppm and the aromatic protons of dianhydrides SiDA (CPI-3a-c) and 6-FDA (CPI-2a-c)

showed signals in the region 7.8-8.2 δ ppm. In the case of copolyimides from ODPA (CPI-1a-c) four protons ortho to carbonyl group showed signals in this region and the signal corresponding to other two protons overlapped with diamine protons in the region 7.5-7.7 δ ppm. In the case of copolyimides with a mixture of dianhdrides the signals corresponding to aromatic protons of diamine were in the region 6.8-7.5 δ ppm and the signals corresponding to dianhydride protons were in the region 7.8-8.2 δ ppm, except in the case of ODPA containing polyimide (CPI-4d) where the two protons ortho to the ether group showed signals in the region 7.5-7.7 δ ppm and the four protons ortho to carbonyl group of dianhydride showed signals in the region 7.8-8.2 δ ppm. In the case of copolyimides from SiDA the silyl – CH$_3$ protons showed a singlet in the region 0.6-0.8 δ ppm. A representative ^{1}H NMR spectra of polyimides containing varying diamine composition with SiDA (CPI-3a-c) are shown in Figures 4(a).26-28 and that based on diamine PPDBN with a mixture of dianhydrides like ODPA and SiDA (CPI-4d) is shown in Figure 4(a).29.

The composition of monomers in copolyimides were calculated from the ^{1}H NMR spectrum in the case of SiDA containing polyimides, CPI-3a-c and CPI-4a-e, by comparing the ratio of the end –CH$_3$ of pentadecyl group (at 0.85 δ ppm) to that of silyl –CH$_3$ (0.75 δ ppm) protons and were found to be in good agreement with the feed ratios. In the case of copolyimides where the silyl -CH$_3$ and pentadecyl -CH$_3$ group merged together, the integration corresponding to silyl -CH$_3$ was estimated from the aromatic protons of SiDA which showed two separate peaks in the region 7.8-8.2 δ ppm. It was not possible to calculate the percentage incorporation of ODA from the aromatic protons since there was an overlapping of peaks in this region and therefore only the percentage incorporation of PPDBN was calculated. All spectra showed the expected integration and multiplicities. From the proton NMR spectra of copolyimides CPI-3a, CPI-3b, CPI-3c and CPI-4d it was found that the percentage incorporation of PPDBN was 5.5%, 20.48%, 41.66% and 50% respectively. In the case of copolyimides CPI-1a-c and CPI-2a-c from dianhydrides ODPA and 6-FDA, the copolyimides composition could not be determined because of the overlapping of aromatic protons and also due to the lack of a reference peak in the aliphatic region that can be compared with the pentadecyl group.
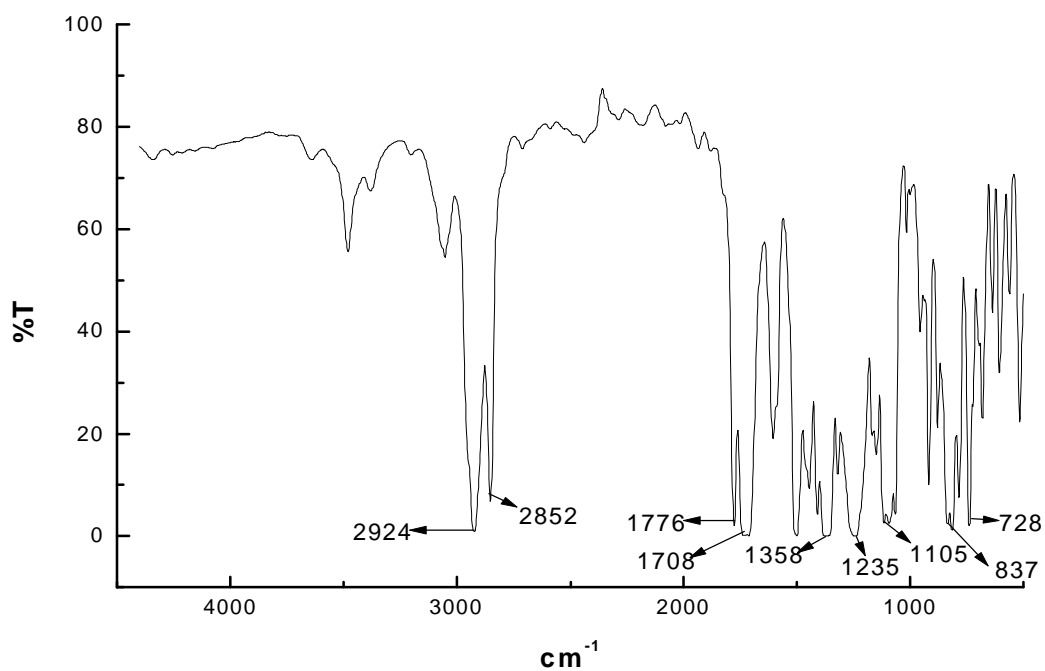
Figure 4(a).25. FTIR spectrum of polymer CPI-3c (Film)
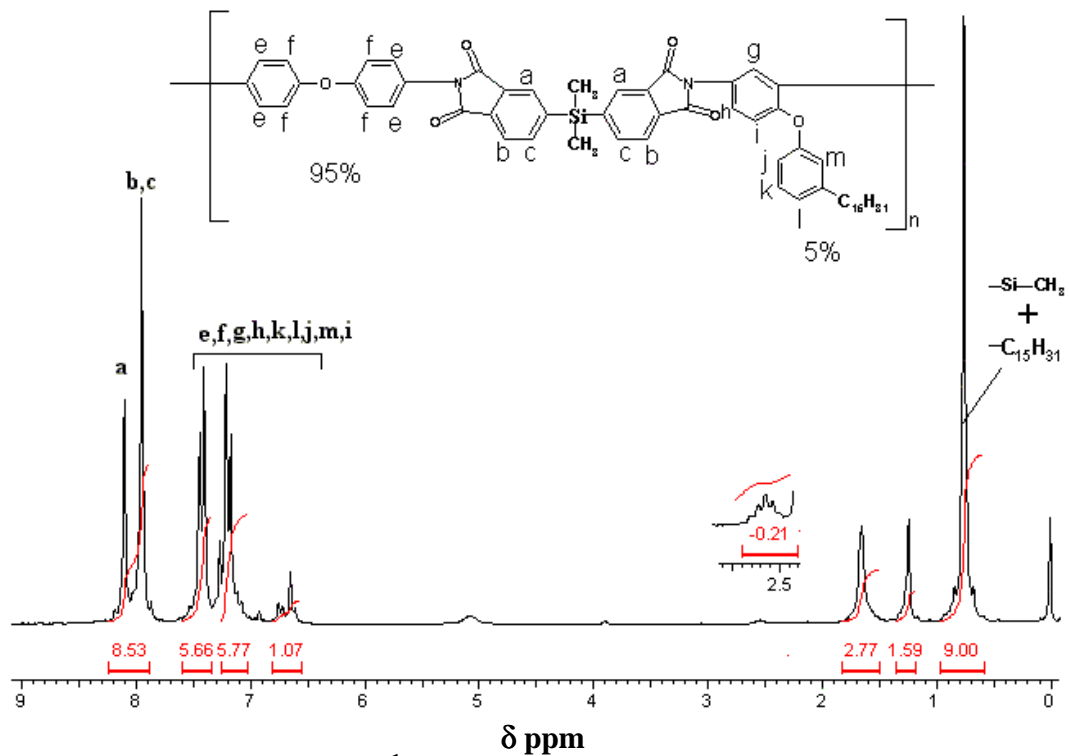
Figure 4(a). 26. ¹H NMR spectrum of CPI-3a in CDCl₃

Figure 4(a). 27. ¹H NMR spectrum of CPI-3b in CDCl₃
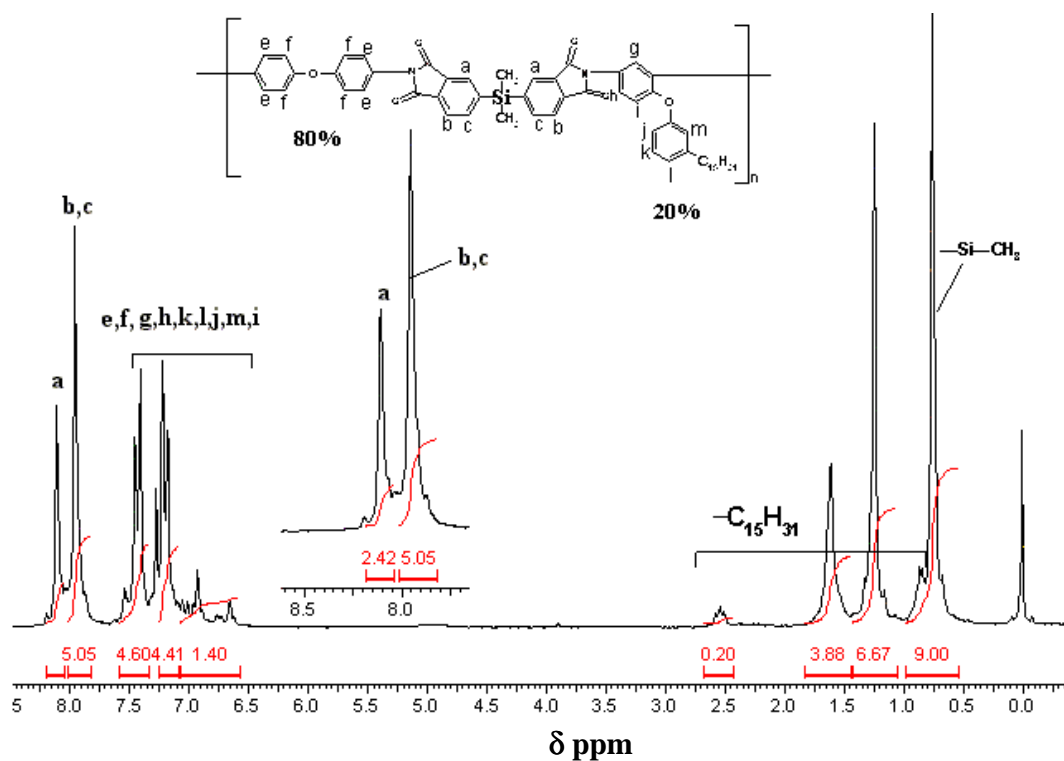
Figure 4(a). 27. ^{1}H NMR spectrum of CPI-3b in CDCl$_3$
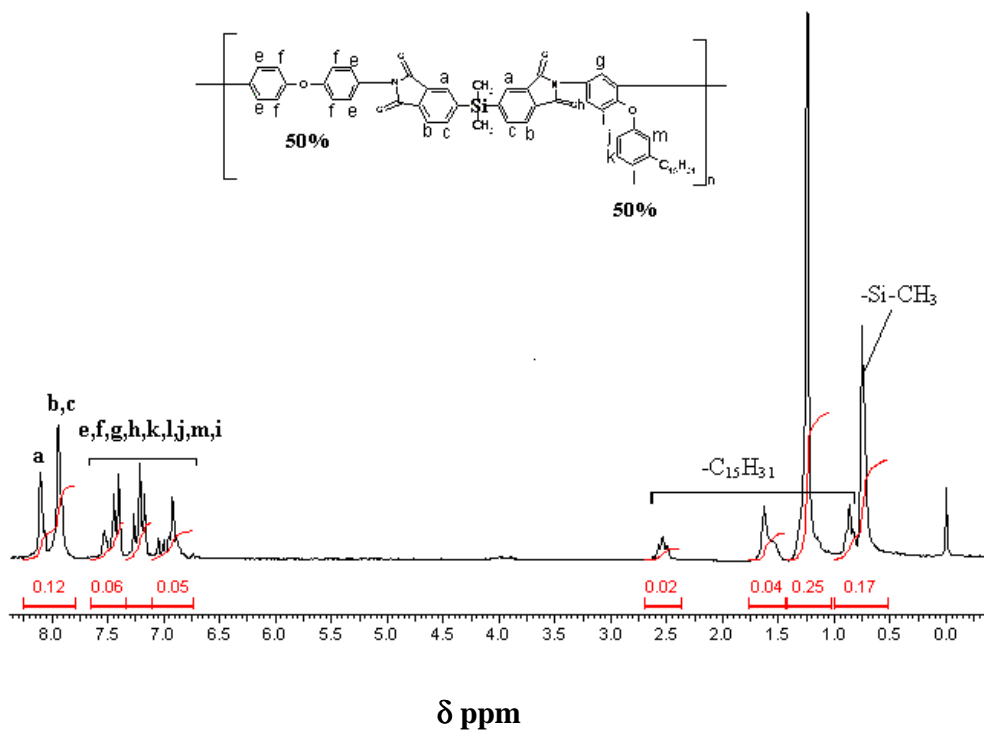
Figure 4(a). 28. ^{1}H NMR spectrum of CPI-3c in CDCl$_3$
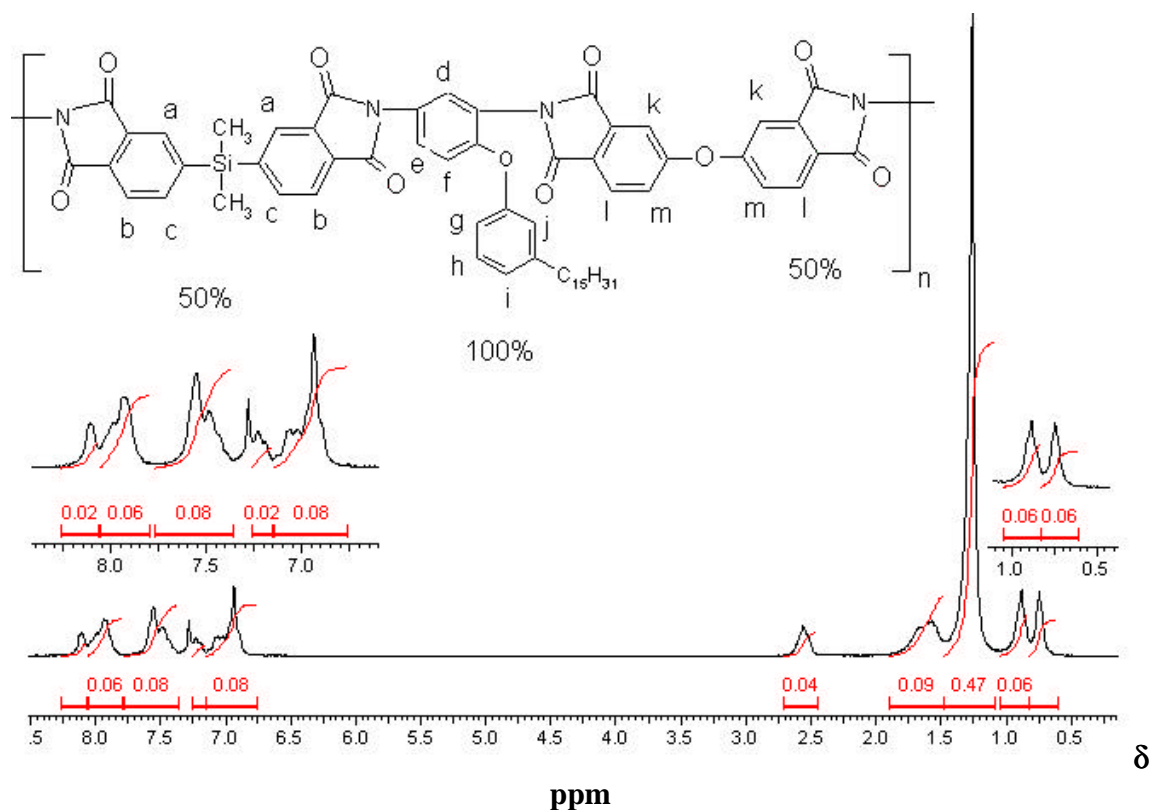
Figure 4(a). 29. ^{1}H NMR spectrum of CPI-4d in CDCl$_3$

4(a).3.4 Properties of copolyimides

The properties of copolyimides were evaluated by solubility measurements, X-ray diffraction, differential scanning calorimetry (DSC) thermogravimetric analysis (TGA) and UV-visible spectroscopy

4(a).3.4.1 Crystallinity of copolyimides

The degree of crystallinity in a polymer is related to its structure and it influences its solubility, mechanical and thermal properties. Polymers derived from symmetrical monomers are generally more crystalline than those from unsymmetrical ones. Highly crystalline polymers generally have low solubility, which limits their application areas and hence polyimides derived from symmetrical monomers have low solubility. Copolymerization is one of the methods used to improve the solubility of these polyimides. Copolymerization with less symmetrical monomers helps in the reduction of inter and intra chain packing without affecting the other properties significantly.

In the present study an attempt was made to reduce the packing density and improve the solubility of polyimides derived from a symmetrical diamine ODA by copolymerizing with a less symmetrical diamine PPDBN. The crystallinity of these copolyimides was evaluated by wide angle X-ray diffraction measurements of film samples. All copolyimides from dianhydride ODPA containing different ratios of diamines ODA and PPDBN (CPI-1a-c) showed amorphous patterns (Figure 4(a).30). The copolyimides from dianhydride 6-FDA with varying composition of diamines ODA and PPDBN (CPI-2a-c) (Figures 4(a).31) and also from dianhydride SiDA were amorphous in nature (Figures 4(a).32). The copolyimides containing a mixture of SiDA and other dianhydrides like PMDA, BPDA, BTDA, ODPA, 6-FDA with diamine PPDBN also showed amorphous nature (Figures 4(a).33).
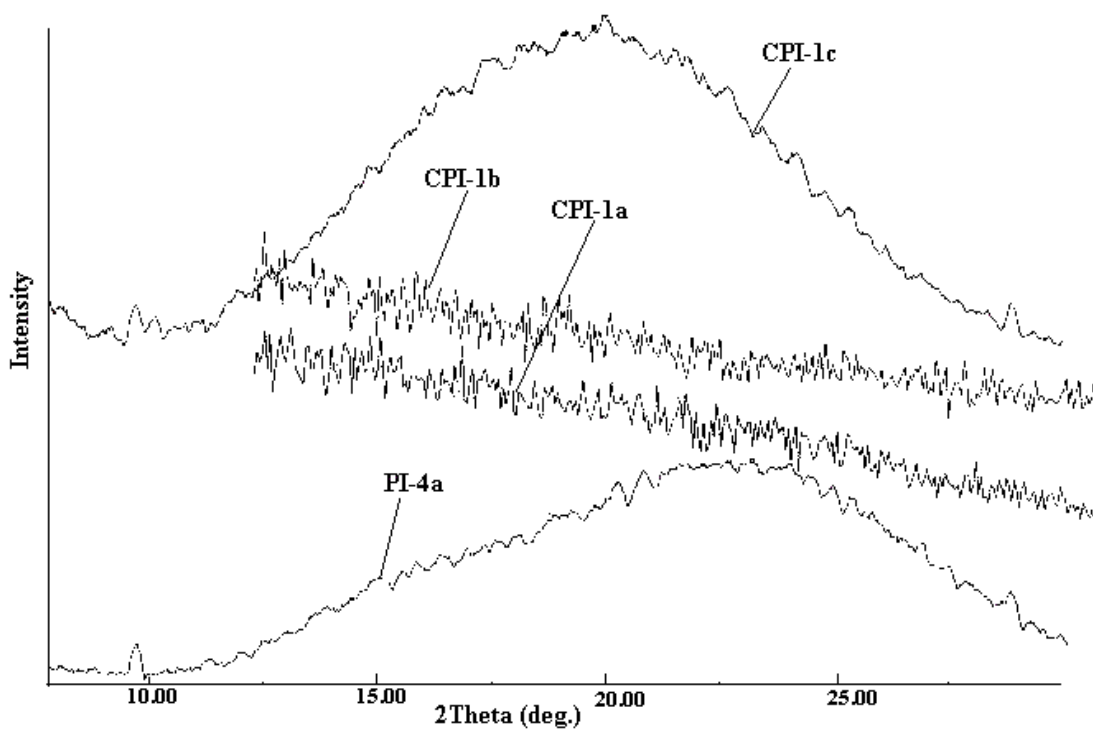
Figure 4(a).30. X-ray diffractograms of homopolyimide from ODA and copolyimides ODA and PPDBN with dianhydride ODPA.
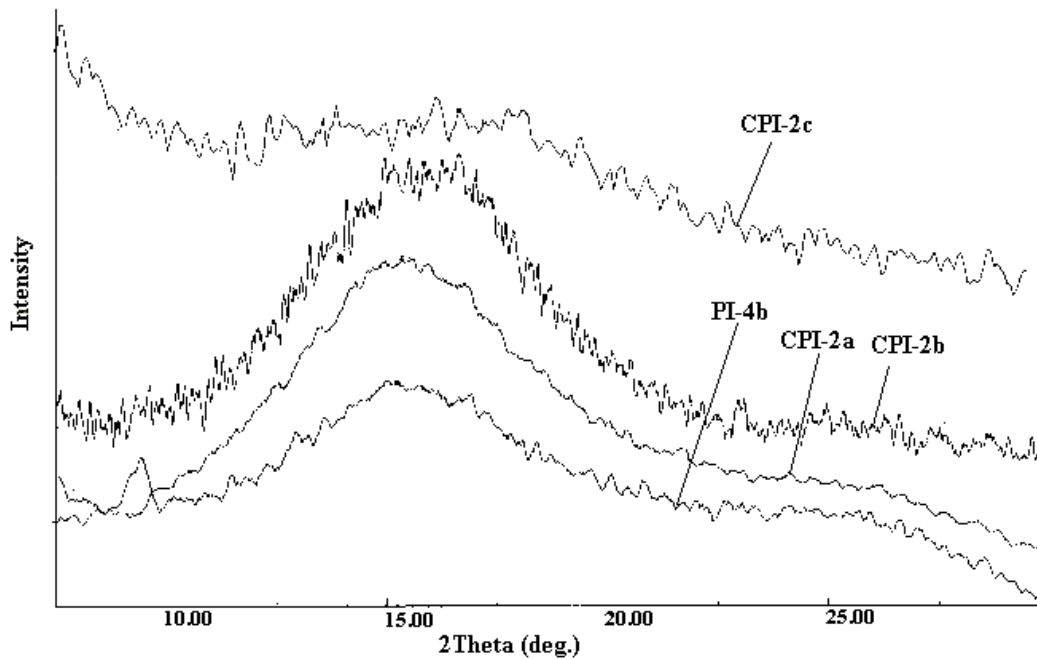
Figure 4(a).31. X-ray diffractograms of homopolyimide from ODA and copolyimides from ODA and PPDBN with dianhydride 6-FDA
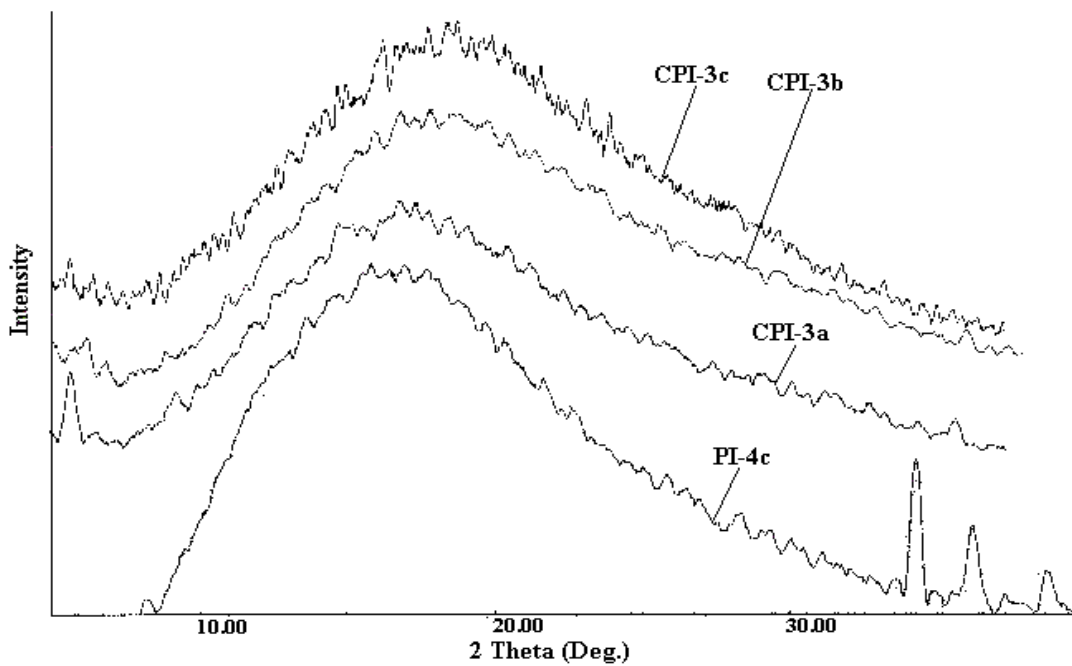
Figure 4(a).32. X-ray diffractograms of homopolyimide from ODA and copolyimides from ODA and PPDBN with dianhydride SiDA
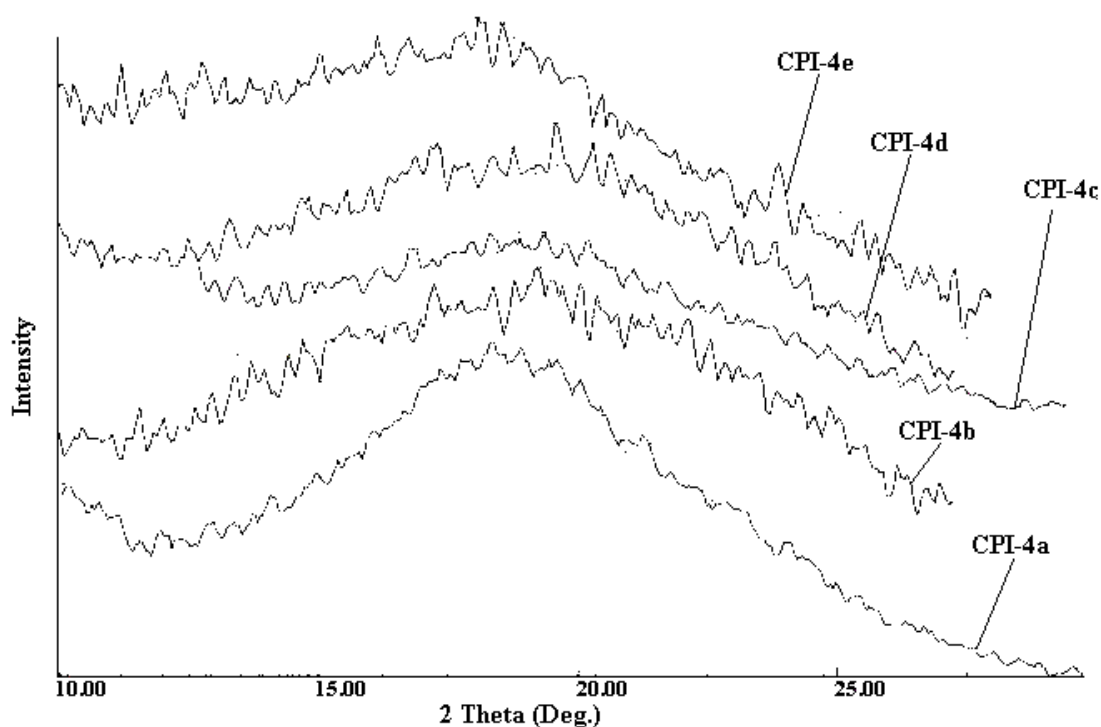
Figure 4(a).33. X-ray diffractograms of copolyimides from PPDBN with a mixture of dianhydrides

4(a).3.4.2 Solubility measurements

The qualitative solubility measurements of the copolyimides are shown in Tables 4(a).13, 14. Incorporation of 5% of pentadecyl group containing diamine did not improve the solubility of the ODPA-ODA homopolyimide (PI-4a) much, but its solubility in NMP, DMAc and pyridine increased (Table 4(a).13). Incorporation of 20% of diamine PPDBN in ODPA-ODA homopolyimide improved its solubility in NMP, DMAc, pyridine and chloroform. The copolyimides CPI-1c from ODPA and 50% of ODA and 50% PPDBN were soluble in a wide range of solvents like NMP, DMAc, DMF, DMSO, pyridine, m-cresol, o-chlorophenol and nitrobenzene and even in low boiling solvents like THF and chloroform where as the homopolyimide of ODPA and ODA were soluble only in m-cresol, o-chlorophenol and nitrobenzene. All the copolyimides from dianhydrides 6-FDA (CPI-2a-c) were soluble in a wide range of polar solvents like NMP, DMAc, DMF, DMSO, pyridine, m-cresol, o-chlorophenol and nitrobenzene and even in low boiling solvents like THF, chloroform where

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as 6-FDA-ODA homopolyimide (PI-4b) was not soluble in most of the above solvents. The copolyimides containing SiDA (CPI-3a-c) and also SiDA-ODA homopolyimide (PI-4c) were soluble in all the above solvents. In general this study shows that incorporation of a small amount of pendant pentadecyl group containing diamine PPDBN in ODA containing homopolyimides helps in the enhancement of their solubility. Also it shows the role of SiDA in enhancing the solubility of both homopolyimides and copolyimides from ODA.

