The objective of this book is to highlight the use cyclopentanone as a starting material to design and produce several difunctional monomers such as aromatic diamines, diacids used to synthesize aromatic high performance polyamides. Important considerations in designing monomers are: i) meta- linkage introduces “kinks” to the main chain which decrease the rigidity of the polyamide backbone and inhibit packing, thus reducing the interchain interactions leading to enhanced solubility, ii) the presence of cardo cyclopentane ring in the polyamide backbone reduces strong molecular interactions of stiff-chain aromatic polyamides, producing an effective chain separation effect and which help in enhanced processability, iii) the presence of flexible methyl group on aromatic ring offers asymmetry to the polyamide backbone leading to constitutional isomerism, which could impart interesting properties to the polyamides. The second objective of this book is to present investigated effect of incorporation of pendent or cardo cyclopentane ring on the properties of polyamides, such as solubility, inherent viscosity, crystallinity, glass transition temperature and thermal stability.

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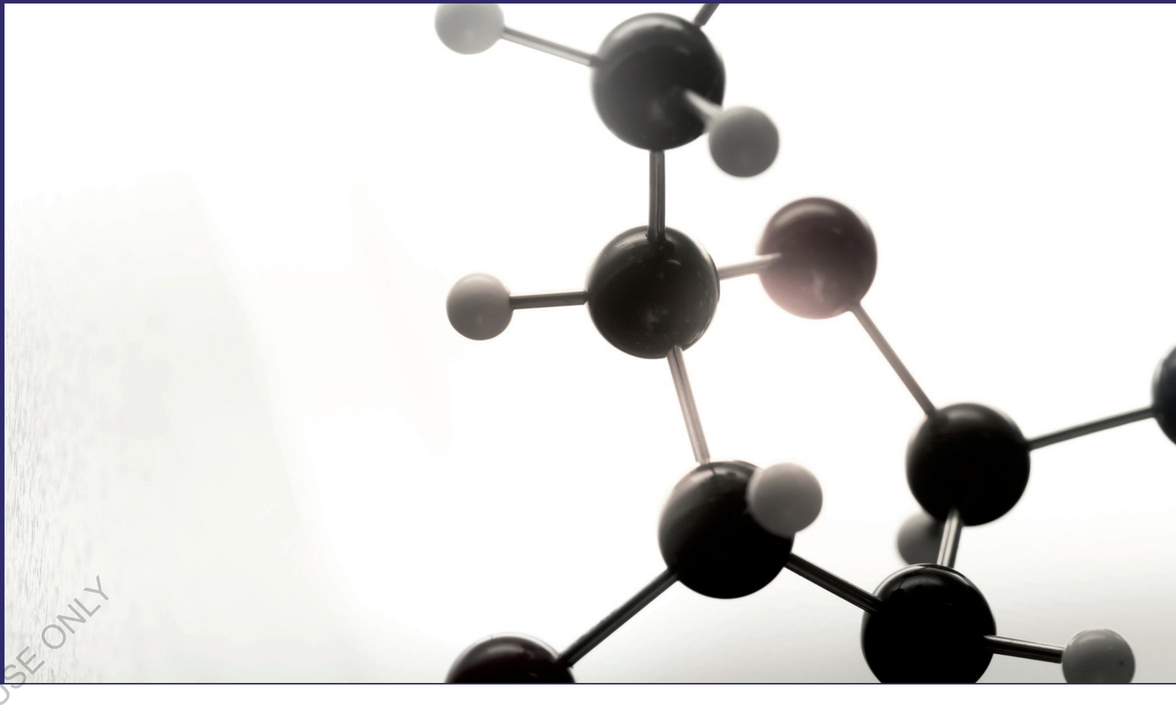
Processable High Performance Polyamides

Ankushrao, Ghanwat



Sanjay Ankushrao
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Synthesis, Characterization and Property of processable high performance polyamides containing cardo moiety

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Contents

Preface

This book is addressed principally to graduates, undergraduates and researchers in the field of polymer chemistry at the beginning of their research careers. The main goal is to bring to their notice some of the synthetic pathways used in high performance aromatic polyamide synthesis. High Performance Polyamides is one of the specialty areas within polymer science. These aromatic polyamides are used as high-strength and flame resistant fibers and coatings, with applications in the aerospace and armament industry, bullet-proof body armor, protective clothing, sport fabrics, electrical insulation, asbestos substitutes, and industrial filters, etc.

Candidly, the whole field of high performance polyamide synthesis could not be covered in a book of this size. A large part of the book is concerned with basics of high performance polymer chemistry, reactions and pathways which lead to the formation of various monomers such as diamines, diacids. The more emphasis has been also given to the synthesis of various polyamides by using newly designed and synthesized monomers. The characteristics and property study of all polyamides and their structure-property relationship has been explained which helps new researcher to learn the design and synthesis of monomer and polyamides therefrom as per need and applications.

We want to take this opportunity to thank our family and friends for constant support throughout the work of this book. Our special thanks to all management staff and colleague from School of Chemical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur and Vivekanand College (Autonomous), Kolhapur, Maharashtra, India.