The solubility behavior of copolyimides from diamine PPDBN containing 50% SiDA and 50% other dianhydrides like PMDA, BPDA, BTDA, ODPA and 6-FDA is shown in Table 4(a).14. The data shows that SiDA helped in the enhancement of solubility of homopolyimides of PPDBN from rigid dianhydrides like PMDA (PI-1a), BPDA (PI-1b) and BTDA (PI-1c) which were not soluble in any solvents tested. The copolyimides were soluble in solvents like NMP, pyridine, THF, chloroform, m-cresol, o-chlorophenol and nitrobenzene. The copolyimides containing 50% SiDA and 50% ODPA (CPI-4d) or 50 % 6-FDA (CPI-4e) were soluble in almost all the solvents tested. Thus this study further shows the role of SiDA in enhancing the solubility of homopolyimides from PPDBN and rigid dianhydrides like PMDA, BPDA and BTDA.

Table 4(a).13. Effect of pendant pentadecyl group on the solubility of polyimides based on ODA

Polymer Code	Diamine (mole %)		Dianhydride	Solvents									
	ODA	PPDBN		NMP	DMAc	DMF	DMSO	Pyrdine	THF	CHCl$_3$	m-cresol	o-Cl-phenol	Nitro benzene
PI-4a	100	-	ODPA	+-	+-	- -	- -	+-	- -	+-	++	++	++
CPI-1a	95	5	ODPA	++	++	- -	- -	+	- -	+ -	++	++	++
CPI-1b	80	20	ODPA	++	++	S	- -	++	S	++	++	++	++
CPI-1c	50	50	ODPA	++	++	++	- -	++	++	++	++	++	++
PI-4b	100	-	6-FDA	+-	+-	+-	- -	+-	+-	+-	++	++	++
CPI-2a	95	5	6-FDA	++	++	++	- -	++	++	++	++	++	++
CPI-2b	80	20	6-FDA	++	++	++	- -	++	++	++	++	++	++
CPI-2c	50	50	6-FDA	++	++	++	- -	++	++	++	++	++	++
PI-4c	100	-	SiDA	++	++	++	- -	++	++	++	++	++	++
CPI-3a	95	5	SiDA	++	++	++	- -	++	++	++	++	++	++
CPI-3b	80	20	SiDA	++	++	++	- -	++	++	++	++	++	++
CPI-3c	50	50	SiDA	++	++	++	- -	++	++	++	++	++	++

++ Soluble at room temperature, + soluble on heating, +- partly soluble even on heating, -- insoluble even on heating, S: swells
NMP: N-methylpyrrolidone, DMAc: N-N'-dimethyl acetamide, DMF: N-N'-dimethyl formamide, DMSO: dimethyl suphoxide,
THF: tetrahydrofuran, CHCl$_3$: chloroform

Table 4(a).14. Solubility properties of copolyimides based on PPDBN with a mixture of dianhydrides

Polymer Code	Diamine	Dianhydride		Solvents									
		50%	50%	NMP	DMAc	DMF	DMSO	Pyridine	THF	CHCl$_3$	m-Cresol	o-Cl-phenol	Nitro benzene
CPI-4a	PPDBN	SiDA	PMDA	++	+	+	- -	++	++	++	++	++	++
CPI-4b	PPDBN	SiDA	BPDA	++	+	+	- -	++	++	++	++	++	++
CPI-4c	PPDBN	SiDA	BTDA	++	+	+	- -	++	++	++	++	++	++
CPI-4d	PPDBN	SiDA	ODPA	++	++	++	- -	++	++	++	++	++	++
CPI-4e	PPDBN	SiDA	6-FDA	++	++	++	- -	++	++	++	++	++	++

++ Soluble at room temperature, + soluble on heating, +- partly soluble even on heating, -- insoluble even on heating

NMP: N-methylpyrrolidone, DMAc: N-N'-dimethyl acetamide, DMF: N-N'-dimethyl formamide, DMSO: dimethyl suphoxide, THF: tetrahydrofuran, CHCl$_3$: chloroform

4(a).3.4.3 Thermal Properties of copolyimides

The thermal stability and glass transition temperatures (T_g) of copolyimides were determined by thermogravimetric analysis and differential scanning calorimetry (DSC) respectively. Both these measurements were carried out in nitrogen at a heating rate of 10^0C per minute. The thermogravimetric curves of these copolyimides containing varying diamine composition and dianhydride composition are shown in Figures 4(a).34–37. The initial decomposition temperature (IDT), the decomposition temperature at 10% weight loss (T_{10}) and the maximum decomposition temperature (T_{max}) in nitrogen for all the polyimides are listed in Tables 4(a).15–18.

In the case of copolyimides containing varying ratios of diamine containing pentadecylphenoxy group and ODA the incorporation of alkyl groups decreased IDT, T_{10} and T_{max} values. In the case of copolyimides from ODPA, ODA and PPDBN the IDT, T_{10} and T_{max} values were lower than that of ODPA-ODA homopolyimide and were in the order CPI-1a > 1b > 1c (Table 4(a).15). Copolyimides from SiDA, ODA and PPDBN (CPI-3a-c) also showed a similar pattern (Table 4(a).17). In the case of copolyimides from 6-FDA, ODA and PPDBN, the IDT and T_{max} of copolyimides incorporating 50% of PPBDN was slightly higher as compared to the copolyimides incorporating 20% PPDBN and could not be explained (Table 4(a).16).

In the case of copolyimides from PPDBN with 50% SiDA and 50% other dianhydrides (CPI-4a-e), the maximum thermal stability was shown by ODPA containing copolyimide (CPI-4d) followed by BPDA, BTDA, 6-FDA and PMDA (Table 4(a).18).

The DSC thermograms of the copolyimides which were recorded at the second heating of polymers at a heating rate of 10^0C per minute are given in Figures 4(a).38-40. It was observed that in the case of copolyimides containing varying diamine composition, the T_g decreased as the amount of alkyl group containing diamine increased (Figure 4(a).38). In the case of copolyimides with a mixture of dianhydrides, the T_g values were in the order BTDA > PMDA > BPDA > ODPA = 6-FDA. Polyimides based on rigid dianhydrides showed higher T_g than those based on flexible dianhydrides (Figure 4(a).40). The DSC thermograms of homopolyimides of ODA synthesized for comparative purpose is given in Figure 4(a).39.
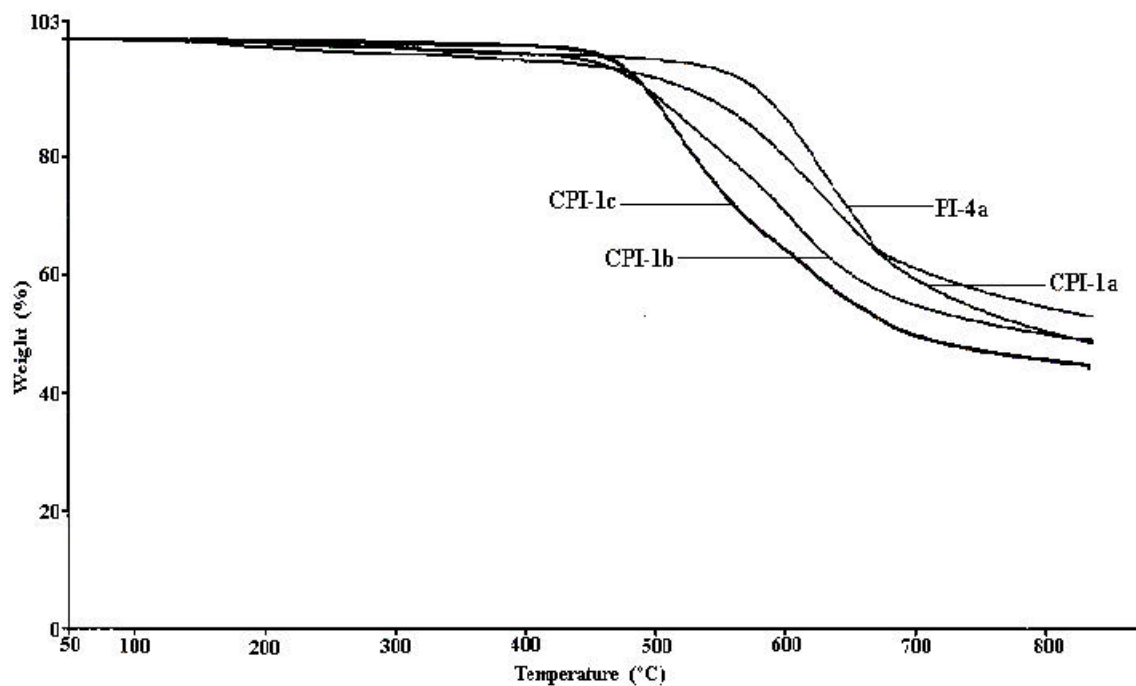
Figure 4(a).34. TG curves of homopolyimide from ODA and copolyimides from ODA and PPDBN with dianhydride ODPA
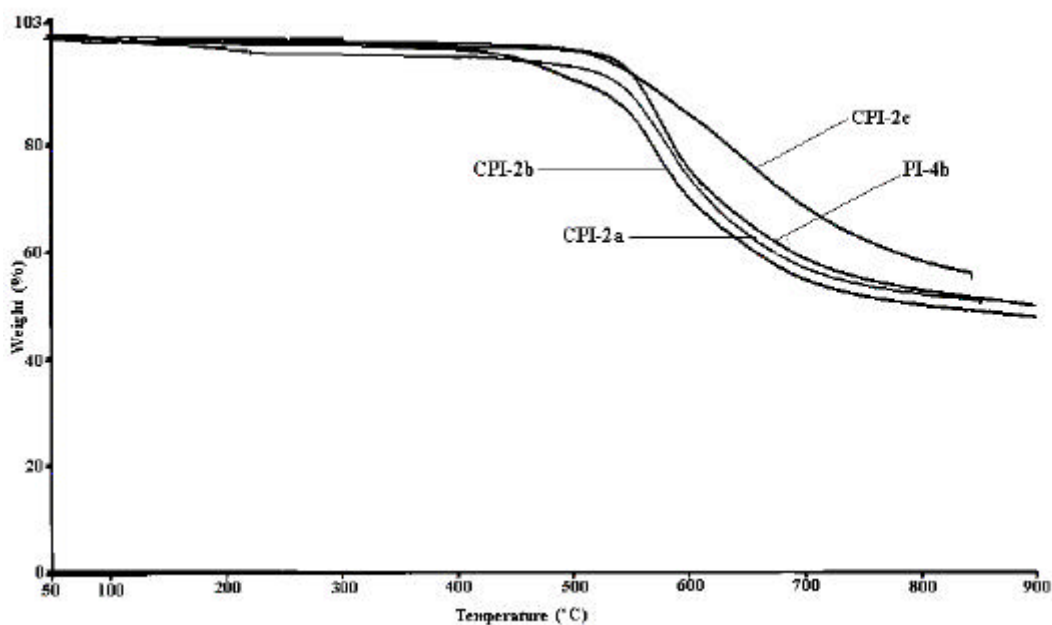
Figure 4(a).35. TG curves of homopolyimide from ODA and copolyimides from ODA and PPDBN with dianhydride 6-FDA

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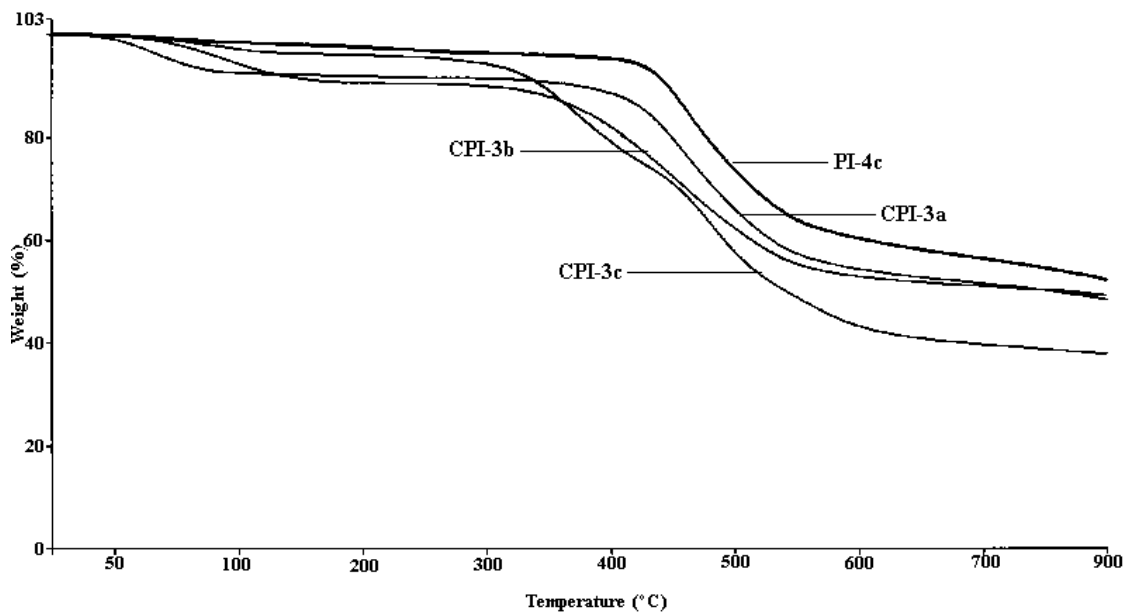
Figure 4(a).36. TG curves of homopolyimide from ODA and copolyimides from ODA and PPDBN with dianhydride SiDA.
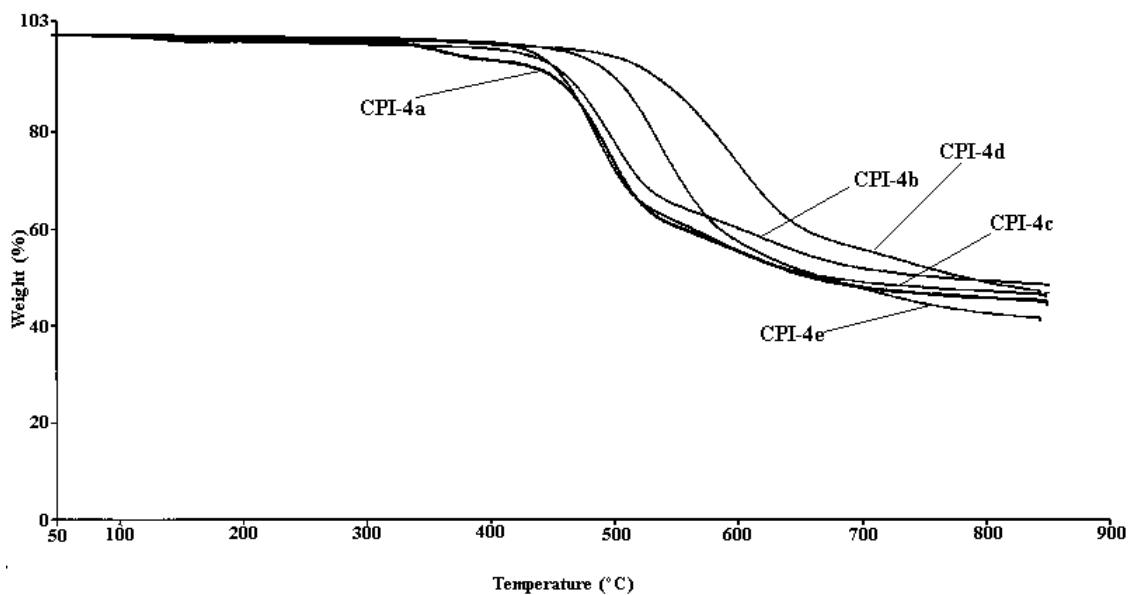
Figure 4(a).37. TG curves of copolyimides from PPDBN with a mixture of dianhydrides

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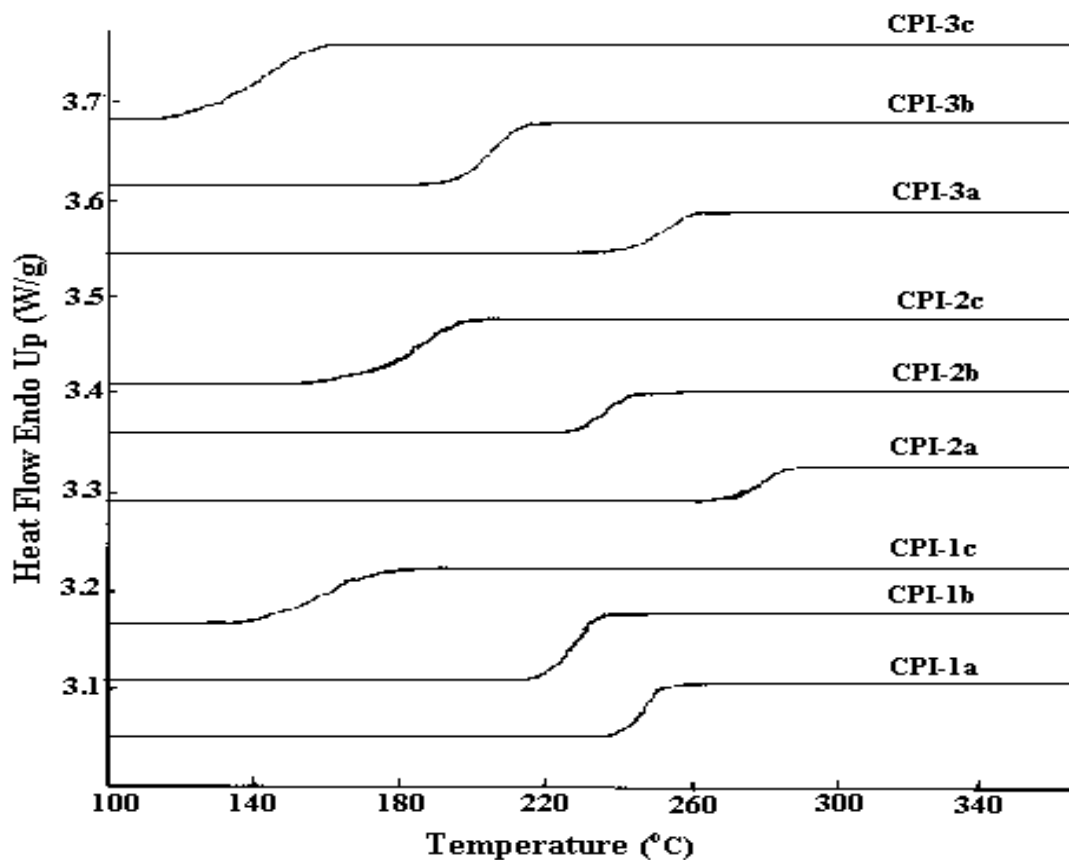
Figure 4(a).38. DSC thermograms of copolyimides from ODA and PPDBN with dianhydrides ODPA, 6-FDA and SiDA
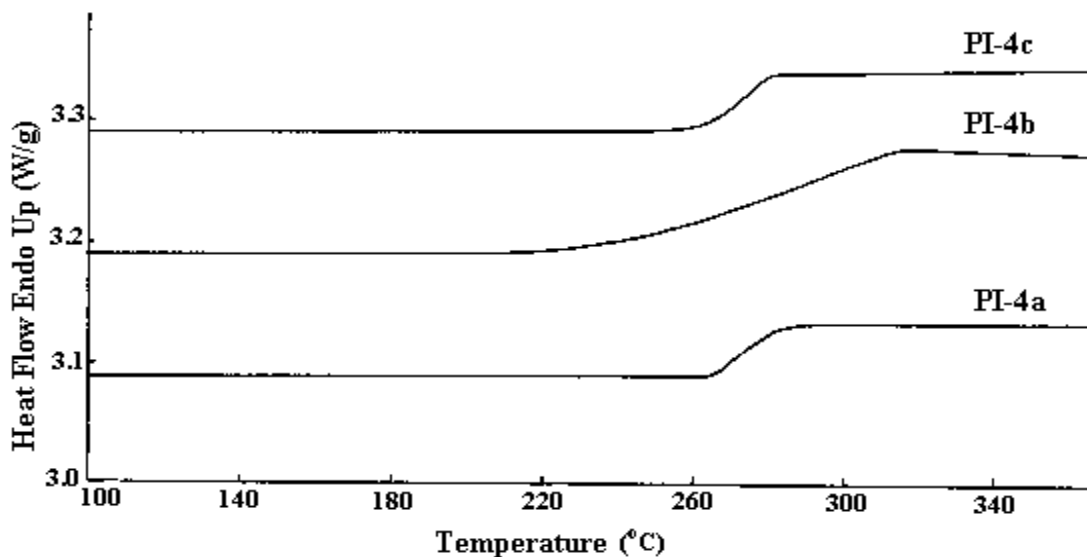
Figure 4(a).39. DSC thermograms of homopolyimides from ODA with dianhydrides ODPA, 6-FDA and SiDA
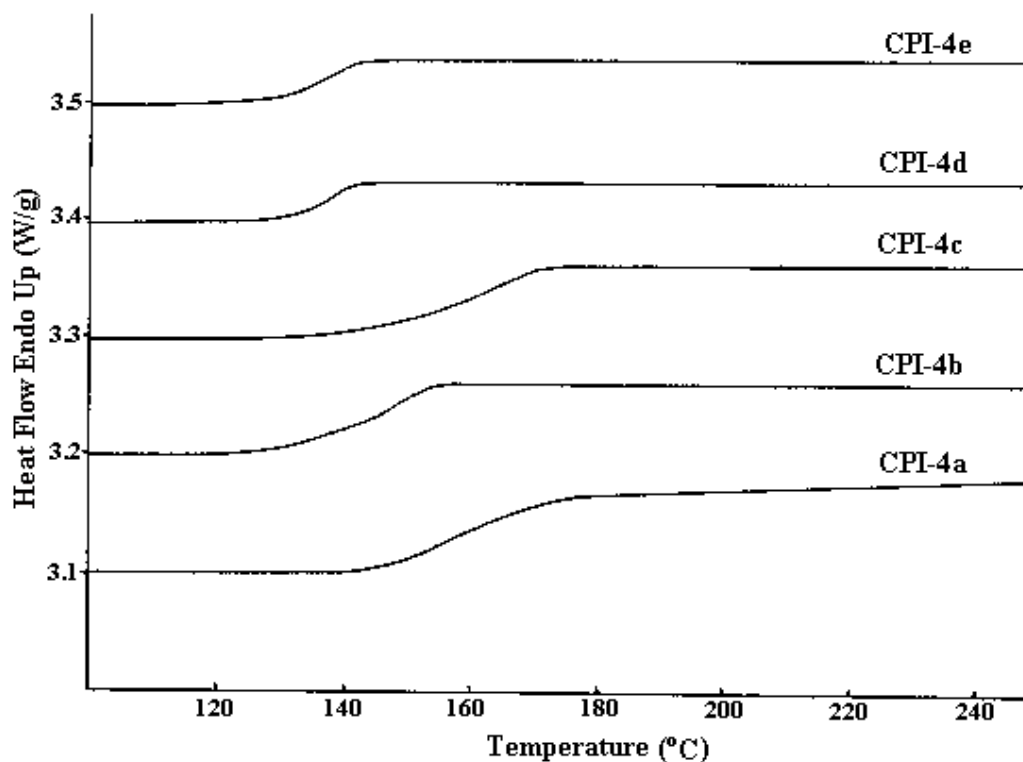
Figure 4(a).40. DSC thermograms of copolyimides from PPDBN with mixture of dianhydrides

Table 4(a).15. Thermal properties of homopolyimides from ODA and copolyimides from PPDBN and ODA with dianhydride ODPA

Polymer code	Dianhydride	Diamine (mole %)		IDT, ^oC	T_{10}, ^oC	T_{max}, ^oC	T_g, ^oC
		ODA	PPDBN				
PI-4a	ODPA	100	–	576	578	623	275
CPI-1a	ODPA	95	5	530	567	638	247
CPI-1b	ODPA	80	20	471	514	601	229
CPI-1c	ODPA	50	50	472	481	513	160

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Table 4(a).16. Thermal properties of homopolyimides from ODA and copolyimides from PPDBN and ODA with dianhydride 6-FDA

Polymer code	Dianhydride	Diamine (mole %)		IDT, ^{o}C	T_{10}, ^{o}C	T_{max}, ^{o}C	T_{g}, ^{o}C
		ODA	PPDBN				
PI-4b	6-FDA	100	–	542	551	575	303
CPI-2a	6-FDA	95	5	536	553	582	284
CPI-2b	6-FDA	80	20	515	550	571	238
CPI-2c	6-FDA	50	50	528	546	654	185

Table 4(a).17. Thermal properties of homopolyimide from ODA and copolyimides from PPDBN and ODA with dianhydride SiDA

Polymer code	Dianhydride	Diamine (mole %)		IDT, ^{o}C	T_{10}, ^{o}C	T_{max}, ^{o}C	T_{g}, ^{o}C
		ODA	PPDBN				
PI-4c	SiDA	100	–	531	538	561	272
CPI-3a	SiDA	95	5	513	520	553	252
CPI-3b	SiDA	80	20	467	475	541	208
CPI-3c	SiDA	50	50	422	432	463	142

Table 4(a).18. Thermal properties of copolyimides based on PPDBN with a mixture of dianhydrides

Polymer code	Diamine	Dianhydride		IDT, ^{o}C	T_{10}, ^{o}C	T_{max}, ^{o}C	T_{g}, ^{o}C
		50%	50%				
CPI-4a	PPDBN	SiDA	PMDA	486	496	539	156
CPI-4b	PPDBN	SiDA	BPDA	510	517	565	144
CPI-4c	PPDBN	SiDA	BTDA	502	507	554	159
CPI-4d	PPDBN	SiDA	ODPA	525	529	597	136
CPI-4e	PPDBN	SiDA	6-FDA	492	496	535	136

4(a).3.4.4 Optical transparencies of copolyimides

The high color associated with polyimides often create problems in their application areas as discussed in Section 4(a).3.2.4. Many structural modifications aimed at improving the solubility of polyimides can in turn modify their transparency. Copolymerization is one of the important modification methods used to improve solubility of polyimides and was therefore expected to improve the optical transparency of polyimides.

In the present study the effect of incorporation of diamine PPDBN in different mole ratios on the optical transparency of several polyimides based on a commercially important diamine ODA with dianhydrides like ODPA, 6-FDA and SiDA was studied using UV-visible spectroscopy of film samples with a thickness of 50 μm. The optical transparency of copolyimides based on PPDBN where 50% of dianhydrides like PMDA, BPDA, BTDA, ODPA and 6-FDA was replaced with SiDA was also determined. The UV-visible spectra of the polyimides are given in Figures 4(a).41-43 and the wavelengths of onset of transmission and cut-off are given in Table 4(a).19.

The UV-visible spectra of copolyimides and homopolyimides (Figure 4(a).41) based on dianhydride ODPA with different ratios of diamines ODA and PPDBN showed that the optical transparency of ODPA-ODA polyimide (PI-4a) increased gradually as the amount of PPDBN diamine increased. All copolyimides based on 6-FDA and PPDBN (Figure 4(a).42) showed higher optical transparency than the homopolyimide PI-4b (6-FDA-ODA). The copolyimides with 5% PPDBN showed the highest transparency in this series and that with 20% PPDBN showed the lowest transparency. Incorporation of PPDBN in SiDA-ODA homopolyimide (PI-4c) also increased its optical transparency (Figure 4(a).43). In this case the copolyimides incorporating 50% PPDBN (CPI-3c) showed lower transparency than those with 5% (CPI-3a) and 20% (CPI-3b) of PPDBN. The onset wavelength of transmission was same in the case of CPI-3a and CPI-3b.
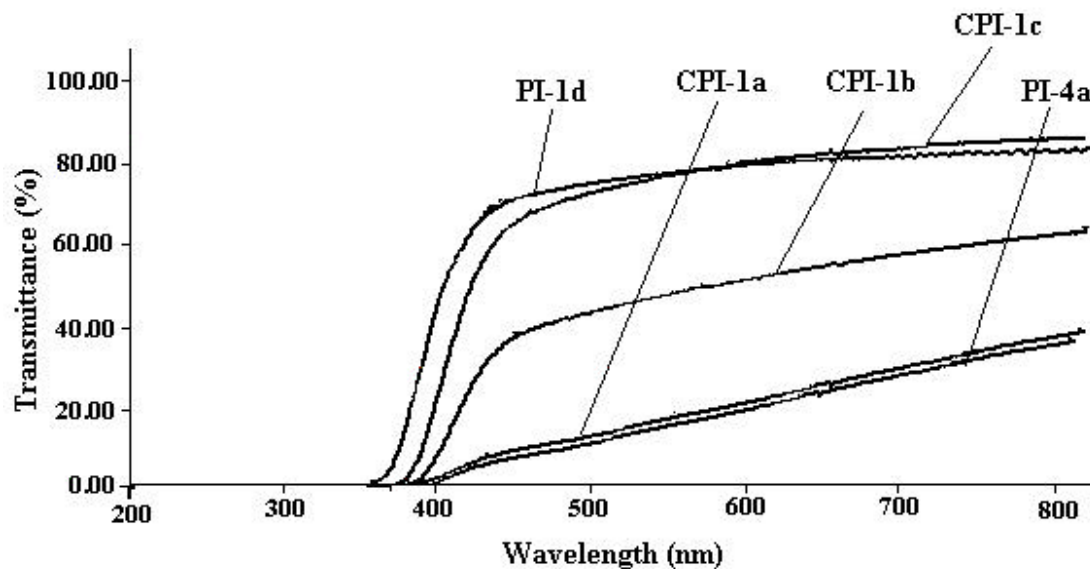
Figure 4(a).41. UV-visible spectra of homopolyimides and copolyimides based on diamines ODA and PPDBN with dianhydride ODPA
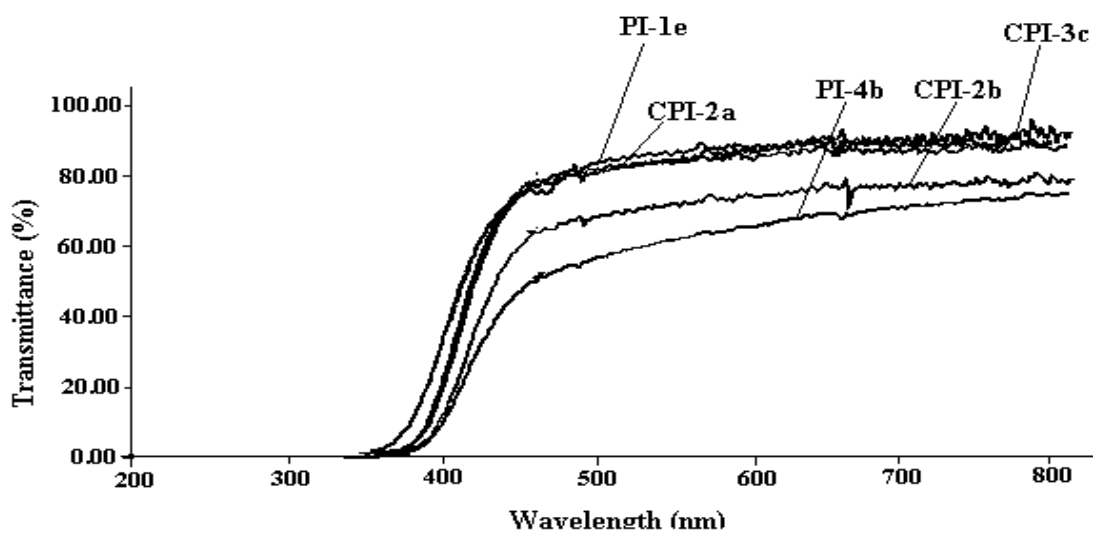
Figure 4(a).42. UV-visible spectra of homopolyimides and copolyimides based on diamines ODA and PPDBN with dianhydride 6-FDA
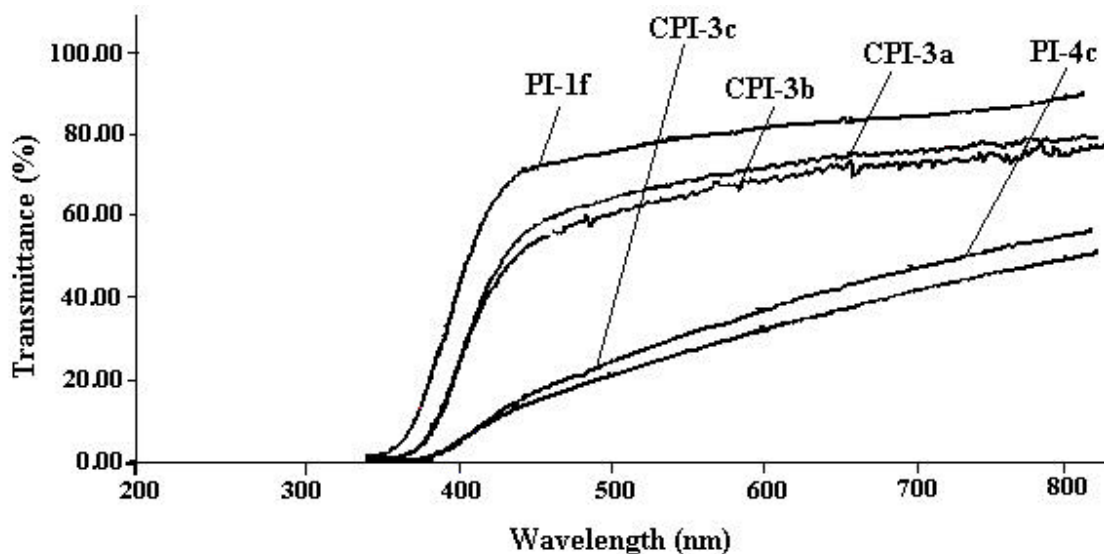
Figure 4(a).43. UV-visible spectra of homopolyimides and copolyimides based on diamines ODA and PPDBN with dianhydride SiDA

Table 4(a).19. Optical transparencies of homo and copolyimides based on PPDBN and ODA with dianhydrides ODPA, 6-FDA and SiDA

Polymer Code	Dianhydride	Diamine (mole %)		Onset (nm)	Cut-off (nm)
		ODA	PPDBN		
PI-4a	ODPA	100	–	383	432
CPI-1a	ODPA	95	5	382	432
CPI-1b	ODPA	80	20	376	450
CPI-1c	ODPA	50	50	368	442
PI-1d	ODPA	–	100	354	424
PI-4b	6-FDA	100	–	372	458
CPI-2a	6-FDA	95	5	362	456
CPI-2b	6-FDA	80	20	368	452
CPI-2c	6-FDA	50	50	364	452
PI-1e	6-FDA	–	100	340	456
PI-4c	SiDA	100	–	380	440
CPI-3a	SiDA	95	5	356	456
CPI-3b	SiDA	80	20	356	446
CPI-3c	SiDA	50	50	374	438
PI-1f	SiDA	–	100	350	442

Copolyimides based on PPDBN with mixture of dianhydrides also showed good transparency with the onset wavelengths in the range 354-386 nm Figure 4(a).44. The onset and cut off transmittance wave lengths for these polyimides are given in Table 4(a).20. The copolyimide CPI-4e (6-FDA/SiDA) showed the highest transparency and CPI-4b (BPDA/SiDA) showed the lowest. All the polyimides transmitted more than 60% of light and the copolyimide CPI-4a showed the highest percentage transmittance of nearly 75%.
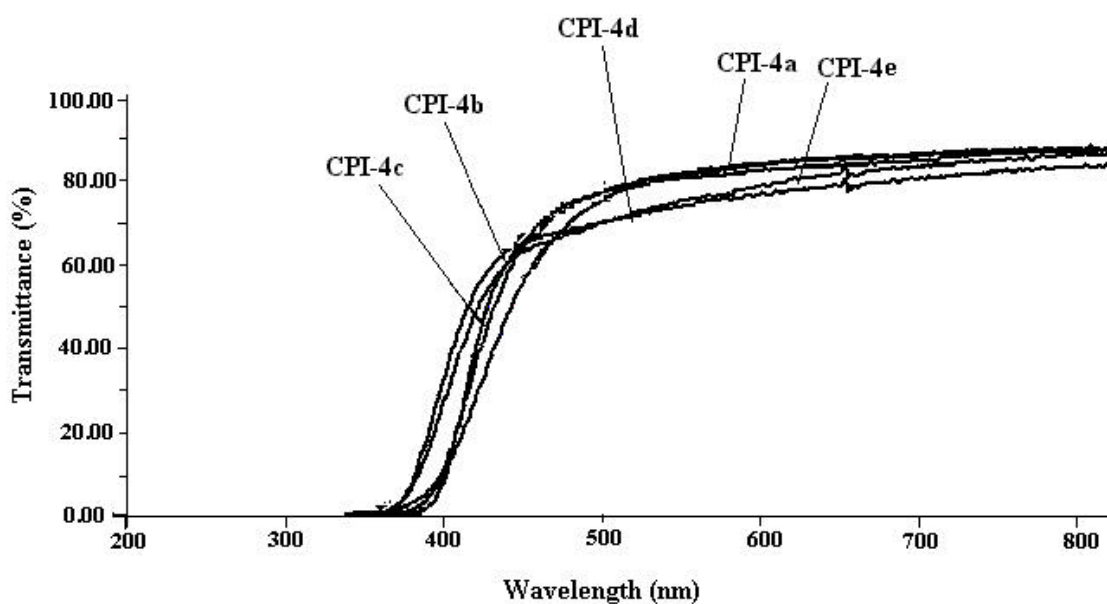
Figure 4(a).44. UV-visible spectra of copolyimides based on diamine PPDBN with a mixture dianhydrides

Table 4(a).20. Optical transparencies of copolyimides based on diamine PPDBN with a mixture dianhydrides

Polymer Code	Diamine	Dianhydrides		Onset (nm)	Cut-off (nm)
		50%	50%		
CPI-4a	PPDBN	SiDA	PMDA	358	498
CPI-4b	PPDBN	SiDA	BPDA	386	470
CPI-4c	PPDBN	SiDA	BTDA	368	466
CPI-4d	PPDBN	SiDA	ODPA	360	438
CPI-4e	PPDBN	SiDA	6-FDA	354	448

4(a).4   Conclusions

1. New series of homopolyimides having pendant pentadecylphenoxy, pentadecylbenzoate and pentadecylphenoxybenzamide groups were synthesized from substituted m-phenylene diamines namely (1) 4-(3-pentadecylphenoxy) benzene-1,3-diamine (PPDBN) (2) 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT) and (3) 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (PPPB) and dianhydrides like PMDA, BPDA, BTDA, ODPA, 6-FDA and SiDA by high temperature one step solution condensation method in m-cresol.

2. The polyimides based on diamine 4-(3-pentadecylphenoxy)benzene-1,3-diamine (PPDBN) showed more solubility than those based on diamines 3-pentadecylphenyl-3,5-diaminobenzoate (PPDBT) and 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide (PPPB). Polyimides from flexible dianhydrides like ODPA, 6-FDA and SiDA have higher solubility than those with rigid dianhydrides like PMDA, BPDA and BTDA.

3. The polyimides based on dianhydrides 6-FDA and SiDA with all the three diamines PPDBN, PPDBT and PPPB and the ODPA based polyimide of PPDBN (PI-1d) were soluble in a wide range of solvents like NMP, DMAc, DMF, m-cresol, chlorobenzene, nitrobenzene, pyridine, THF and chloroform, whereas the polyimides based on unsubstituted m-phenylene diamines were insoluble in these solvents indicating that the incorporation of bulky pendant groups leads to a significant improvement in solubility. The polyimides based on diamines PPDBT and PPPB with ODPA showed lower solubility than those based on PPDBN indicating that the nature of pendant groups influences the solubility.

4. These polyimides exhibited reasonably good thermal stability indicating that incorporation of pendant alkyl group does not affect the thermal stability significantly.

5. The glass transition temperatures (T_g) of the polyimides were dependent on both the monomers.

6. New series of copolyimides incorporating PPDBN and ODA in different mole ratios, with dianhydrides such as ODPA, 6-FDA and SiDA and copolyimides based on diamine

PPDBN with 50% of SiDA and 50% other dianhydrides such as PMDA, BPDA, BTDA, ODPA, 6-FDA were also synthesized by high temperature one step solution condensation method in m-cresol.

7. The solubility of ODA containing homopolyimides was found to improve with the incorporation of PPDBN.

8. The glass transition temperature and thermal stability of homopolyimides based on ODA decreased gradually with the incorporation of PPDBN.

9. The solubility properties of homopolyimides based on diamine PPDBN with dianhydrides PMDA, BPDA and BTDA improved significantly by the incorporation of silicon. The copolyimides in which 50% of these dianhydrides were replaced by silicon containing dianhydride, SiDA showed high solubility in all test solvents like NMP, DMAc, DMF, m-cresol, chlorobenzene, nitrobenzene, pyridine, THF and chloroform whereas the homopolyimides PMDA-PPDBN, BPDA-PPDBN and BTDA-PPDBN were not completely soluble in any of these solvents.

10. Most of the homo ad copolyimides were found to have good optical transparency. The incorporation of PPDBN improved the optical transparency of homopolyimides based on ODA.

11. In general this study shows that incorporation of bulky pendant groups and silicon improves the solubility properties of polyimides without affecting the thermal properties significantly.

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Chapter 4

Part-B

Possible Applications of Polyimides from Cardanol

4(b).1 Introduction

The excellent properties of polyimides like good mechanical properties, high thermal stability, good chemical resistance, good abrasion resistance and high glass transition temperature makes them useful candidates for a wide range of applications. The large free volume and high selectivity of polyimides make them useful as gas separation membranes and their ability to align liquid crystal molecules in liquid crystal display devices makes them useful as liquid crystal alignment layers. They also satisfy the requirements for electronic applications such as high glass transition temperatures, low coefficient of thermal expansion, low dielectric constant and good planarising properties and hence are also used as inter layer dielectrics in electronic devices. These properties are mainly influenced by the structure of polyimide and those having pendant alkyl groups have gained particular attention in these areas. The pendant alkyl group in a polyimide can increase the permeability by increasing the free volume, improve the alignment properties by the hydrophobic interaction with liquid crystals and lower the dielectric constant by increasing the hydrophobicity. Thus the objective of the present study was to find out the possible application of polyimides and copolyimides discussed earlier in different fields like

1. Alignment layers for liquid crystal display devices

2. Inter layer dielectrics in electronics industry

3. Gas separation membranes

where the alkyl groups are known to improve the properties.

4(b).1.1 Application of Polyimides as Liquid Crystal Alignment layers

4(b).1.1.1 Introduction

Liquid crystal molecules usually form an angle with the boundary surface, which is called the tilt bias angle and exerts strong influence on the liquid crystal display performance. The displays with low pretilt angle may show undesirable scattering effects whereas displays with large pretilt angle on the other hand often show disturbing interference colors.[1] Therefore to optimize the display performances it is necessary to control the pretilt angle. The tilt bias angle required for the twisted nematic LCD's is 1° to 3° and for super twisted nematic LCD's is 5° to 14°.

The uniform alignment of liquid crystal molecules is difficult to obtain by merely injecting the liquid crystal between upper and lower substrates. Therefore an alignment film is generally provided between the substrates for uniform alignment. One method of obtaining liquid crystal molecular alignment is by controlled gradient vapor deposition of the inorganic materials without using rubbing treatment. This method is utilized in laboratory scale preparation only because of the difficulty in large-scale production and low yield. Alternatively, organic alignment films obtained by coating an organic polymer, followed by rubbing with a piece of polar cloth are generally used.[2] Among organic polymers, mainly polyimides have been used since they have good chemical resistance, good abrasion resistance and good thermal stability and can be applied by spin coating method. However all polyimides do not have the desired pretilt angle. Pretilt angle is dependent on the structure of both polyimide and liquid crystal and is affected by both electronic interaction and steric repulsion between liquid crystal molecules and the alignment layer polymer surface.[3] The stronger the electronic interaction, the smaller the liquid crystal pretilt angle and the greater the steric repulsion, the larger the pretilt angle. It has been reported in literature that incorporation of alkyl group in the main chain,[4] incorporation of alkyl group in the side chain,[5] incorporation of pendant $–CF_3$[6] or nitrile[7] groups and irradiation with slanted UV light lead to higher tilt bias angles.[8]

The phenomenon of orientation of liquid crystals on an alignment layer is not yet fully understood. It is suggested that the orientation of polymer chains near the film surface, which

are generated by rubbing, plays a key role in aligning liquid crystals at the surface.[4] Requirement of a polyimide alignment layer for liquid crystal display application are good solubility, high monomer purity and a low polarity structure with 2-4° tilt bias angle.

From the foregoing discussions it is evident that polyimides having alkyl groups in the main chain or side chain can provide high pretilt angle required for liquid crystal display applications. Therefore in this study an attempt was made to evaluate the pretilt angle properties of polyimides having pendant pentadecylphenoxy groups synthesized from cashew nut shell liquid. Two polyimides based on diamine PPDBN with dianhydrides ODPA and SiDA were chosen for this study, since it was also an objective to evaluate the effect of different bridging groups on the pretilt angle properties of PPDBN based polyimides.

4(b).1.1.2 Experimental

➢ **Preparation of liquid crystal cells**

Liquid crystal cells were prepared to measure the pretilt angle of LC molecules aligned on the PI films. The alignment films were deposited first by spin coating of a dilute solution of polyimide in trichloroethane on the substrates and then cured at 120°C for 2 h.

The polyimide films were then rubbed with a rubbing machine using a rayon cloth. The cells were mounted with antiparallel rubbing directions, using two 15 μm Mylar strips along two edges and then sealed with an epoxy resin. The cell was then filled with the nematic liquid crystal and the pretilt angle measured as described below.

➢ **Measurements**

Pretilt angles were determined by the crystal rotation method[9] in an automated optical bench. The measurements were all performed at room temperature. A schematic representation of the measurement is shown in Figure 4(b).1. The liquid crystal cell is rotated around an axis perpendicular to the director, and the incident light should be polarized at an angle of 45° from the axis. The light transmitted through the crystal at various angle of incidences is obtained in the form of a sine curve Figure 4(b).2. The angle of incidence (ϕ_{sym}) for which the optical retardation is maximum is noted from this transmission versus angle of incidence curve.
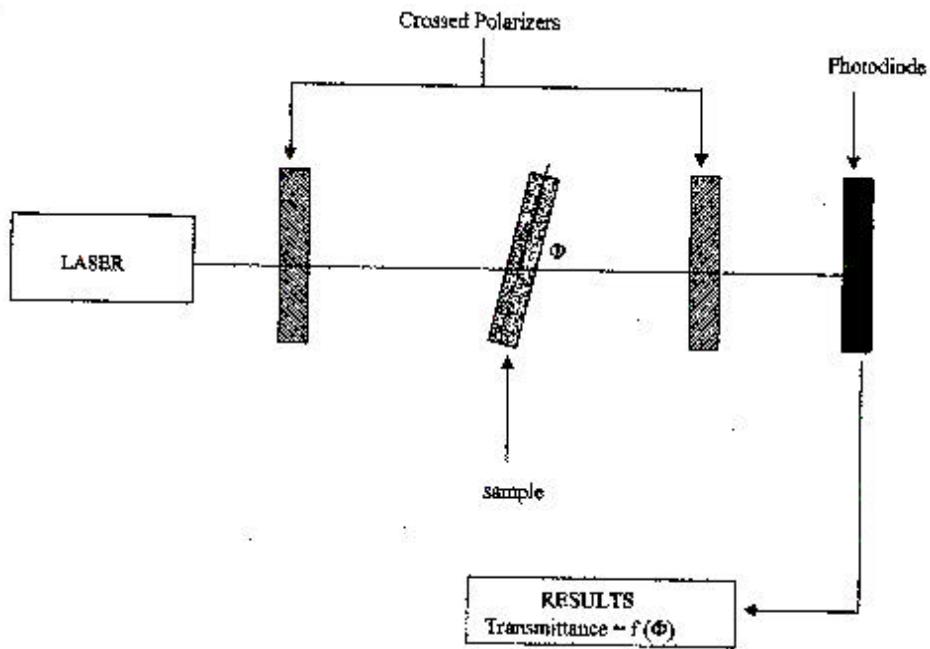
Figure 4(b).1. Schematic representation of pretilt angle measurement by crystal rotation method
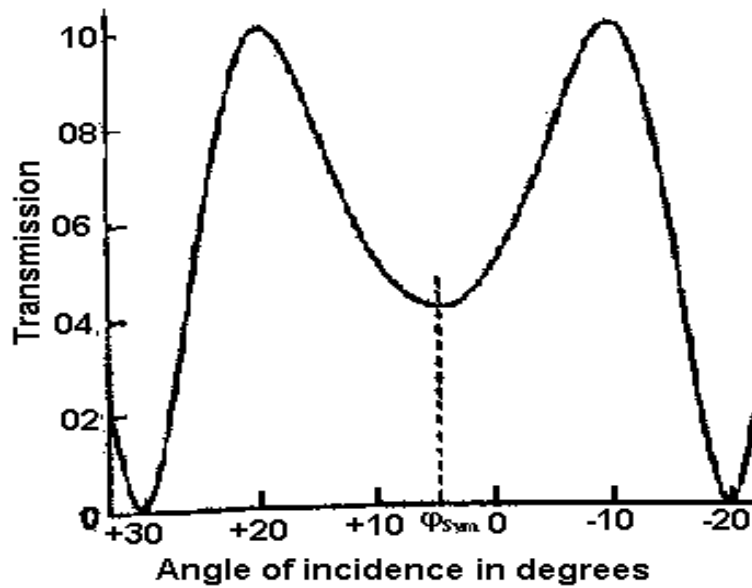
Figure 4(b).2. Transmission versus angle of incidence curve for a homogeneously oriented cell Preparation of LC cells

The maximum optical retardation is taken as the point where there is an approximately symmetrical transmittance curve as shown in Figure 4(b).2. For the relationship between

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symmetry point of the transmission versus rotation curves and the pretilt angles the following simplified equation was used.

$$\sin 2\boldsymbol{b} \;=\; \frac{-2\sin\Phi_{sym}}{(n_0 + n_e)\sqrt{1-(\sin\Phi_{sym}/n_0)^2}} \tag{4.1}$$

were, β is the pretilt angle measured for the samples, Φ_{sym} is the symmetry angle found for the transmssion versus angle of incidence curves, while n_o and n_e are the ordinary and extraordinary refractive indexes of the liquid crystal used.

4(b).1.1.3 Results and discussion

The liquid crystal cells were prepared as given in experimental section and the measurements were done by crystal rotation method. The pretilt angle was then calculated from the obtained incident angle for which the optical retardation is maximum (ϕ_{sym}) and the two anisotropic refractive indices n_o and n_e of the liquid crystal, using the Equation 4.1.

The transmission versus angle of incidence curves obtained for polyimide PI-1d (ODPA-PPDBN) and PI-1f (SiDA-PPDBN) with liquid crystal ZL13961 are shown in Figures 4(b).3 and 4. The ϕ_{sym} and the pretilt angle values obtained for polyimides PI-1d and PI-1f for liquid crystal ZLI1557 are given in Table 4.1. It was found that the pretilt angle obtained for the polymer PI-1d (4.3°) was very much higher than that obtained for PI-1f (0.15°).

Table 4(b).1. Pretilt angle values obtained for polymers PI-1d and PI-1f with liquid crystal ZLI1557

Polymer code	Liquid crystalline mixture	ϕ_{sym} (degrees)	Pretilt angle (degrees)
PI-1d	ZLI1557	13.37	4.3
PI-1f	ZLI1557	0.46	0.15

Although a mechanism for the origin of pretilt angle is not clear so far, the conformational structures of polyimides near the surface and the interaction of liquid crystals with the surface are considered to be essential factors. The single chain conformational structures of polyimides PI-1d (ODPA-PPDBN) and PI-1f (SiDA-PPDBN) obtained using

Hyperchem program Version 5.0 are shown in Figures 4(a).13 (Page No. 194) and 15 (Page No. 195). A large difference in conformations was observed as the dianhydride was changed from ODPA to SiDA. The difference in the steric interaction between the alignment layer and the liquid crystal molecules due to the conformational changes in the polyimide is considered to play a significant role in generating the observed pretilt angles. In the case of PI-1d (ODPA-PPDBN) the alkyl groups oriented in opposite directions at an angle with respect to the main chain whereas in the case of PI-1f (SiDA-PPDBN) the alkyl groups showed a random orientation. This ordered orientation of alkyl groups may be a possible reason for the high pretilt angle observed for PI-1d (ODPA-PPDBN).

Further it is reported in literature that to obtain a high pretilt angle, the rod-like liquid crystal molecules should be partially attracted and partially repelled by the polyimide alignment layer.[6] These attractive and repulsive forces are mainly dependant on the dianhydride and diamine structure. In the present study the attractive forces that should be mainly considered are the dispersion forces between the aromatic moieties in the polyimide and liquid crystal molecules and the repulsive forces can be mainly attributed to the interaction between hydrophobic alkyl group in the polyimide and liquid crystal molecules. It is expected that the liquid crystal molecules are attracted by the aromatic moieties and at the same time repelled by the alkyl chains causing a tilt from the polyimide surface. In the case of PI-1f (SiDA-PPDBN) alkyl groups are present in both the dianhydride and diamine moiety and therefore the main interactive forces operating all over the polymer surface will be the repulsive forces and thus can result in a very low pretilt angle. However in the case of ODPA containing polyimide, the alkyl groups exist only in the diamine moiety and the liquid crystal molecules are attracted by the dianhydride moiety. This difference in the interaction of a single unit may be a possible reason for higher pretilt angle in ODPA containing polyimide PI-1d (ODPA-PPDBN).

The polyimide PI-1d, having a pretilt angle value of 4.3° was found to be useful for application in liquid crystal display devices and therefore the pretilt angle of this polyimide with eight other liquid crystals were also measured and the angle of incidence versus transmittance curves obtained in each case are shown in Figures 4(b).5-11 and the pretilt angle values are summarized in Table 4(b).2.
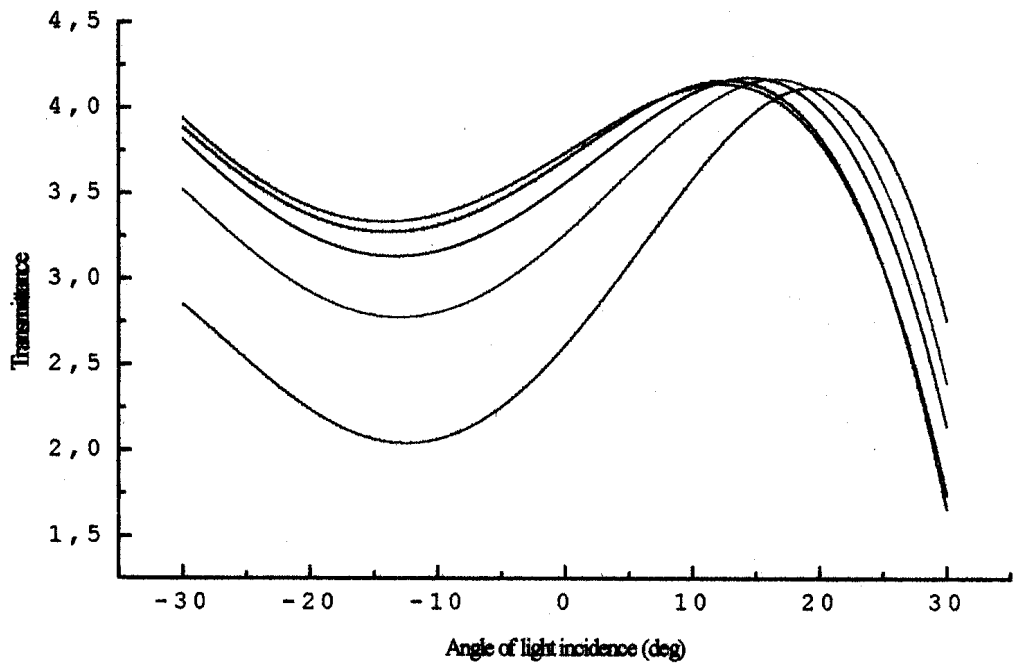
Figure 4(b).3 Angular dependence of transmittance with PI-1d as alignment layer and ZLI1557 as liquid crystal mixture
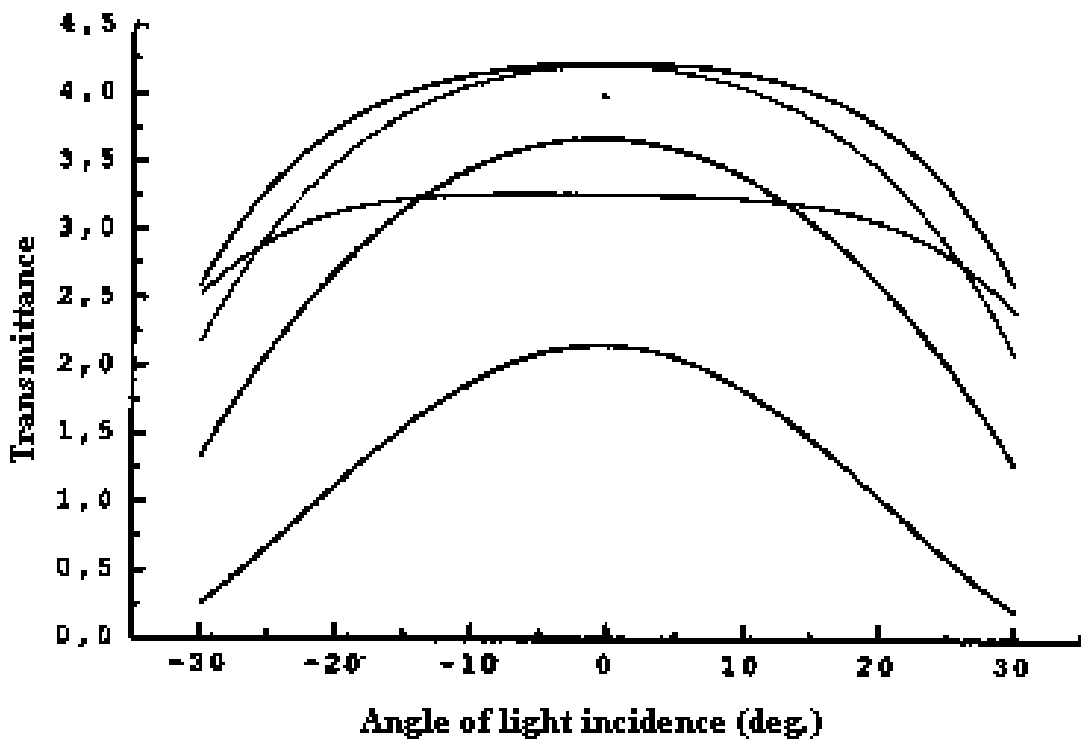
Figure 4(b).4. Angular dependence of transmittance with PI-1f as alignment layer and ZLI1557 as liquid crystal mixture

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Table 4(b).2. Pretilt angle values obtained for polymer PI-1d with different liquid crystals

Polymer code	Liquid crystalline mixture	ϕ_{sym} (degrees)	Pretilt angle (degrees)
PI-1d	ZLI1557	13.37	4.3
PI-1d	ZLI1701	10.89	3.52
PI-1d	ZLI3201-100	11.36	3.64
PI-1d	ZLI2806	12.22	4.11
PI-1d	ZLI2359	19.5	6.6
PI-1d	TL202	6.23	2.2
PI-1d	TL205	3.58	1.25
PI-1d	ZLI3961	1.48	0.46

The pretilt angle of polyimide PI-1d (ODPA-PPDBN) varied from 0.46^o-6.6^0 for different liquid crystals. The difference is due to the fact that pretilt angle depends on the interaction between the liquid crystal and the polymer, which in turn is influenced by the structure of both liquid crystal and the polymer. A high pretilt angle was obtained with the liquid crystal ZLI2359. Since the liquid crystals used were commercial samples their structures were not known and therefore it was not possible to correlate the observed pretilt angle with the liquid crystal structure. In general this study shows the influence of polyimide structure on its liquid crystal alignment properties.
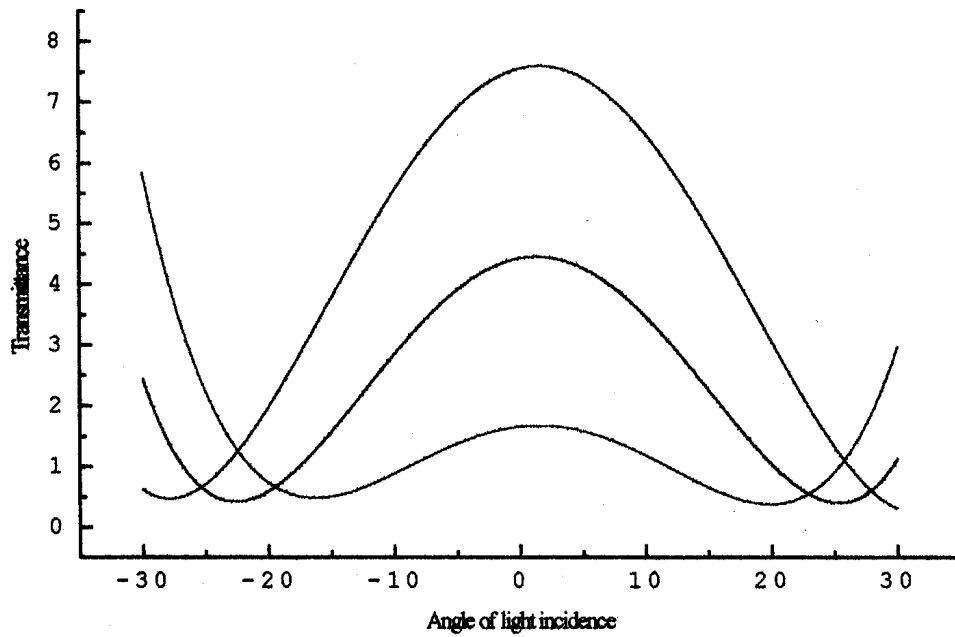
Figure 4(b).5. Angular dependence of transmittance with PI-1d as alignment layer and ZLI3961 as liquid crystal mixture
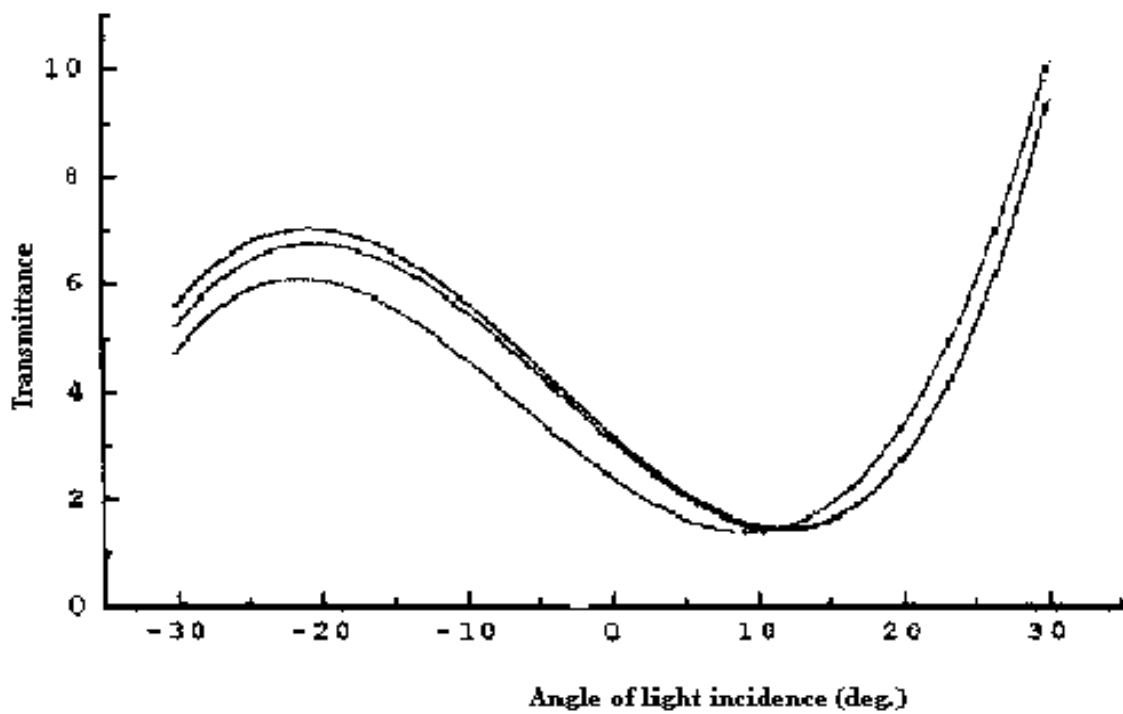
Figure 4(b).6. Angular dependence of transmittance with PI-1d as alignment layer and ZLI1701 as liquid crystal mixture

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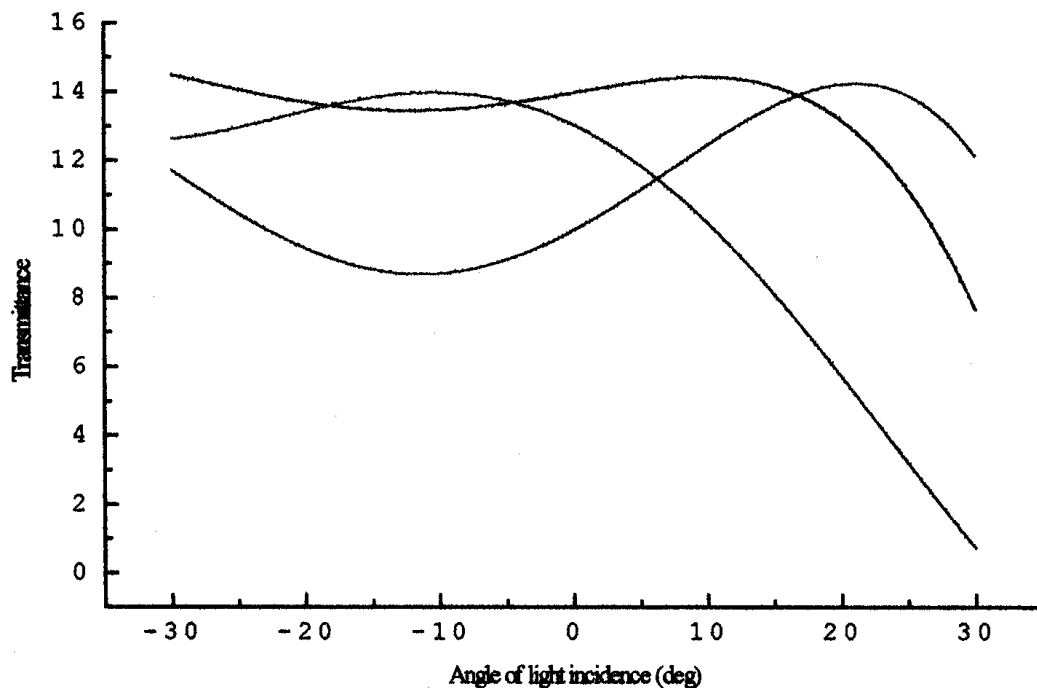
**Figure 4(b).7. Angular dependence of transmittance with PI-1d as alignment
layer and ZLI3201-100 as liquid crystal mixture**
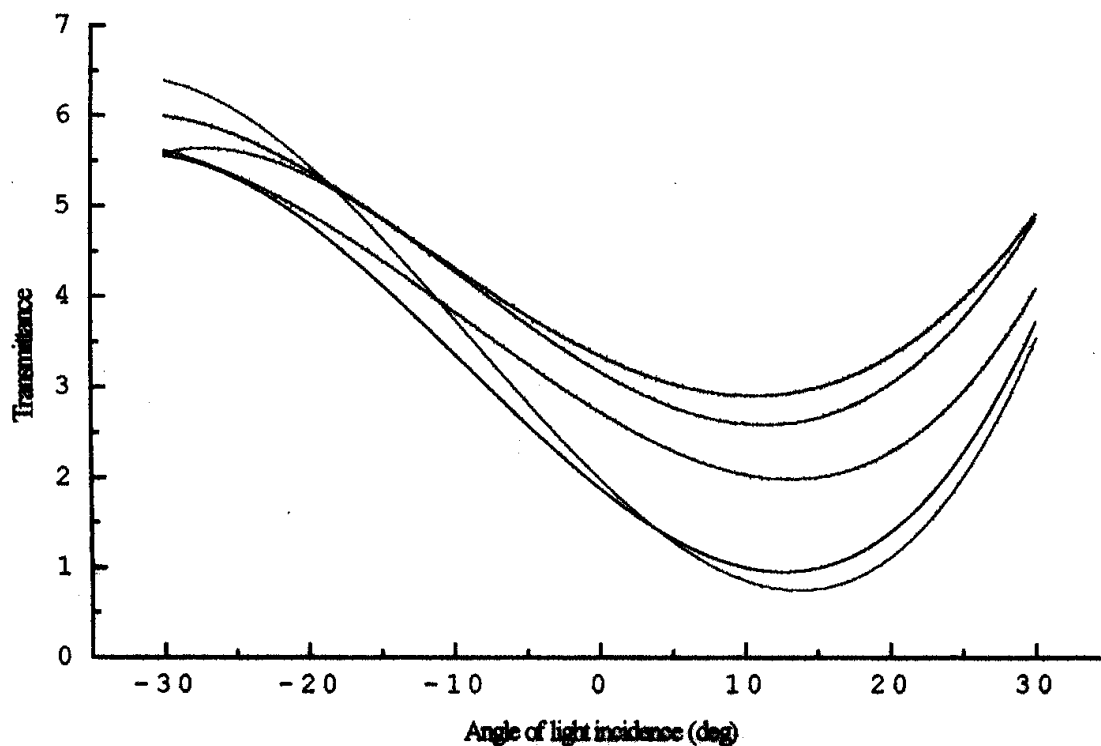
**Figure 4(b).8. Angular dependence of transmittance with PI-1d as alignment
layer and ZLI2806 as liquid crystal mixture**

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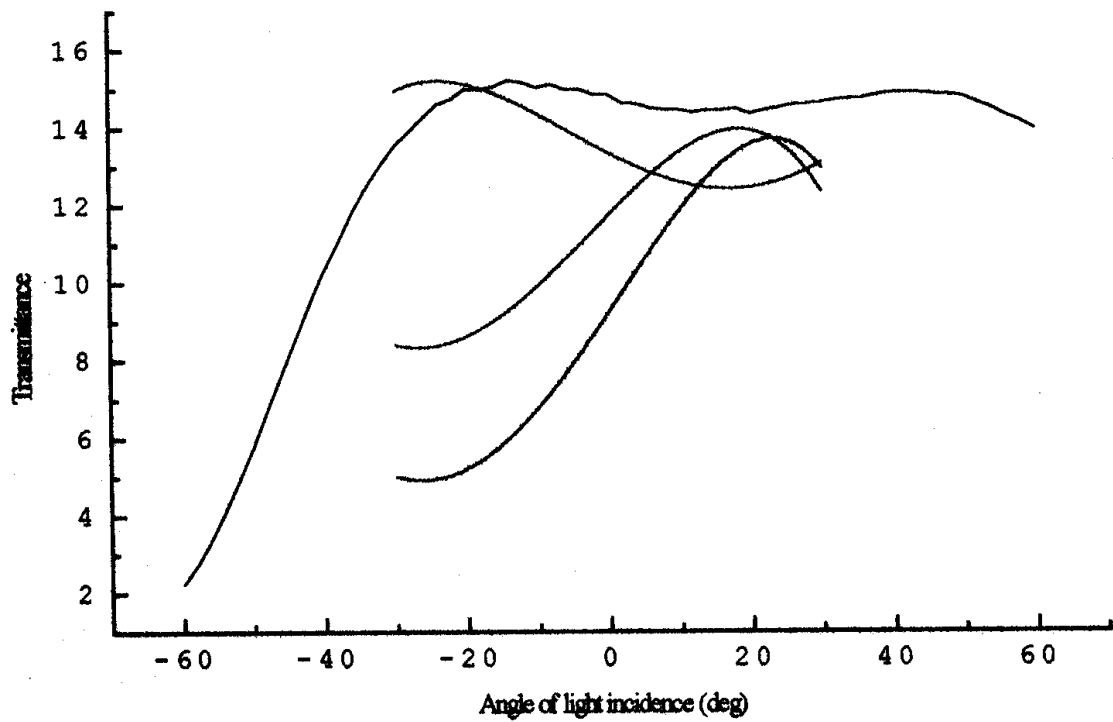
Figure 4(b).9. Angular dependence of transmittance with PI-1d as alignment layer and ZLI2359 as liquid crystal mixture
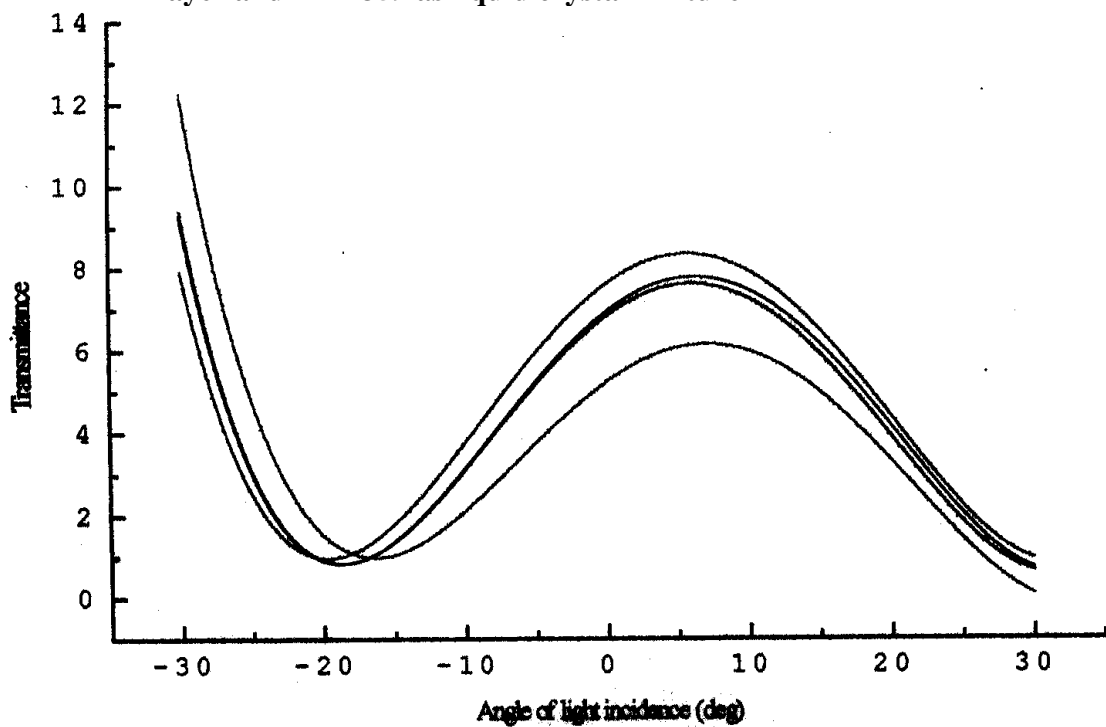
Figure 4(b).10. Angular dependence of transmittance with PI-1d as alignment layer and TL202 as liquid crystal mixture
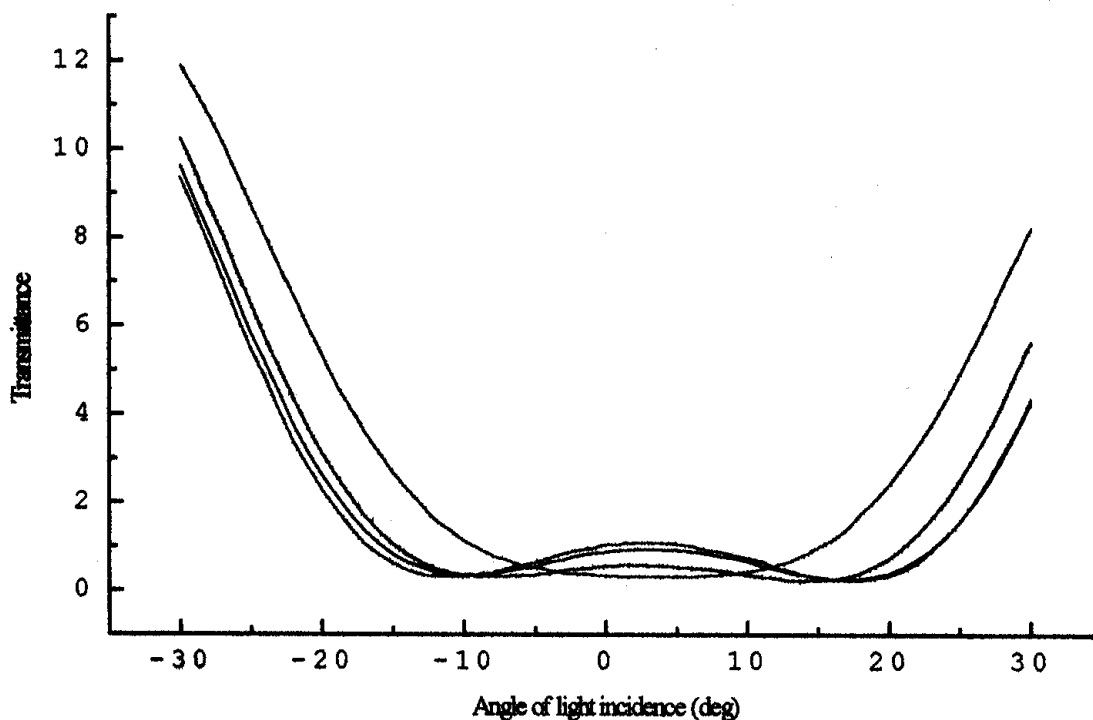
Figure 4(b).11. Angular dependence of transmittance with PI-1d as alignment layer and TL205 as liquid crystal mixture

4(b).1.1.4 Conclusions

1. The alignment properties of two polyimide alignment layers ODPA-PPDDN and SiDA-PPDDN synthesized from cashew nut shell liquid were studied for use in liquid crystal display devices.

2. Pretilt angle of these polyimides were dependant on their molecular structure and also on the structure of liquid crystal. The attractive and repulsive interactions that exist between the liquid crystal molecules and the polyimide alignment layer play a major role in the alignment properties of these polyimides.

3. The polyimide PI-1f (SiDA-PPDBN) having alkyl groups on both the diamine and dianhydride showed a low pretilt angle because of the high repulsive interaction and low attractive interactions. Polyimide PI-1d (ODPA-PPDBN) having alkyl group only in the diamine part showed a high pretilt angle of 4.3^o for a liquid crystal mixture ZLI1557 because of the balance in attractive and repulsive forces that exist between the alignment

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layer and liquid crystal molecules. Pretilt angle of this polyimide alignment layer could be increased to 6.6^o by changing the liquid crystal mixture.

4. The polyimide ODPA-PPDBN was soluble in low boiling solvents like trichloroethane, chloroform and THF and formed transparent flexible films at room temperature. This polyimide had good adhesion to the substrate and high pretilt angle and hence has potential as alignment layers for a super twisted nematic liquid crystal device.

4(b).1.2 Application of polyimides as dielectric materials

4(b).1.2.1 Introduction

Polyimides are a class of polymers used extensively in microelectronics. They are particularly used as interlayer dielectrics in integrated circuit fabrication because of their low permittivity, low losses over a wide frequency range and high breakdown voltages.[10]

Several polyimides containing the commercial diamines like oxydianiline and m-phenylene diamines and dianhydrides like PMDA, BPDA and 6-FDA have been studied extensively for use in electronics industry because of their excellent properties. Other polyimides containing siloxane,[11] fluorine,[12] alkoxy[13] and alkyl[14] groups have also been recognized to have good dielectric properties. It is known that alkyl group in a polymer reduces its dielectric constant. The polyimides of this study based on cashew nut shell liquid containing long alkyl groups were expected to have low dielectric constant. Therefore it was an objective of this study to measure the dielectric constant of these polyimides and to find out their application as interlayer dielectrics in electronics industry. In this study the dielectric constant measurements were made for some homopolyimides, synthesized from 4-(3-pentadecyphenoxy)benzene-1,3-diamine (PPDBN) and dianhydrides like ODPA (PI-1d), 6-FDA (PI-1e) and SiDA (PI-1f) for a range of frequencies to compare the effect of ether, silicon and fluorine group along with pendant alkyl groups on the dielectric properties of the resulting polyimides. To compare the effect of percentage incorporation of PPDBN on the dielectric properties of some commercially important polyimides like 6-FDA-ODA (PI-4b), the dielectric constant measurements were also done for some copolyimides containing 6-FDA, ODA and PPDBN. The dielectric constant of 6-FDA-ODA polyimide though reported in literature was also measured for comparison under identical conditions.

4(b).1.2.2 Experimental

➢ **Preparation of samples for capacitance measurements**

The samples were made from 1 cm^2 polyimide films having a thickness of 45-50 μm. Both sides of the films were coated with conducting silver paste and then the films were sandwiched between two 1 cm^2 copper foils. Then a point contact was made on both sides of the copper foil using a thin copper wire and silver paste and the cells were then mounted on a

small piece of glass plate with the help of a cellophane tape. These cells were then directly used for capacitance measurements.

➢ **Measurements**

The dielectric constants were calculated from the capacitance values obtained using an HP model 4192A Impedance Analyzer. A schematic representation of an impedance bridge used for measuring capacitance is shown in Figure 4(b).12. 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 and consists of a series of variable capacitances and variable resistances. 'Det' represents the null detector; usually a lock-in amplifier. After the insertion of sample in the circuit the variable capacitance (C_3) and resistance (R_3) standards are adjusted to obtain a zero voltage at the null detector. From this null detector condition, the real and imaginary components of the unknown impedance is calculated.
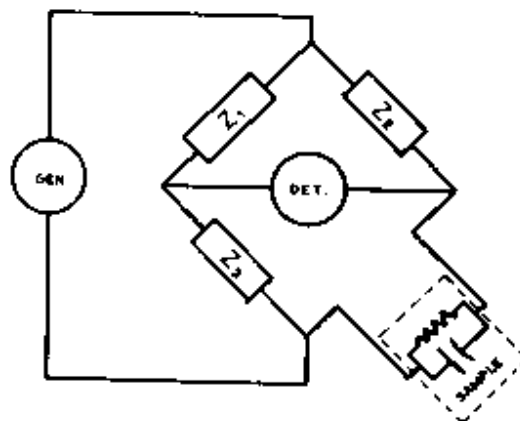
Figure 4(b).12. Schematic diagram of a typical impedance-bridge circuit

The measurements were carried out for a range of frequencies varying from 10 kHz to 13 MHz at room temperature. From the obtained capacitance values the dielectric constants were calculated using the following equation

$$\varepsilon = Cd \Big/ \varepsilon_o A \qquad (4.2)$$

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

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4(b).1.2.3 Results and discussion

The term dielectric constant (ε) is generally used to describe the general dielectric behavior of a material; 'ε' is most commonly defined as the ratio of capacitance in a capacitor filled with dielectric material to the capacitance of the identical capacitor filled with vacuum. The magnitude of dielectric constant depends on the number and strength of all the dipoles in the material. Since the mobility of dipoles depends on temperature, the dielectric constant is temperature dependent. In an ac field, the dielectric function has two components; the real component ε' is called the dielectric constant and the imaginary component ε'' is known as the dielectric loss factor. Usually in impedance analyzers the dielectric loss tangent tan δ is obtained instead of ε''. Dielectric loss factor can be obtained from tan δ using the equation

$$\varepsilon'' = \tan \delta \; x \; \varepsilon' \hspace{4cm} (4.3)$$

In the present study capacitance measurements were done for some samples for a range of frequencies at room temperature. The dielectric constants calculated using Equation 4.2 and the dielctric loss tangent tan δ are listed in Table 4(b).3. The dielectric loss factors were calculated using the equation 4.3 and to understand the impedance behavior of these polyimides the dielectric constants (ε') were plotted against the dielectric loss factor (ε'') and the results are shown in Figures 4(b).13-18.

It was observed that in the case of polyimides PI-1d (ODPA-PPDBN), PI-1f (SiDA-PPDBN) and CPI-2c (6-FDA-ODA(50%)-PPDBN(50%)) the electrode processes were mainly diffusion controlled in the high frequency range (1MHz to 13 MHz) as indicated by the linear dependence on frequency. In the case of PI-1e (6-FDA-PPDBN (Figure 4(b).14)) a strong frequency dependent dispersion was observed indicating more complex electrode processes. The ε''-ε' plots of polyimides CPI-2b (6-FDA-ODA(80%)-PPDBN(20%) (Figure 4(b).17)) and PI-4a (6-FDA-ODA (Figure 4(b).16)) showed a semicircular arc indicating an interfacial charge transfer process that can be modeled by an equivalent RC circuit.[15]

Table 4(b).3. Dielectric properties of polyimides and copolyimides from PPDBN

Frequency	PI-1d		PI-1e		PI-1f		PI-4b		CPI-2b		CPI-2c	
	ODPA-PPDBN		6-FDA-PDBN		SiDA-PDBN		6-FDA-ODA		6-FDA-ODA(80 %)-PPDBN (20 %)		6-FDA-ODA(50 %)-PPDBN (50 %)	
	ε	Tan δ	ε	Tan δ	ε	Tan δ	ε	Tan δ	ε	Tan δ	ε	Tan δ
13 MHz	0.48195	-0.0218	1.26945	-0.0216	1.695	0.0021	1.43344	0.0344	1.27792	0.0593	0.81743	0.0038
12	0.56763	-0.0153	1.3446	-0.0207	1.94925	0.0042	1.63494	0.034	1.41736	0.0588	0.93985	0.0093
11	0.65035	-0.0105	1.3905	-0.0202	2.1974	0.0084	1.83334	0.0333	1.60272	0.0568	1.05532	0.0129
10	0.73057	-0.0065	1.43235	-0.0165	2.45165	0.0082	2.02306	0.0321	1.78192	0.0591	1.16368	0.0212
9	0.80672	-0.0038	1.4733	-0.0173	2.66251	0.0067	2.201	0.0306	1.95216	0.0516	1.26784	0.0273
8	0.87633	-0.0019	1.50615	-0.0179	2.88014	0.008	2.3653	0.0294	2.1112	0.0457	1.3636	0.0212
7	0.94059	0.0013	1.53495	-0.0087	3.05846	0.0092	2.51596	0.0287	2.27528	0.0416	1.45376	0.0181
6	0.99889	0.0032	1.5759	-0.0031	3.23203	0.0115	2.65236	0.0279	2.42536	0.0391	1.54672	0.0157
5	1.05009	0.0046	1.5921	8E-4	3.39814	0.01	2.77202	0.0271	2.54184	0.0362	1.61784	0.0163
4	1.09293	0.006	1.52685	0.004	3.52696	0.0104	2.87742	0.0259	2.64544	0.0342	1.68168	0.0172
3	1.12863	0.0062	1.57185	0.0051	3.6212	0.0114	2.98034	0.027	2.73504	0.0321	1.73264	0.0166
2	1.15362	0.0065	1.593	0.0071	3.70595	0.0118	3.05474	0.0251	2.81736	0.031	1.7724	0.0184
1	1.17198	0.0079	1.60785	0.0145	3.76561	0.0116	3.11798	0.0226	2.89072	0.0298	1.81048	0.0176
900 kHz	1.17351	0.0071	1.60695	0.0148	3.77171	0.0115	3.11612	0.0227	2.9148	0.0293	1.8144	0.0177
800	1.17453	0.0076	1.5219	0.0151	3.77646	0.0119	3.1248	0.0226	2.92152	0.0286	1.81776	0.0175
700	1.17606	0.0075	1.5228	0.0154	3.78188	0.012	3.13286	0.0223	2.93048	0.0285	1.82224	0.0174
600	1.17759	0.0137	1.50525	0.0156	3.78799	0.0119	3.1403	0.0216	2.94	0.0282	1.82616	0.0174
500	1.20411	0.0093	1.476	0.0153	3.79409	0.0119	3.14774	0.0212	2.95008	0.0278	1.83008	0.0168
400	1.20666	0.0096	1.4814	0.015	3.80155	0.012	3.15642	0.0206	2.96016	0.0275	1.83512	0.0167
300	1.21584	0.015	1.49715	0.0145	3.80968	0.0123	3.16572	0.0201	2.9736	0.0256	1.84128	0.0169
200	1.22043	0.0141	1.48815	0.0122	3.82256	0.0126	3.193	0.0183	2.99096	0.0246	1.84912	0.0177
100	1.22553	0.0125	1.47375	0.0112	3.84494	0.0138	3.22772	0.0175	3.03632	0.0273	1.86648	0.0175
90	1.22604	0.0125	1.4823	0.0116	3.84833	0.0145	3.23206	0.0174	3.04136	0.0272	1.86368	0.017
80	1.22604	0.012	1.4796	0.0117	3.85646	0.0144	3.2364	0.0173	3.04696	0.0269	1.86536	0.0171
70	1.22553	0.0119	1.47285	0.0128	3.86189	0.0146	3.24012	0.0171	3.05368	0.0268	1.8676	0.0174
60	1.22706	0.0085	1.4652	0.0132	3.86528	0.0154	3.24136	0.0167	3.05928	0.0272	1.87096	0.0188
50	1.23165	0.0091	1.45305	0.0133	3.8768	0.0161	3.24756	0.0162	3.06768	0.0268	1.87992	0.0195
40	1.23165	0.0086	1.4346	0.0133	3.88969	0.014	3.255	0.0156	3.07776	0.0266	1.88384	0.0184
30	1.23369	0.0072	1.72485	0.0132	3.89986	0.0155	3.27236	0.0146	3.08896	0.0261	1.88888	0.0184
20	1.23573	0.0055	1.35	0.0135	3.91613	0.0159	3.28476	0.0132	3.108	0.026	1.89952	0.0201
10	1.23777	0.003	1.0782	0.0137	3.94528	0.0171	3.30646	-	3.1416	0.026	1.91296	0.021
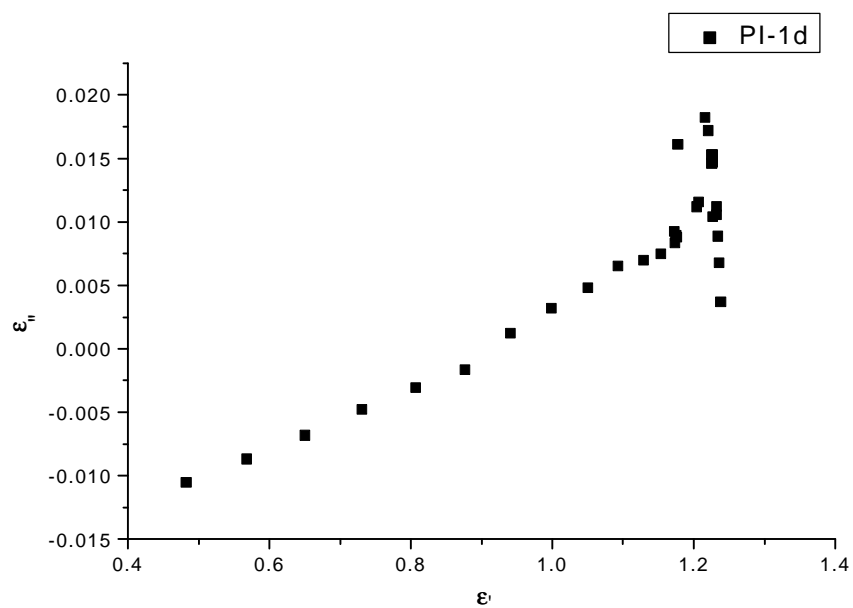
Figure 4(b).13. Impedance behavior of ODPA-PPDBN
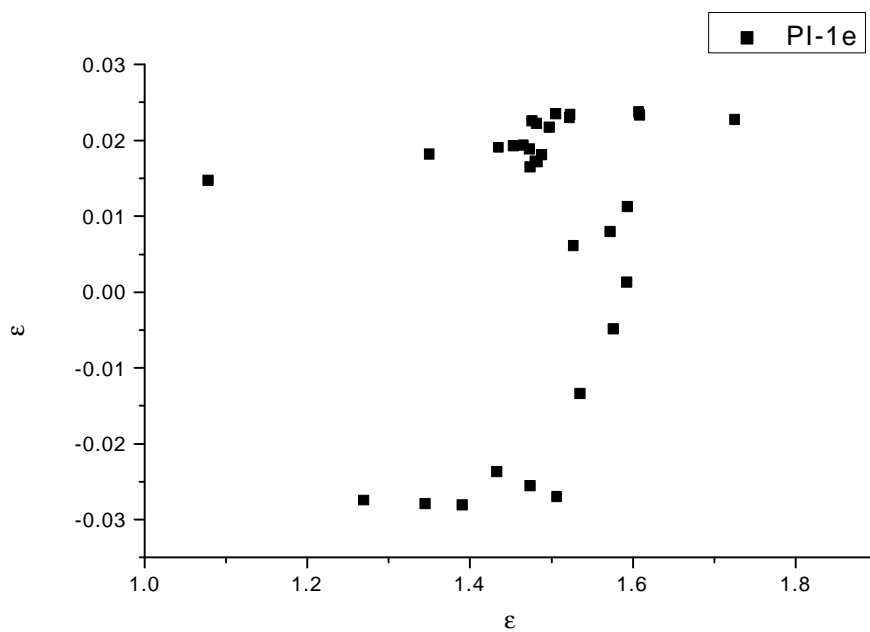
Figure 4(b).14. Impedance behavior of 6-FDA-PPDBN

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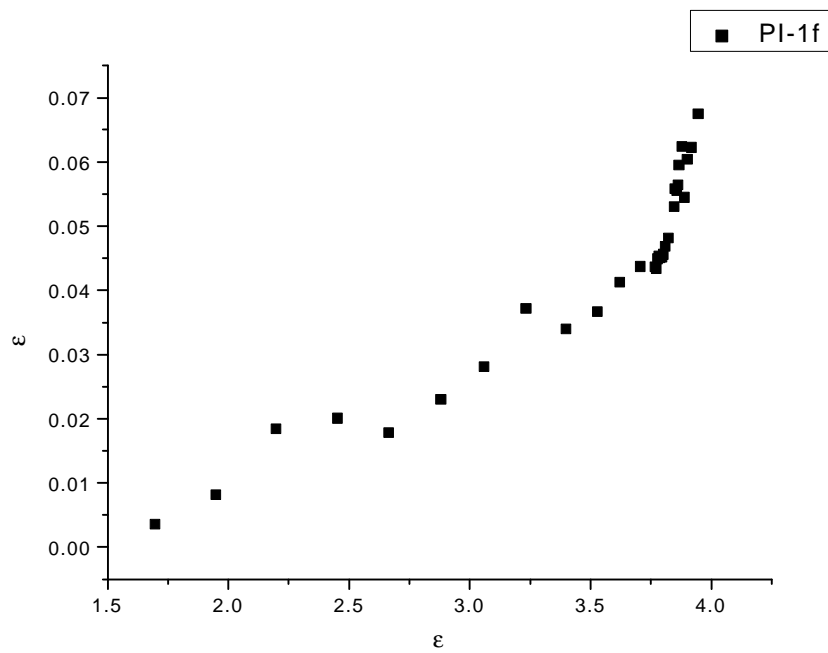
Figure 4(b).15. Impedance behavior of SiDA-PPDBN
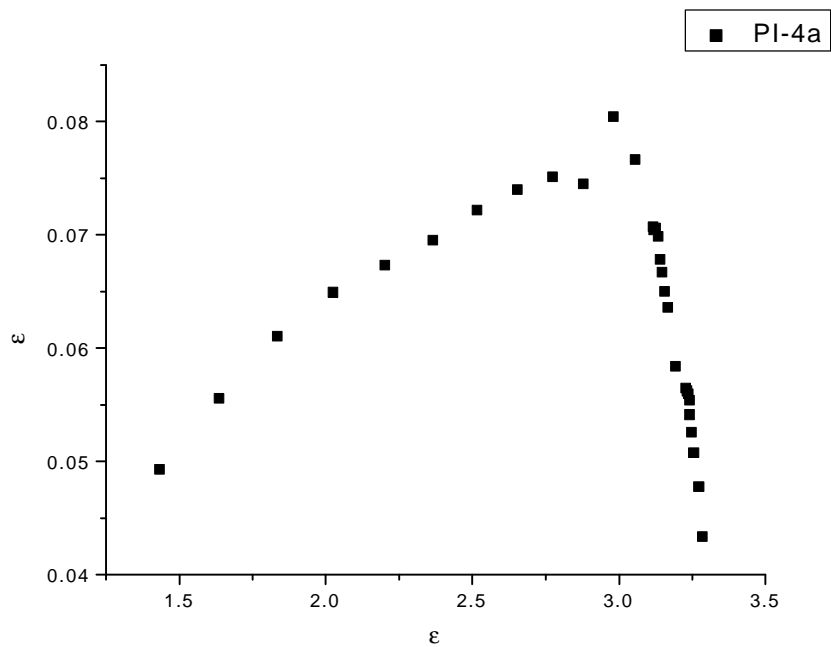
Figure 4(b).16. Impedance behavior of 6-FDA-ODA

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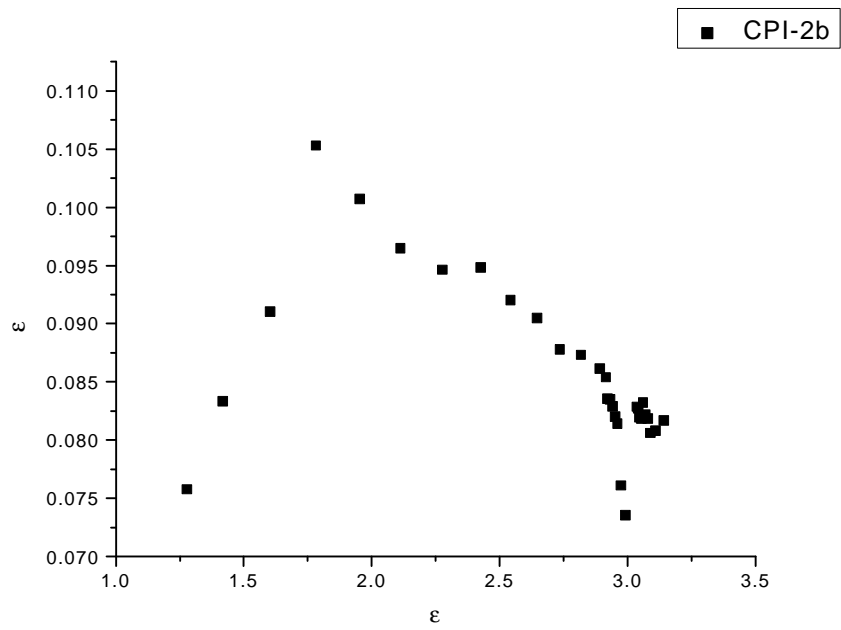
Figure 4(b).17. Impedance behavior of 6-FDA-ODA-80-PPDBN-20
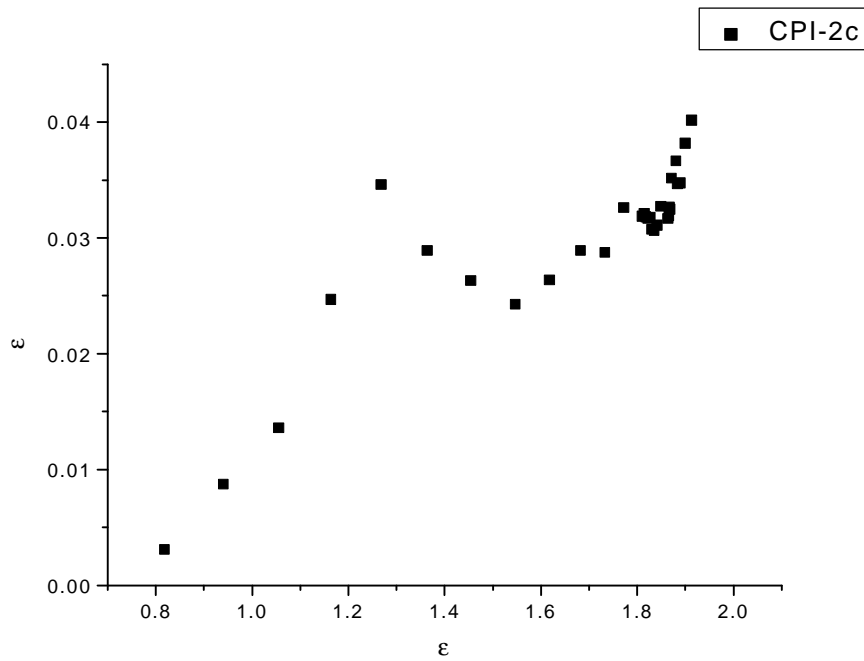
Figure 4(b).18. Impedance behavior of 6-FDA-ODA-50-PPDBN-50

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The variation of dielectric constant with frequency is given in Figures 4(b).19 and 20 and it was observed that in the low frequency range (10 kHz to 900 kHz) the dielectric constant was independent of frequency and in the high frequency range (1 MHz to 13 MHz) the dielectric constant of PI-1f, PI-4a and CPI-2b varied with frequency, whereas the frequency dependence of dielectric constant in the case of polyimides PI-1d and CPI-2c was not significant and was much lower as compared to the commercial polyimide PI-4a. The dielectric constant of polyimide PI-1e remained almost constant over the whole frequency range of 10 kHz to 13 MHz.

Among the homopolyimides the one synthesized from dianhydride ODPA (PI-1d) gave the least value of dielectric constant, followed by 6-FDA (PI-1e) and then SiDA (PI-1f). In the case of polyimides PI-1d (ODPA-PPDBN) and PI-1e (6-FDA-PPDBN) the dielectric constant values were in the range 0.4-1.2 and 1.07-1.7, which are much lower than most commonly used interlayer dielectrics. The dielectric constant of SiDA containing polyimide PI-1f (SiDA-PPDBN) was higher than the dielectric constant of the commercial polymer 6-FDA-ODA but was lower than that of silicon dioxide, a commonly used dielectric, having a dielectric constant in the range 4 -10. Generally fluorine containing polyimides have low dielectric constant compared to non fluorinated ones. However in the present study it was observed that the polyimide PI-1d (ODPA-PPDBN) based on ODPA showed lower dielectric constants as compared to PI-1e based on 6-FDA. This may be because of the difference in the orientation of alkyl groups. It is possible that in a particular conformation the alkyl groups may be masking the polarity induced on the polyimide surface by the imide linkages. This can lead to an increase in hydrophobicity and reduction in dielectric constant of the polyimide.

The study of dielectric constant of copolyimides showed that incorporation of alkyl group containing diamine PPDBN in the 6-FDA-ODA (PI-4a) polyimide leads to a decreased in the dielectric constant. As the mole percentage of the PPDBN diamine was increased, the dielectric constant gradually decreased showing the effect of incorporation of alkyl group on the dielectric properties of 6-FDA-ODA (PI-4a) polyimide. All the tested polyimides except PI-1f and CPI-2b had dielectric constants below 2. Such low dielectric constants are difficult

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to obtain and this shows that these polyimides are potential candidates for use in electronic industry as interlayer dielectrics.

The variation in dielectric loss tangent with frequency in the low frequency range (10-900 kHz) and high frequency range (1-13 MHz) are shown in Figures 4(b).21 and 22. No general trend was observed in this case. In the low frequency range (10 kHz to 900 MHz) the dielectric loss factor showed some variation with frequency up to 200 kHz and after that it was independent of frequency up to 900 kHz except in the case of polyimide PI-1d (ODPA-PPDBN). In the case of PI-1d the dielectric loss tangent showed strong frequency dependent fluctuations up to a frequency of 900 kHz (Figure 4(b).21).

In the high frequency range (1 MHz to 13 MHz) the dielectric loss tangent of polyimides PI-4b (6-FDA-ODA) and CPI-2b (6-FDA/20% PPDBN/80% ODA) increased as the frequency increased (Figure 4(b).22) and in the case of polyimides PI-1d (ODPA-PPDBN) and PI-1e (6-FDA-PPDBN), the dielectric loss tangent showed a gradual decrease with increase in frequency. There was no significant change in the dielectric loss tangent of PI-1f (SiDA-PPDBN) with frequency. The dielectric loss tangent of CPI-2c (6-FDA/ 50% PPDBN/ 50% ODA) was independent of frequency up to 6 MHz and then showed an increase up to 9 MHz and afterwards gradually decreased.
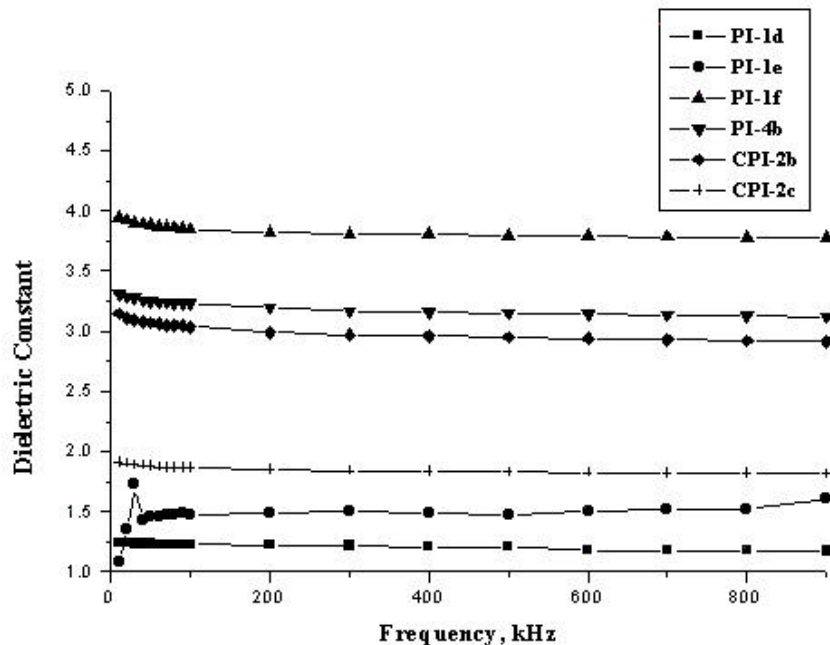
Figure 4(b).19. Variation of dielectric constant with frequency in the frequency range 10 kHz to 900 kHz
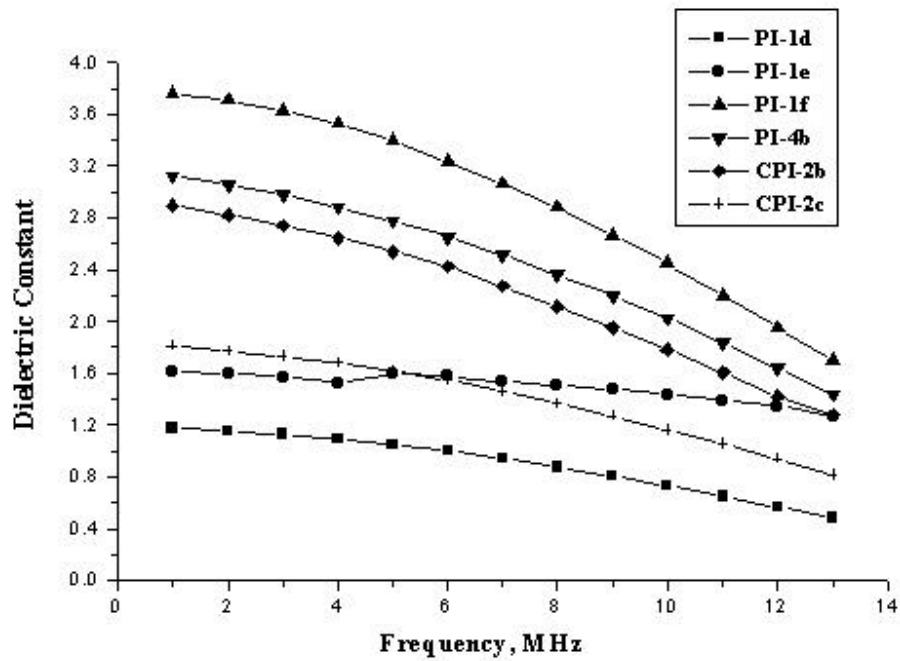
Figure 4(b).20. Variation of dielectric constant with frequency in the frequency range 1 MHz to 13 MHz
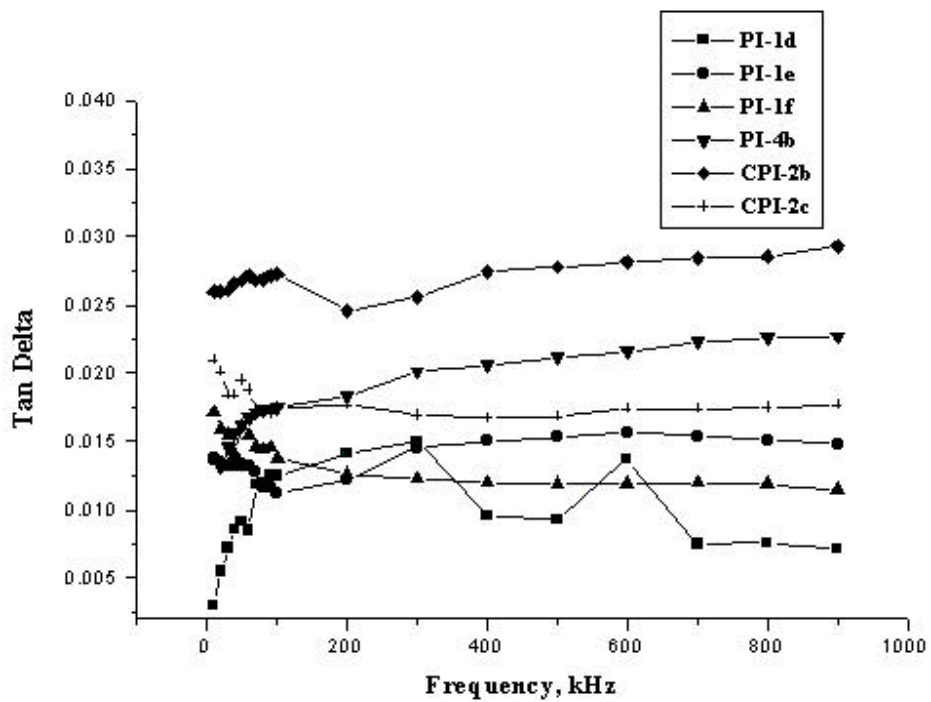
Figure 4(b).21. Dielectric loss factor versus frequency in the frequency range 10 kHz to 900 kHz
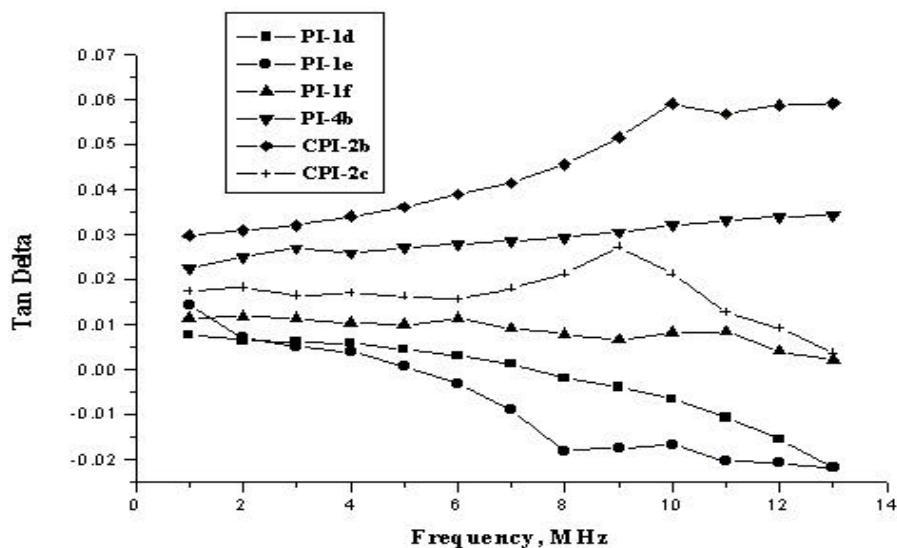
Figure 4(b).22. Dielectric loss factor versus frequency in the frequency range 1MHz to 13 MHz

4(b).1.2.4 Conclusions

1. All homopolyimides based on diamine PPDBN showed low dielectric constants. The dielectric constants of polyimides with dianhydrides ODPA, 6-FDA and SiDA were in the order ODPA < 6-FDA < SiDA.

2. Polyimides PI-1d (ODPA-PPDBN), PI-1e (6-FDA-PPDBN), and CPI-2c (ODPA-PPDBN (50%)-ODA (50%)), showed dielectric constants less than 2 which were almost independent of frequency.

3. A combination of fluorine or ether along with pendant pentadecyl phenoxy group was found to decrease the dielectric constant significantely.

4. The incorporation of PPDBN in 6-FDA-ODA polyimide decreased its dielectric constant indicating the effect of pendant pentadecyl groups on the dielectric constant.

5. The electrode processes were either diffusion controlled or charge transfer controlled depending on the structure of the polyimide.

6. All the polyimides in this study showed dielectric constant lower than that of the polyimide 'H' film ($\varepsilon = 3.5$) based on pyromellitic dianhydride and oxydianiline, which is one of the most preferred dielectrics in high performance applications. Therefore the potential application of these materials in the microelectronics and related fields are foreseen.

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4(b).1.3 Application of polyimides as gas separation membranes
4(b).1.3.1 Introduction

Polyimides have attracted much attention as gas separation materials because of their gas separation properties and other excellent physical properties. The relationship between the structures and the gas permeability properties of the polyimides have been investigated extensively in order to prepare gas separation membranes with high gas permeability and permselectivity.[16] Bulky groups in the main chain generally lead to an increase in free volume and hence high permeability coefficients.[17] High chain stiffness, as indicated by the high glass transition temperatures is expected to improve the selectivity.[17] It has been reported in the literature that the alkyl group ortho to a diamine moiety increases the permeability without decreasing the permselectivity[18] but the effect of a long alkyl group which is a substituent of another pendant group which in turn is connected to the main chain *via* different flexible connecting groups, on the permeability and selectivity properties of corresponding polyimides is not reported. Therefore in this study the effect of different pendant groups like pentadecylphenoxy, pentadecylbenzoate and pentadecylphenoxybenzamide on the gas permeability properties of different homopolyimides incorporating these groups was investigated.

Oxydianiline containing polyimides are commercially important polymers with a wide range of applications. These polyimides are known to have good selectivity, but their permeabilities are generally low. This is due to the close packing of chains that exist in these polyimides that result in a reduced free volume. It is reported in literature that an increase in free volume without affecting the rigidity of the main chain can result in polymers with high permeability and selectivity. In this regard the diamines in this study seems to be interesting. Copolymerization with rigid diamines containing flexible side groups is an effective method to improve the free volume while maintaining the overall rigidity of the main chain. Therefore in this study the effect of incorporation of pendant alkyl group on the permeability properties of some ODA containing polyimides like ODPA-ODA, 6-FDA-ODA and SiDA-ODA was also investigated by determining the permeability properties of copolyimides based on 4-(3-pentadeylphenoxy)benzene-1,3-diamine and ODA in different mole ratios with dianhydrides like ODPA, 6-FDA and SiDA.

Gas permeability of a polymer membrane is governed mainly by free volume, d-spacing, glass transition temperature, surface morphology of the polymer and solubility and diffusivity of gases. To study the structure-property relationship, it is essential to determine all these factors. The objective of the present work was to find out the possibilities of using the polyimides based on CNSL, containing pendant pentadecyl groups for gas separation and not the study of structure-property relationship. Hence all the parameters required for the study of structure-property relationship were not determined. However an attempt was made to interpret the observed results with the available data of d-spacing and molecular modeling.

4(b).1.3.2 Experimental

The gas permeability measurements were made as described in Chapter 3, Section 3.2.2.1 and the permeability coefficient (P) and the ideal separation factor for various gases were calculated.

4(b).1.3.3 Results and discussion

The permeability coefficients of four gases O_2, N_2, H_2, CO_2 and the ideal separation factor for different pairs of gases at $30 \pm 0.1^o C$ for different homopolyimides and copolyimides are given in Tables 4.(b).4–7.

The permeability data of homopolyimides from diamines PPDBN, PPDBT and PPPB with dianhydrides ODPA, 6-FDA and SiDA given in Table 4.(b).4 shows the influence of different pendant groups like pentadecylphenoxy, pentadecylbenzoate and pentadecylphenoxybenzamide groups on the permeability and selectivity properties of the respective polyimides for different gases like oxygen, nitrogen, hydrogen and carbon dioxide. In the case of homopolyimides, it was observed that the permeability was dependant on the d-spacing values (d_{sp}) for gases like O_2, N_2 and CO_2. Permeability of hydrogen deviated from this trend because hydrogen has got low solubility in many polymers and this affect the permeability of hydrogen significantly compared to other gases.

Table 4.(b).4. Effect of different pendant groups on the permeability properties of polyimides from dianhydrides ODPA, 6-FDA and SiDA

Polymer Code	Dianhydrides	Diamines	d-spacing, A^o	Permeability Coefficients, barrer				Selectivity				
				P_{O2}	P_{N2}	P_{H2}	P_{CO2}	P_{O2}/P_{N2} α_1	P_{CO2}/P_{N2} α_2	P_{H2}/P_{N2} α_3	P_{H2}/P_{CO2} α_4	P_{H2}/P_{O2} α_5
PI-1d	ODPA	PPDBN	4.45	2.75	0.8	8.1	16	3.4	20	10.13	1.97	2.94
PI-1e	6-FDA	PPDBN	5.15	5.6	1.6	25	32.7	3.5	40.88	31.25	1.3	0.22
PI-1f	SiDA	PPDBN	5.08	3.56	0.9	20	8.6	3.95	9.55	22.22	2.32	5.62
PI-2d	ODPA	PPDBT	4.32	1.17	0.27	15	3.9	4.3	14.44	55.55	3.85	12.82
PI-2e	6-FDA	PPDBT	4.91	4.7	1.1	34	17	4.27	15.45	30.91	2.0	7.23
PI-2f	SiDA	PPDBT	5.18	0.23	m	m	m	m	m	m	m	m
PI-3d	ODPA	PPPB	4.52	3.77	1.28	20.75	13.7	2.94	10.70	16.21	1.51	5.50
PI-3e	6-FDA	PPPB	4.06	n	n	n	n	n	n	n	n	n
PI-3f	SiDA	PPPB	4.68	n	n	n	n	n	n	n	n	n

m = the membrane broke on application of pressure for a longer time

n = The membrane did not have strength at all and broke on application of small pressure

In the case of polyimides with ODPA the one based on diamine PPPB (PI-3d) having the highest d_{sp} value showed highest permeability for all the four gases and the one with diamine PPDBT (PI-2d) with minimum d_{sp} value showed lowest permeability for gases like O_2, N_2 and CO_2. The permeability of PI-1d (ODPA-PPDBN) was in between that of PI-3d (ODPA-PPPB) and PI-2d (ODPA-PPDBT). Accordingly the O_2/N_2 selectivity was highest for PI-2d (ODPA-PPDBT), which had the lowest permeability for O_2 and N_2, and the selectivity was lowest for PI-3d (ODPA-PPPB), which had the highest permeability. The selectivity of PI-1d was in between these two. It is reported in literature that bulky pendant groups increase the permeability and reduces the selectivity due to increase in the free volume.[19] Therefore it was expected that the high permeability of polyimides from diamine PPPB in this study may be due to its longer side chain, which can increase the free volume considerably. The single chain conformation of polyimide PI-2d (ODPA-PPDBT) obtained using "Hyperchem 5.0" showed a packing of main chain and pendant alkyl groups (Figure 4(a).16, Page No. 196). Therefore it can be assumed that the high selectivity in the case of PI-2d may be due to the restricted mobility of the side chain as well as the main chain. The lowest selectivity of PI-3d (Figure 4(a).17, Page No. 196) may be due to the increase in free volume resulting from the anti-parallel orientation of alkyl groups with respect to the main chain. The H_2 permeability was lowest for the polyimide synthesized from PPDBN (PI-1d). It was observed that the hydrogen permeability was not governed by the d-spacing values, which represents the inter chain and intra chain packing in the polyimide, but was dependant on solubility of hydrogen in the particular polyimide. The H_2 permeability in the case of ODPA based homopolyimides were in the order PI-3d> PI-2d> PI-1d. The low permeability of H_2 in the case of polyimide PI-1d may be due to its low solubility. The selectivity for CO_2/N_2 was in the order PI-1d > 2d > 3d. PI-2d also had higher selectivities for other pair of gases like H_2/N_2, H_2/CO_2 and H_2/O_2. The selectivity for CO_2/N_2 for polyimide PI-1d was twice than that of PI-3d whereas the H_2/N_2 and H_2/O_2 selectivities of PI-1d were lower by ~37% and 46.547 % respectively. The selectivity of H_2/CO_2 of PI-1d was 23 times higher than that of PI-3d. In the case of the polyimides based on dianhydride 6-FDA, the permeability of PI-3e (6-FDA-PPPB) could not be determined as the film was brittle. A comparison of the permeability properties of PI-1e (6-FDA-PPDBN) and PI-2e (6-FDA-PPDBT) showed that the permeability of PI-1e was higher

than PI-2e for gases O_2, N_2 and CO_2 where as the permeability of H_2 was lower by ~36%. PI-1e had high selectivity for the pair of gases CO_2/N_2 and H_2/N_2. The selectivity for H_2/N_2 in the case of PI-2e was comparable with that of PI-1e where as the selectivity of CO_2/N_2 was less than half. The polyimide PI-2e with oxygen permeability of 4.7 and O_2/N_2 selectivity of 4.27 may be useful in the separation of oxygen and nitrogen. The polyimides based on SiDA with diamines PPPB (PI-3f) and PPDBT (PI-2f) were brittle even though they formed a good transparent film and therefore the permeability and selectivity studies were done only for PI-1f based on diamine PPDBN.

Often the gas permeability properties of polyimides can be modified by copolymerization. These properties are generally dependant on the ratio of monomers and the structure of both diamines and dianhydrides. To study the possibility of improving the permeability and selectivity properties of some ODA based polyimides the permeability properties of some copolyimides containing different ratios of ODA and PPDBN with dianhydrides ODPA, 6-FDA and SiDA were studied and are shown in Tables 4.(b).5–7.

In the case of copolyimides containing ODA and PPDBN with dianhydrides like ODPA, 6-FDA and SiDA the permeabilities and selectivities did not show a general trend. Incorporation of 5% of alkyl group containing diamine PPDBN in ODPA-ODA increased the permeability of O_2 by nearly 20 times, N_2 by 24 times, H_2 by 4 times and CO_2 by 5.7 times and the selectivity values for O_2/N_2, CO_2/N_2, H_2/N_2, H_2/CO_2 and H_2/O_2 decreased by 28%, 76%, 83%, 27% and 78% respectively (Table 4(b).5). The incorporation of 20% (CPI-1b) PPDBN resulted in an increase in permeability and selectivity as compared to homopolyimide, however the permeability was lower than that of CPI-1a incorporating 5% PPDBN. Further incorporation of 50% PPDBN in ODPA-ODA homopolyimide resulted in an increase in permeability and decrease in selectivity for most of the gases. The permeability of O_2, N_2, H_2 and CO_2 increased by 14 times, 19 times, 8 times and 43 times respectively and the selectivities of O_2/N_2, H_2/N_2, H_2/CO_2 and H_2/O_2 decreased by 33%, 55.68 %, 80.5% and 37.89%, whereas the CO_2/N_2 selectivity increased 2.28 times when 50% of ODA was replaced by PPDBN.

The incorporation of 5% of PPDBN in 6-FDA-ODA homopolyimide resulted in a decrease in permeability and increase in selectivity for different gases (Table 4(b).6) except in the case of H_2/CO_2 where the selectivity decreased by 15 %. When PPDBN content was increased to 20%, the permeability increased with an increase in selectivity as compared to homopolyimides. This polyimide showed high permeability towards hydrogen and gave a high selectivity value of 50 for the pair of gases H_2/N_2. This membrane may be useful in the separation of N_2 and H_2. The CPI-2c containing 50% PPDBN and ODA showed an increase in permeability but the selectivities were decreased. The highest permeability was observed for hydrogen and the lowest for nitrogen.

Incorporation of 5% of PPDBN (CPI-3a) in SiDA-ODA (PI-4c) homopolyimide resulted in a decrease in permeability where as the selectivity was not affected (Table 4.(b).7). The highest permeability was shown by carbon dioxide and the highest selectivity was obtained for the pair of gases CO_2/N_2 and H_2/N_2. Permeability of polyimides containing 20% of PPDBN (CPI-3b) was lower than that of the homopolyimide SiDA-ODA, but was higher than that of CPI-3a containing 5% PPDBN. The selectivity for the pair of gases O_2/N_2, CO_2/N_2 and H_2/N_2 increased where as that for H_2/CO_2 and H_2/O_2 decreased. Incorporation of 50% PPDBN (CPI-3c) increased the permeability but decreased the selectivity of homopolyimide PI-4c significantly.

Table 4(b).5. Effect of incorporation of pendant alkyl group on the permeability properties of ODPA-ODA homopolymer

Polymer Code	Dianhydrides	Diamines, mole %		d-spacing, A^o	Permeability Coefficients, barrer				Selectivity				
		ODA	PPDBN		P_{O2}	P_{N2}	P_{H2}	P_{CO2}	P_{O2}/P_{N2} α_1	P_{CO2}/P_{N2} α_2	P_{H2}/P_{N2} α_3	P_{H2}/P_{CO2} α_4	P_{H2}/P_{O2} α_5
PI-4a	ODPA	100	-	3.96	0.2	0.065	3.9	0.58	3.33	8.9	60.0	6.72	19.5
CPI-1a	ODPA	95	5	_	3.9	1.6	16.4	3.34	2.4	2.09	10.25	4.91	4.21
CPI-1b	ODPA	80	20	_	0.59	0.11	9.8	1.76	5.36	16	89.09	5.57	16.61
CPI-1c	ODPA	50	50	4.49	2.7	1.23	32.7	25	2.2	20.33	26.59	1.31	12.11
PI-1d	ODPA	-	100	4.45	2.75	0.8	16	8.1	3.4	10.13	20.0	1.98	5.82

Table 4(b).6. Effect of incorporation of pendant alkyl group on the permeability properties of 6-FDA-ODA homopolymer

Polymer Code	Dianhydrides	Diamines, mole %		d-spacing, A°	Permeability Coefficients, barrer				Selectivity				
		ODA	PPDBN		P_{O2}	P_{N2}	P_{H2}	P_{CO2}	P_{O2}/P_{N2} α_1	P_{CO2}/P_{N2} α_2	P_{H2}/P_{N2} α_3	P_{H2}/P_{CO2} α_4	P_{H2}/P_{O2} α_5
PI-4b	6-FDA	100	-	5.81	2.1	0.65	20	4.5	3.2	6.92	30.77	4.44	9.52
CPI-2a	6-FDA	95	5	5.74	1.55	0.46	16.2	4.3	3.38	9.34	35.22	3.77	10.45
CPI-2b	6-FDA	80	20	5.54	2.2	0.4	20	5.2	5.5	13.0	50.0	3.85	9.09
CPI-2c	6-FDA	50	50	5.4	2.3	0.55	21.50	7.3	4.18	13.27	39.09	2.95	9.35
PI-1e	6-FDA	_	100	5.15	5.6	1.6	32.7	25	3.5	15.63	20.44	1.31	5.84

Table 4(b).7. Effect of incorporation of pendant alkyl group on the permeability properties of SiDA-ODA homopolymer

Polymer Code	Dianhydrides	Diamines, mole %		d-spacing, Aº	Permeability Coefficients, barrer				Selectivity				
		ODA	PPDBN		P_{O2}	P_{N2}	P_{H2}	P_{CO2}	P_{O2}/P_{N2} α_1	P_{CO2}/P_{N2} α_2	P_{H2}/P_{N2} α_3	P_{H2}/P_{CO2} α_4	P_{H2}/P_{O2} α_5
PI-4C	SiDA	100	-	5.36	0.92	0.19	3.4	15	4.8	17.89	17.89	0.22	3.69
CPI-3a	SiDA	95	5	5.22	0.625	0.13	2.2	9.4	4.8	16.92	16.92	0.23	3.49
CPI-3b	SiDA	80	20	5.19	0.89	0.15	2.8	10.8	5.9	18.67	18.67	0.26	3.15
CPI-3c	SiDA	50	50	4.98	5.45	2.7	6.3	18	2.0	2.33	2.33	0.35	1.16
PI-1f	SiDA	-	100	5.08	3.56	0.9	8.6	20	3.95	9.56	9.55	0.43	2.42

4(b).1.3.4 Conclusions

1. The structure of diamine influences the permeability properties. Polyimides based on PPPB showed high permeability towards gases like O_2, N_2 and CO_2 whereas polyimides based on PPDBT exhibited low gas permeability.

2. Polyimides based on diamines PPDBN and PPDBT with dianhydride 6-FDA having comparatively high permeability of O_2 and good selectivity for the gas pair O_2/N_2 seem to be promising membrane materials for the separation of O_2 and N_2.

3. The incorporation of 5% of PPDBN in ODA based homopolyimides either increased or decreased the permeability and selectivity depending on d-spacing values. Incorporation of 20% of PPDBN increased the selectivity irrespective of the nature of dianhydrides. Incorporation of 50% PPDBN increased permeability with a decrease in selectivity.

4(b).1.4 Application of Polyimide as Coating Materials for Transmission Electron Microscopy (TEM) Grids

4(b).1.4.1 Introduction

It is known that the surface morphology of polymer membranes is one of the important parameters that influence the gas permeability properties. In this regard the surface morphology of some polyimides and copolyimides were studied by TEM to investigate the relationship between surface morphology and gas permeability properties. However, good correlations were not obtained. During this study it was observed that the surface morphology of thin films of these polyimides having large number of hole like structures were similar to the surface morphology of polymeric materials used for the coating of copper grids in TEM studies. Therefore studies were extended for investigating the possible application of these polyimides as coating materials for TEM grids since the commercially available materials are very expensive.

Most samples for transmission electron microscopy must be supported on some kind of a thin electron transparent film, to hold the specimen in place while in the objective lens of the TEM. Only samples that are self supporting do not need some support film. The selection of the right support film is very important to obtain a good contrast of the final image.

The polymer support films generally used are commercial grade resins that have been carefully selected and used alone or as a mixture of two or more grades of commercial materials.[20] The most widely used resin is known under the trade name Formavar®. This is otherwise known as polyvinyl formal and is a good support film. Other resins include Parlodion® and collodion sometimes known as gun cotton or nitrocellulose and also Pioloform® and Butvar® which generically are polyvinyl butyral. Even though Formavar® is the most widely used support film and is stronger than the other support film materials, the ability of the film to withstand heating effects is not as good as for Pioloform™. Formavar® in the solid form is not hazardous whereas when dissolved in a solvent the product becomes flammable and therefore hazardous, meaning it is more expensive to ship.

Depending on the kind of samples being studied sometimes polygrids are needed to have completely unobstructed regions of samples without the effect of any substrate films. In those instances, the data is only taken from the portions of the samples essentially suspended

over "holes" and in the case of lacey films, over the open areas of the lacey network. A typical holey and lacey Formavar[®] custom filmed grid coated in the EM Laboratories of structure probe, Inc. and SPI Supplies are shown in Figure 4(b).23 and 24. These holey and lacy grids were obtained by varying the concentration of coating solution.[20]
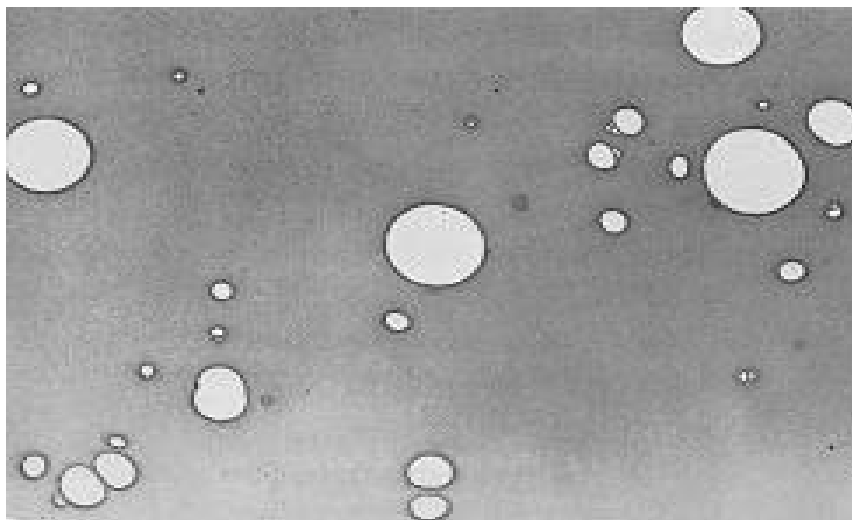
Figure 4(b).23. Custom coated holey Formvar[®] filmed grid coated in the EM laboratories of Structure Probe, Inc. and SPI Supplies
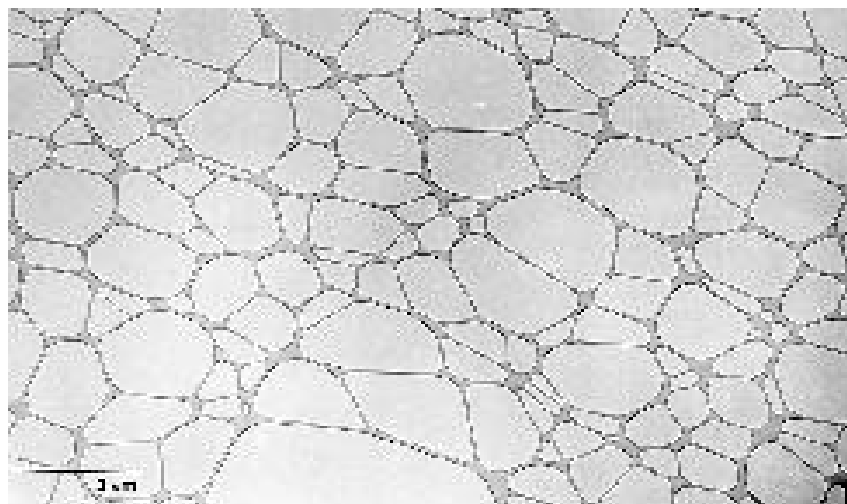
Figure 4(b).24. Lacey Formvar custom filmed grid coated in the EM laboratories of Structure Probe, Inc. and SPI Supplies

The commercially available coated grids for TEM are very expensive. Due to the resemblance of these Formavar[®] grids with the morphology of the polyimides obtained in this study it was decided to find out the application of these polyimides as coatings for TEM grids. The homo

and copolyimides based on ODA and PPDBN with SiDA were chosen for the study since all of them had high solubility in chloroform.

4(b).1.4.2 Sample Preparation

Thin films of polyimide suitable for TEM study were prepared as follows. One drop of a 0.33% polyimide solution was deposited on the top of a copper grid and allowed to dry. This was then kept overnight at room temperature and used for TEM studies. To obtain a more uniform film another method was also used. The films were first made on water surface by adding a solution of polyimide in chloroform carefully to water. The thin film floating on the water surface after the evaporation of solvent was then picked up with the grid.

4(b).1.4.3 Results and discussion

The transmission electron micrographs of grids coated with homo and copolyimides (coated by directly depositing the polymer solution on grid) based on ODA and PPDBN with SiDA (PI-4a, CPI-3a-b and PI-1f) are shown in Figures 4(b).25-30. All the films had morphology with hole like structures as in the case of commercial coating films for grids. But the number and size of holes in a given area varied depending on the percentage of PPDBN in SiDA-ODA. Among the different homo and copolyimides studied, the copolyimide CPI-3b (SiDA-ODA(80%)-PPDBN(20%)) showed more resemblance with the commercial grids. In this case the holes were distributed over a large area and the holey region showed more transparency than the other parts of film (Figure 4(b).21). Therefore for further studies only this polyimide was used.

Further studies were carried out on CPI-3b to find out the possibility of making grids with more even holes and also with a lacey network. Since it is reported that more uniform films can be obtained by casting the polymer solution on water surface[20] in this case thin polyimide films were made on the water surface and then picked up with the grid. Films were also made from polyimide solutions of different concentrations to investigate the change in nature of holes with concentration. It was observed that by using different concentrations of the polyimide solution either holey or lacey grids could be obtained. A holey grid with more uniform holes was obtained by using a polyimide solution of 0.1% concentration and a lacey grid was obtained when the concentration of CPI-2b was 0.07%. Both the grids are shown in

Figures 4(b).31 and 32. It is reported that the minimum concentration used in the case of commercially available grids for obtaining a stable coating is 0.2% and hence this is considered to be the limit for reducing the concentration and hence thickness of the film in the case of commercially available coating materials. But in this study we could obtain stable films from a concentration as low as 0.07%. Thus it was possible to make different types of grids with stable coatings depending on the requirements by just varying the concentration of coating solution.

Since it was found that among the SiDA based polyimides, the one incorporating 80% ODA and 20% PPDBN is a good quality TEM coating material, the copolyimides CPI-1b and CPI-2b based on ODA(80%) and PPDBN (20%) with dianhydrides like ODPA and 6-FDA were also tested. The transmission electron micrographs of these polyimides (Figures 4(b).33 and 34) showed a morphology with uniform transparent holes. Therefore they were also expected to have potential as coating materials for TEM grids.

In order to investigate the feasibility of these polyimides as probable TEM grid coatings, transmission electron micrographs of some samples were studied on grids coated with CPI-3b. The material particularly of interest was MCM-41 mesoporous zeolite. The TEM micrograph of this material on collodion coated grid is shown in Figure 4(b).35. This material was expected to have some fine line like structures. But this fine structure was not visible on collodion coated grid due to poor clarity. Many experiments carried out by varying the coating thickness did not help in improving the clarity and therefore it was decided to take the TEM of this sample on grids coated with the polyimide CPI-3b. The results were excellent and it was observed that the polyimide CPI-2b coated grids gave better clarity and even the fine structure of the material could be observed as shown in Figure 4(b).36.

Further studies are going on to optimize the coating conditions to obtain a stable and uniform film. Once these conditions are optimized, this material can infact replace the commercially available coating materials which are very expensive.

4(b).1.4.4 Conclusions

1. Copolyimides based on 20% PPDBN and 80% ODA with dianhydrides SiDA, ODPA and 6-FDA were found to be promising materials as coatings for TEM grids.

2. Morphology of films were dependent on the concentration of coating solution and therefore different type of grids could be made by varying the concentration of coating solutions.

3. This coating materials derived from cashew nut shell liquid can possibly replace the commercially available coating materials because of their excellent properties and low cost.

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20. Obtained from the website www.2spi.com.
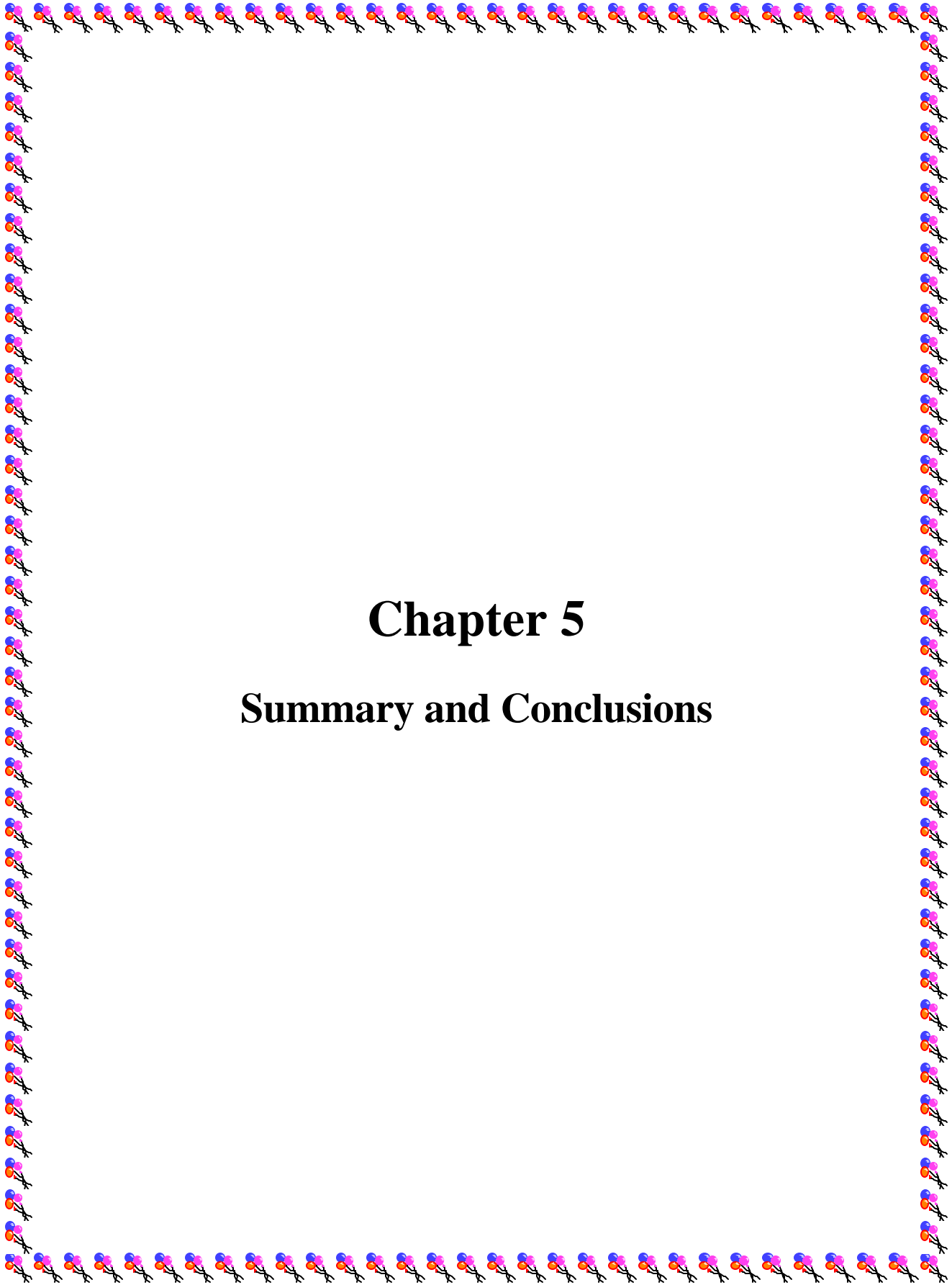
Chapter 5

Summary and Conclusions

5.1 Summary of the work

A summary of the main findings of the present investigations presented in the previous chapters of the thesis and conclusions are given below.

In recent years the synthesis of polymers from renewable resource has attracted considerable attention of researchers all over the world. Cardanol, a natural alkylphenol from cashew nut shell liquid (Anacardium occidentale), a potential natural source for biomonomers, cannot even today be said to have found its niche in terms of an appropriate industrial application. Considerable research work have been done by scientists all over the world to find out the multifarious uses of CNSL and recent investigations have revealed that the constituents of CNSL possess special structural features, which can be chemically transformed into specialty and high value products/ polymers. This study is a part of the ongoing program concerned with the utilization of cashew nut shell liquid for the synthesis of value added products. Thus the main objective of this work was to synthesize some futuristic polymers like polyimides and polyamides that can have specialty application in the field of gas separation membranes, alignment layers for liquid crystal displays and low dielectric materials for interlayer application in semiconductor devices from cardanol. It was expected that the unique pentadecyl group at the m-position in cardanol would improve the solubility, gas permeability properties, pretilt angle and dielectric properties of the resulting polyamides and polyimides.

Aromatic polyimides and polyamides constitute a major class of thermally stable polymers. These polymers possess outstanding thermal stability in addition to other favorable properties such as excellent radiation and solvent resistance, mechanical and electrical properties over a wide temperature range.[1, 2] However these polymers are processable only under extreme conditions, which limit their application areas. Recently significant synthetic effort has been centered on improving the processability and solubility of polyimides and polyamides through the synthesis of structurally modified diamines.[3]

To achieve the above objectives three new diamines namely (1) 4-(3-pentadecylphenoxy)benzene-1,3-diamine (2) 3-pentadecylphenyl-3,5-diaminobenzoate and (3) 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl)benzamide were synthesized in high purity and yields from cardanol. Since it is known that the incorporation of silicon can also

improve the solubility of polyimides and polyamides some silicon containing monomers like bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and bis(4-chlorocarbonylphenyl)dimethylsilane was also synthesized.

Several polyamides were synthesized from these substituted m-phenylene diamines and diacid chlorides namely bis (4-chlorocarbonylphenyl)dimethylsilane (DMSC), terephthaloyl chloride (TPCl) and isophthaloyl chloride (IPCl). The effect of different pendant groups on the solubility, thermal stability, crystallinity and gas permeability properties of these polyamides was investigated. Polyimides having pendant pentadecylbenzoate groups showed better solubility and permeability properties than the polyamides containing pendant pentadecylphenoxy and pentadecylphenoxybenzamide groups. The polyamides based on silicon containing diacid chloride, DMSC showed higher solubility than those based on terephthaloyl and isophthaloyl chlorides. Incorporation of pendant alkyl group did not affect the thermal stability of these polymers significantly. Pendant pentadecylphenoxybenzamide and pentadecylbenzoate groups did not have much effect on the T_g, however the (T_g) was lowered by the incorporation of silicon and pentadecylphenoxy group.

Several new polyimides were also synthesized from these diamines and different dianhydrides. The effect of variation of dianhydrides on the different properties like crystallinity, solubility, glass transition temperature, thermal stability and optical transparency was investigated. Copolymerizaton with some conventional diamine like 4,4'-oxydianiline (ODA) was also done by varying the amine composition to find out the effect of varying ratios of alkyl group on the properties of these ODA based polyimides which are commercially important. Some copolyimides containing 50% SiDA and 50 % other dianhydrides with diamine PPDBN were also synthesized to study the effect of incorporation of silicon on the solubility. The possible application of some of the polyimides as gas separation membranes, alignment layers for liquid crystal display devices, as interlayer dielectrics with low dielectric constant and as coating materials for TEM grids were also explored.

It was observed that the incorporation of alkyl group improved the solubility of polyimides without affecting the thermal stability significantly. Copolymerization helped in

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the improvement of solubility, optical transparency, permeability and dielectric properties of several commercially important polyimides based on ODA. Incorporation of silicon enhanced the solubility and improved the optical transparency the polyimides, wheras the thermal stability and T_g reduced to some extent. The pretilt angle of the polyimides was found to be dependent on the electronic and steric interactions between the polymer chain and liquid crystals. Polyimides PI-1d having favorable interaction with the liquid crystals gave high pretilt angle. TEM grids coated with copolyimides based on ODA and PPDBN showed better clarity than the commercially available polymer coated grids. The existing commercially available grid coating materials are very expensive and the thermally stable polyimides suggested in this study can be a cheaper alternative for TEM grid coatings.

In general this study shows the effective use of a renewable resource cardanol, which is a byprodut of cashew industry in the synthesis of high value products like polyimides and polyamides that can have application as gas separation membranes, alignment layers for liquid crystal display devices, interlayer dielectrics in electronics industry and coatings for transmission electron microscopy grids.

5.2 Conclusions

The conclusions drawn from the present study are given below.

➢ Three new m-substituted phenylene diamines having pendant ether, ester and amide groups along with alkyl and phenyl were synthesized in high yields and purity from cardanol, which in turn is a byproduct of cashew industry.

➢ Many novel polyamides based on these diamines were synthesized and characterized.

➢ Several novel homo and copolyimides were also synthesized and the structure property relationship was studied.

➢ The solubility, thermal properties and crystallinity of polymers are dependent on the nature of both monomers. It was observed that incorporation of pendant bulky groups along with pendant flexible connecting groups in polyamides improved the solubility by without affecting the thermal properties significantly. Here the solubility was found to be dependent on the nature of pendant groups

- Polyimides synthesized from flexible dianhydrides like ODPA, 6-FDA and SiDA and the diamines containing bulky pendant groups show higher solubility than those synthesized from rigid dianhydrides like PMDA, BPDA and BTDA indicating that bulky pendant groups do not improve the solubility of polyimides synthesized from rigid dianhydrides and rigid diamines significantly.

- The thermal stability and glass transition temperatures were dependent on both the monomers. The introduction of alkyl groups decreased the glass transition temperatures to some extent.

- Silicon containing monomers like bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride and bis(4-chlorocarbonylphenyl)dimethylsilane were also synthesized and characterized. Several polyamides, homopolyimides and copolyimides based on these silicon containing monomers showed improved solubility, whereas the thermal stability and T_g decreased to some extent.

- All homo and copolyimides containing pendant bulky groups and silicon showed good optical transparency.

- The tilt bias angles of polyimides PI-1d and PI-1f were determined. The polyimide PI-1d having high solubility, good adhesion, good pretilt angle and high optical transparency seemed to be a potential alignment layer for liquid crystal display devices.

- The gas permeability studies on several polyamides, polyimides and copolyimides showed that, in general gas permeability increases with the incorporation of pendant bulky groups without affecting the selectivity significantly. The incorporation of silicon also improved the permeability. Copolymerization with PPDBN helped in improving the permeability properties of ODA based polymers to some extent.

- The dielectric properties of homo and copolyimides were also evaluated. It was observed that the incorporation of alkyl groups decreased the dielectric constant significantly and the polyimides PI-1d, PI-1e and CPI-2c having dielectric constants lower than 2 in the frequency range 900 kHz to 13 MHz were found to be potential candidates for use as interlayer dielectrics in electronics industry.

- Transmission electron microscopy grids coated with the polyimides based on cardanol gave better clarity as compared to those coated with commercially available coating

materials. These polyimides can be a cost effective alternative for the existing grid coating materials, which are very expensive

➢ The solubility, permeability, dielectric constant and pretilt angle were found to be dependent on the orientation of alkyl groups and the overall conformation of the polymer.

➢ Copolymerization seemed to be a powerful tool for systematically modifying the existing properties of a polymer. The solubility, permeability, morphology and dielectric constant of some commercially important oxydianiline containing polyimides were modified by the incorporation of diamines with pendant bulky groups.

5.3 Perspectives

In general this study opens up a new cost effective and efficient route for the synthesis of novel polyimides and polyamides from a renewable resource cardanol, which have potential in applications like alignment layers for liquid crystal display devices, gas separation membranes, low dielectric materials and coating for transmission electron microscopy grids.

Some suggestions are made for the future work.

The polyamides and polyimides based on cardanol were found to have several applications. Based on the observations in this work several new diamines can be designed and new polymers synthesized to have a further improvement in the properties.

Though it is known that often copolyimides gives higher pretilt angle than homopolyimides, the potential of copolymerization in improving the pretilt angle of the homopolyimides was not explored due to the non availability of the instrument. Further studies can be done to evaluate the pretilt angle properties of the copolyimides. The polyimides particularly of interest are 80:20 copolymers of ODA and PPDBN with different dianhydride because it was observed that different properties of copolyimides deviate from the general trend at this composition. This may be due to drastic change in the overall conformation of the polyimide and needs further investigation

The morphology studies of polyimides seemed to be interesting. Even though in this study we attempted to study the morphology of some polyimides by TEM, good correlations were not obtained. The polyimides showed a morphology in which several hole like structures were distributed all over the film. It was observed that the number and distribution of these so

called "holes" changes with the alkyl group content. Therefore it was assumed that the formation of these holes might be influenced by the free volume and orientation of alkyl groups. Detailed studies are required to find out the effect of pendant group on the formation and distribution of these holes. Literature reports some atomic force microscopy studies on polyimide alignment layers to find out the changes taking place on the alignment surface during rubbing process.[4] They observed some cluster like structures on the films, which could be oriented with the help of a rubbing machine. It will be interesting to study whether the morphology of the polyimides in the present study can be influenced by the rubbing process. If these holes orient depending on the rubbing strength, their dependence on the structure of the polyimide can be confirmed. This will give a clear idea about the observed pretilt angle and permeability properties of these homo and copolyimides. Another important point to be noted is that if they are real holes embedded in the film containing entrapped air they can influence the dielectric property also. A new concept to decrease the dielectric constant of thin organic films has been recently investigated by many researchers. The process is based on the in situ production of micro-voids within the bulk of dielectric film to introduce as far as possible, a sizeable amount of air with a permittivity of 1.0. A detailed study on the morphology will therefore explain the observed low dielectric constants of the polyimides based on cashew nut shell liquid also.

A preliminary attempt to explain the structure property relationships of the polymers in this study based on model structures seemed to be somewhat successful. Detailed modeling studies can help to envisage the dependence of solubility, permeability, pretilt angle and dielectric constant of polymers on orientation of alkyl groups and overall conformation.

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Appendix 1
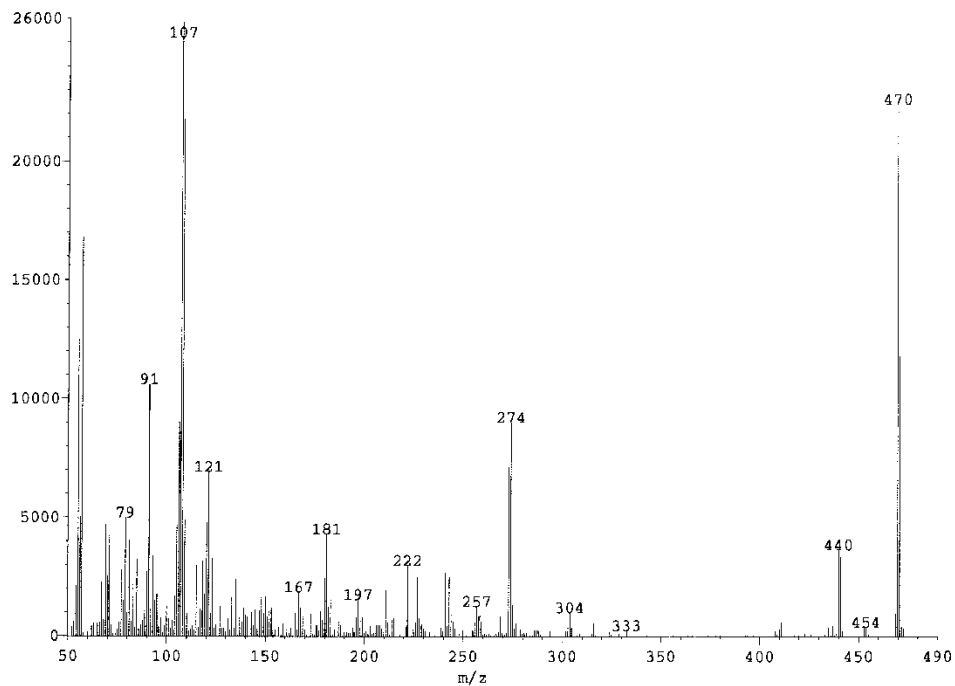
Figure A.1. Mass spectrum of 1-(3-pentadecylphenoxy)-2,4-dinitrobenzene (1b)
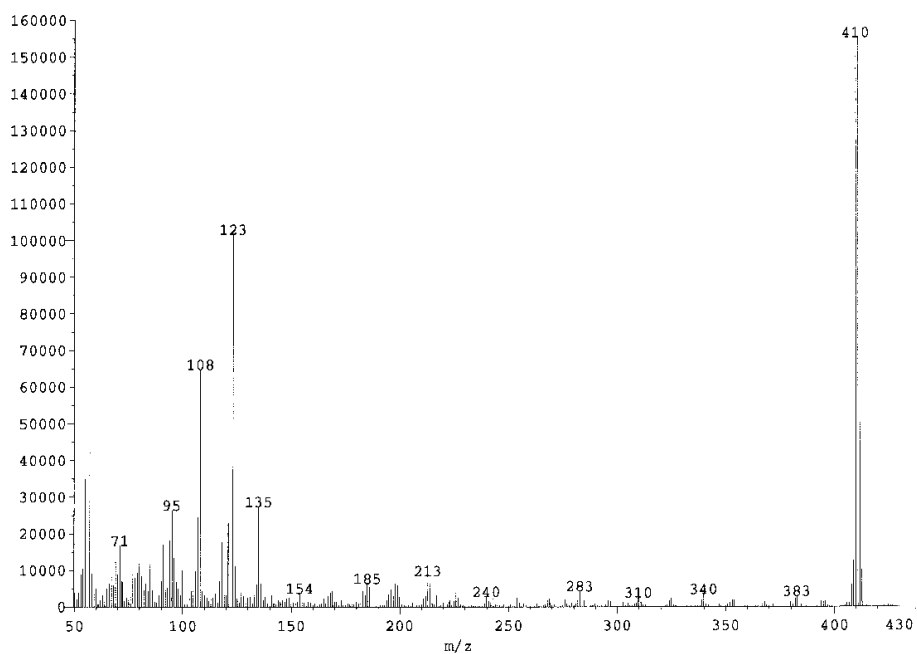
Figure A.2. Mass spectrum of 4-(3-pentadecylphenoxy)benzene-1,3-diamine (1c)

Figure A.3. Mass spectrum of 3-pentadecylphenyl-3,5-dinitrobenzoate (2b)

Figure A.4. Mass spectrum of 3-pentadecylphenyl-3,5-diaminobenzoate (2c)

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Figure A.5. Mass spectrum of 3,5-dinitro-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3c)

Figure A.6. Mass spectrum of 3,5-diamino-N-(4-(3-pentadecylphenoxy)phenyl) benzamide (3d)

LIST OF PUBLICATIONS

1. Synthesis and characterization of silicon containing polyimides
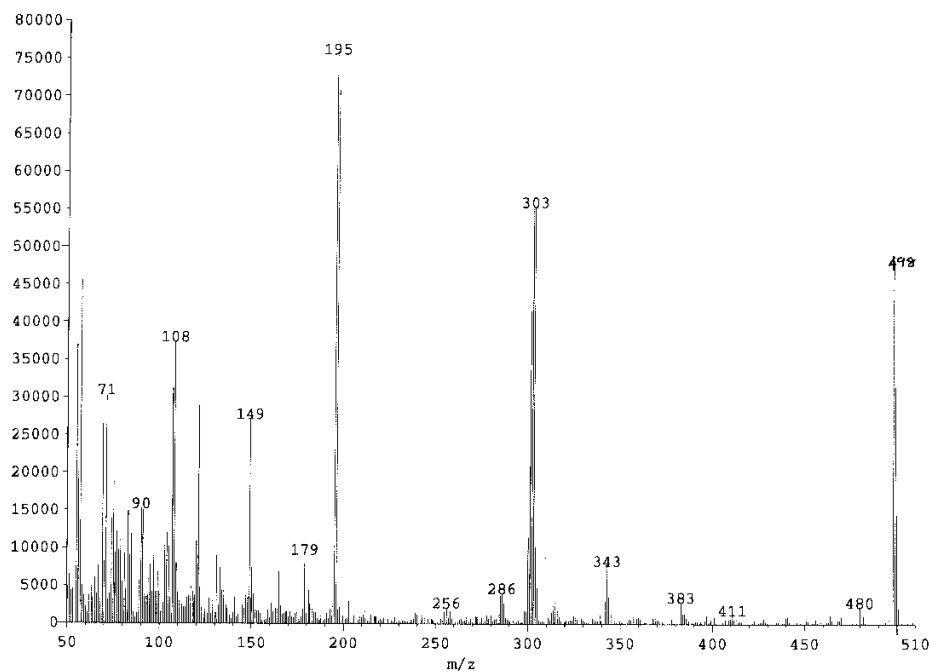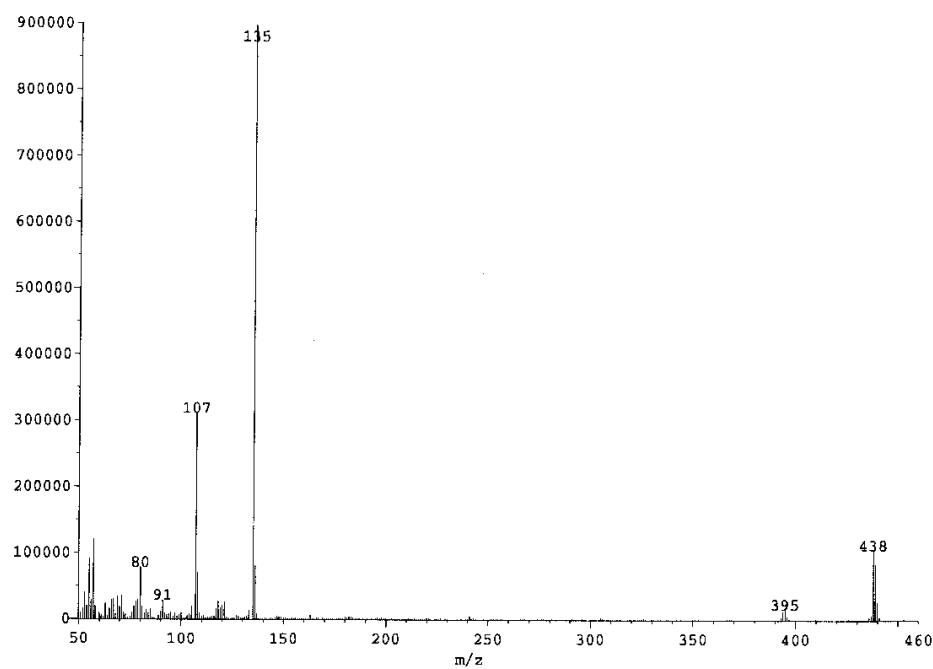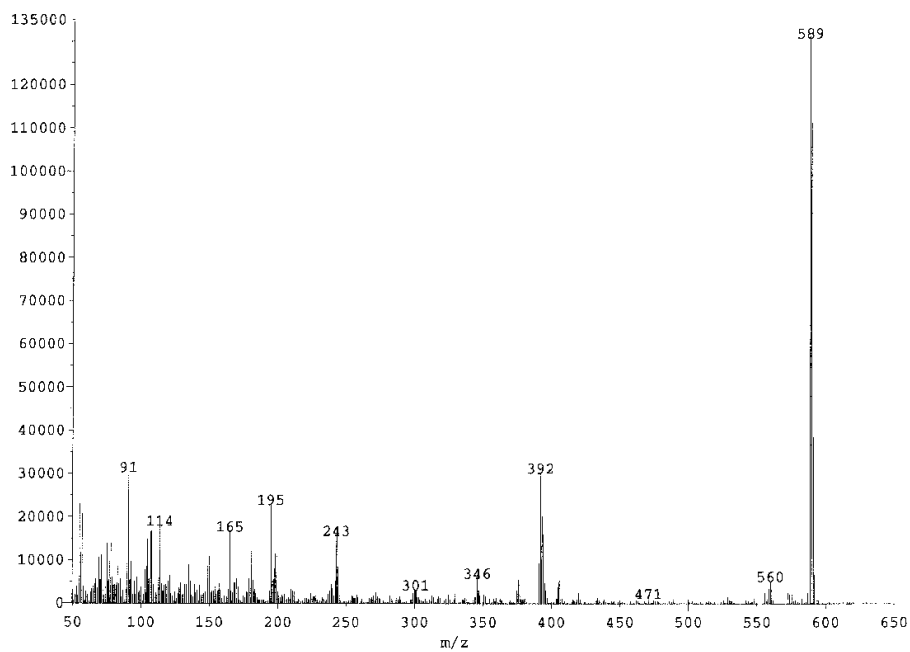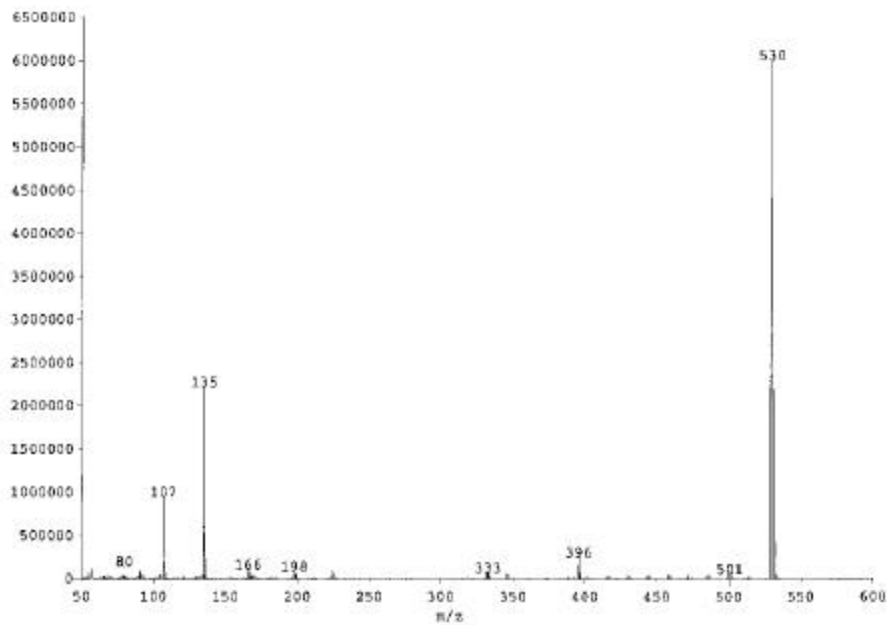   Jinu S. Mathew, Sreelatha S. Panicker, S. P. Vernekar
    In Proceedings of Polymer International Symposium on 'Polymers Beyond AD
    2000', Replika Press Pvt. Ltd., New Delhi, 1999

2. Synthesis and characterization of silicon containing poly (arylates)
    Sreelatha S. Panicker, Jinu S. Mathew, S. P. Vernekar
    In Proceedings of Polymer International Symposium on 'Polymers Beyond AD
    2000', Replika Press Pvt. Ltd., New Delhi, 1999

3. Synthesis, characterization and applications of polyimides containing pendant
    pentadecylphenoxy groups
    Jinu S. Mathew, M. B. Sabne, S. P. Vernekar (To be communicated)

4. Synthesis, characterization and applications of polyimides containing pendant
    pentadecylbenzoate groups
    Jinu S. Mathew, Sreelatha S. Balamurugan and S. P. Vernekar (To be
    communicated)

5. Synthesis, Characterization and Applications of polyimides containing pendant
    pentadecylphenoxybenzamide groups
    Jinu S. Mathew, Sreelatha S. Balamurugan and S. P. Vernekar (To be
    communicated)

6. Synthesis, characterization and applications of polyamides from diamines based   on
    cashew nut shell liquid
    Jinu S. Mathew, M. B. Sabne, and S. P. Vernekar (To be communicated)

7. Dielectric properties of homo and copolyimides containing pendant bulky aralkyl
    substituents
    Jinu S. Mathew and S. P. Vernekar (To be communicated)

LIST OF PATENTS

1. New substitited dinitro compounds and a process for the preparation thereof.
    Jinu S. Mathew, S. P. Vernekar and Reges Mercier (Indian and US patents applied)

2. New substituted phenylene diamino compounds and a process for the preparation
    thereof.
    Jinu S. Mathew, S. P. Vernekar and Reges Mercier (Indian and US patents applied)

3. Novel polyimides and a process for the preparation thereof
    Jinu S. Mathew, S. P. Vernekar, Reges Mercier and Rachid Kerboua (Indian and US
    patents applied)

4. Novel polyimides with low dielectric constant from cashew nut shell liquid
    Jinu S. Mathew and S. P. Vernekar (Indian and US patents applied)

5. Novel Polyimides having pendant pentadecylbenzoate and pentadecylphenoxy benzamide groups and a process for the preparation thereof
    Jinu S. Mathew, Sreelatha S. Balamurugan, M. B. Sabne and S. P. Vernekar (Indian and US patents applied)

6. Thermally stable polyimide coating materials for TEM grids with high clarity
    from cashew nut shell liquid
    Jinu S. Mathew, R. Pasricha, M. M. Bhadbhade and S. P. Vernekar (Indian and US patents applied)

Synopsis

In recent years, the synthesis of polymers from renewable resources has attracted considerable attention of research workers through out the world. This necessitates a look at the renewable natural resources that can serve as alternative feed stocks for monomers of the polymer industry. In this respect, cashew nutshell liquid, an agricultural byproduct abundantly available in the country, holds considerable promise as a source of unsaturated hydrocarbon phenol, an excellent monomer for polymer production[1]. Cardanol, a natural alkylphenol from cashew nut shell liquid (Anacardium occidentale) (CNSL), a potential natural source for biomonomers, have not even today found its niche in terms of an appropriate industrial application. Recent investigations, however, revealed that the constituents of CNSL possess special structural features, which can be chemically transformed into specialty and high value products/ polymers. Though there have been few attempts on the synthesis, chemical modification, and functionalization of cardanol and its polymers, only few reports are available on the use of cardanol in the synthesis of high value polymers used in speciality applications such as alignment layers for liquid crystal display devices and gas separation membranes. As part of the ongoing program concerning utilization of CNSL from Anacardium occidentale as starting material for the preparation of useful compounds, we attempted the synthesis of some futuristic products like polyimides and polyamides having specialty applications, from cardanol.

Aromatic polyamides and polyimides constitute a major class of thermally stable polymers. These polymers possess outstanding thermal stability in addition to other favorable properties such as excellent radiation and solvent resistance, mechanical and electrical properties over a wide temperature range.[2, 3] This resulted in the synthesis of a large number of polyimides and polyamides with diverse structures. However these polymers due to strong enthalpic interactions and minimal increase in conformational entropy associated with their dissolution or melting are basically processable only under extreme conditions, which limit their application areas. Thus the enhancement of solubility of these polymers without sacrificing their excellent properties became the object of wide spread study. [4, 5] Attempts to improve the solubility of polyamides and polyimides have been numerous and a number of strategies have been adopted. These strategies have mainly focussed on chemical modifications, mainly by preparing new monomers that provide less molecular order,

torsional mobility and lower intermolecular bonding. Of the vaious alternatives to design novel processable polyamides and polyimides, some general approaches have been universally adopted[5,6]. These include (1) introduction of aliphatic or other kinds of flexible linkages that reduce chain stiffness (2) Introduction of bulky side substituents, which help for the separation of the polymer chains and hinder molecular packing and crystallization (3) use of enlarged monomers containing angular bonds, which suppress coplanar structures (4) use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers, which lower regularity and molecular ordering (5) Copolymerization of two or more diamines or dianhydrides.

There are examples of polyamides and polyimides in the literature from meta substituted diamines having pendant alkyl, aryl, ether, ester or amide groups. These substituents are known to favorably modify the solubility of the polymer. It is possible that a combination of one or more of the above substituents may provide better solubility for the polymer. Therefore we planned to prepare polyamides and polyimides containing pendant pentadecyl phenyl group and any of the other flexible groups like ether, ester or amide. To achieve this a naturally occurring meta substituted long chain phenol, cardanol, a byproduct of cashew industries, is made use of to synthesis diamines and corresponding polyamides and polyimides. With these objectives, the following specific problems were chosen for the present work.

- Synthesis and characterization of meta phenylene diamines containing at least one pendant pentadecyl group along with phenoxy, benzoate or benzamide pendant groups, utilizing cardanol from cashew nut shell liquid

- Synthesis and characterization of polyamides from diamines having pendant bulky groups

- Synthesis, characterization and applications of polyimides from diamines having pendant bulky groups.

Chapter 1 presents a detailed review of literature on the application of a naturally available and economically viable biomonomer, cardanol, (a constituent of cashewnut shell liquid) in the production of specialty and high value polymers. Emphasis is given for different

types of polymers that have been synthesized from cardanol. This chapter also discusses the scope and objective of the thesis in detail.

Chapter 2 presents a detailed study on the synthesis of different dinitro compounds and the corresponding diamino compounds from cardanol, which are useful monomers in the synthesis of processable polyamides and polyimides The diamines synthesized were (i) 4-(3-pentadecylphenoxy)benzene-1,3-diamine (ii) 3-pentadecylphenyl-3,5-diaminobenzoate (iii) 3,5-diamino-N-(4-(3- pentadecylphenoxy) phenyl) benzamide. These diamines were characterized using NMR, IR and elemental analysis.

Chapter 3 presents a detailed study on the synthesis and characterization of polyamides from the substituted meta phenylene diamines mentioned in *chapte*r 2. The polyamides were characterized by IR spectroscopy, inherent viscosity, elemental analysis, solubility tests, X-ray diffraction studies, differential scanning calorimetry and thermogravimetric analysis. These polyamides were found to have better solubility than the corresponding polyamides prepared from unsubstituted meta phenylene diamine. Even though the T_g values were comparatively lower than the corresponding unsubstituted polyamides, all the polyamides synthesized in the present work have good thermal stability. X-ray diffraction studies showed an amorphous nature for most of the polymers.

Chapter 4 presents a detailed study on the synthesis and characterization of homopolyimides and copolyimides from the substituted meta phenylene diamines. In the case of homopolyimides six different dianhydrides were condensed with these diamines by a high temperature one step process. The dianhydrides used are pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylicdianhydride (BPDA), 3,3',4,4'-benzophenone tetracarboxylicdianhydride (BTDA), bis(3,4-dcarboxyphenyl)etherdianhydride (ODPA), 1,1,1,3,3,3-hexafluoro-2,2-bis(3,4-dcarboxyphenyl)propanedianhydride (6-FDA), bis(3,4-dicarboxyphenyl) dimethylsilanedianhydride (SiDA). These polyimides were found to have better solubility than the corresponding polyimides prepared from unsubstituted meta phenylene diamine. Eventhough the T_g values were comparatively lower than the corresponding unsubstituted polyamides, all the polyamides synthesized in the present work

have good thermal stability. X-ray diffraction studies showed an amorphous nature for most of the polymers. To study the effect of copolymerization on the different properties of the above polyimides some copolyimides were synthesized from 4-(3-pentadecylphenoxy)benzene-1,3-diamine and oxydianiline by reacting with anhydrides ODPA, 6-FDA and SiDA by a one step high temperature process. The application of these polymers as gas separation membranes and as alignment layer for liquid crystals is also discussed.

Key references

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