1.1 Introduction to Polymers

Man’s discovery for new and improved materials has been expanding with time and it can be said to be undying. The materials that have come up into familiarity and acceptance with the ages since the emergence of man’s existence on the mother planet, the earth are: pieces of rocks, sand, soil, stones and various ceramic items; skins and bones of animals; horns, nails; leaves, wood and plant fibres, covering grass and cotton, coir, straw, hemp, jute, wool, hair and many other fibres of plant and animal origin; silk fibre of insect origin; natural adhesive/film-forming gums and resins (e.g. agar, rosin, algies, shellac etc.); fossil fuels, viz., lignite, coal, natural gas and petroleum; quartz, glass, metals and alloys extracted from minerals and ores. Polymers, as a class of materials with potential for use as resins, plastics, rubbers and composites, and as laminates, adhesives and coatings came nearly in the end of the series of discoveries and developments of materials. Unfolding of the science of polymer-based materials and polymers really had its beginning and progress in the second and third decade of the twentieth century.

Even if polymers introduced very late in the chain of materials, they cover a major place and crucial position in our materials map today. As far as concerning application prospects, performance characteristics, property range and diversity, they proffer novelty and versatility that cannot match by any other kind of materials. Polymers have gone deep and wide in moulding the now a day human civilization and culture. Even though scientists, particularly the chemists used to talk earlier about polymers of early twentieth century, there remained a lot of confusion over the basic understanding of the structures of polymer molecules. It was a common experience for chemists working with polymers that, most such materials were very viscous and sticky under melt or solution conditions. One could readily draw them into fine filaments or spread the melt or solution into thin films. In solution, they were recognized more as colloids or associated molecules. Attempts to find their molecular weights from dilute solutions in suitable solvents by cryoscopy often produced doubtful and uncertain and sometimes very high values. For cellulose derivatives, rayon and natural rubber molecular weights ranging 45,000-50,000 or even higher were measured. Such high molecular weight values realized that the relevant polymer molecules were really very large; but this thing was not accepted in view of a total lack of structural concept about such large or big molecules. The chemists continued to prefere the concept of large associations of much smaller molecules of short chain or cyclic structures. A state of growing crisis and confusion imparted fresh encouragement to the thinking about the shape, size, complexity and behavioral patterns of the molecular systems called polymers [1, 2].

Polymers form a very important class of materials without which the life seems to be very difficult. The Polymer is a Greek word (poly means much or many and mer means part), and represents a big molecule constructed by repeating structural units of same or different molecules associated through covalent chemical bonds. In other words polymers are huge molecules of high molecular weight called macromolecules, which are prepared by linking together of a large number of small molecules, called monomers. The reaction where monomers associate and form polymer is known as polymerization. Polymers are substances in which molecules have higher molar masses with variety of physical and chemical properties.

1.1.1 Classification of Polymers

- **Based on Source of Polymer**

a) **Natural Polymers**: These are naturally occurring polymers originate in plants and animals. e.g. proteins, cellulose, starch, resins and rubber

b) **Semi-synthetic Polymers**: These polymers are derived from natural polymers by some chemical modifications. e.g. Cellulose derivatives as cellulose acetate, cellulose nitrate, etc.

c) **Synthetic Polymers**: Synthetic polymers are man-made polymers synthesized in the laboratories or industries used in daily life.

e.g. Polyethylene, polyvinyl chloride, nylon, terylene, Teflon bakelite, synthetic fibres (nylon 6, 6), synthetic rubbers (Buna-S), polypropylene, etc.

- **Based on Backbone of the polymer chain**

a) **Organic Polymer:** A polymer whose backbone chain is fundamentally made of carbon atoms is termed as organic polymer. The atoms attached to the side valencies of the backbone carbon are usually those of hydrogen, oxygen, nitrogen, etc. The majority of synthetic polymers are organic.

b) **Inorganic Polymers**: A Polymer whose backbone contains no carbon atom is called inorganic polymers.

e.g. Glass, silicone rubber, zeolites, polyphosgene, sulfur nitride, etc.

- **Based on Structure of Polymers**

a) **Linear Polymers:** These polymers contain long and straight chains. Linear polymers are comparatively soft, often rubbery substances and often likely to soften (or melt) on heating and to dissolve in certain solvent. e.g. high density polyethylene, linear PVC, polystyrene, etc.

b) **Branched Polymers:** These polymers comprise linear chains having some branches. e.g., low density polythene, starch, glycogen, etc.

c) **Cross-linked Polymers:** These are usually formed from bi-functional and tri-functional monomers and comprise strong covalent bonds between numerous linear polymer chains. Cross linked polymers infusible and insoluble. e.g. vulcanized rubber, urea-formaldehyde resins, phenol-formaldehyde, melamine formaldehyde, epoxy resin, etc.

- **Based on Composition of Polymers**

a) **Homopolymer:** A polymer resultant from the polymerization of a single type of monomer.

b) **Copolymer:** When two different types of monomers are linked in the same polymer chain, the polymer is called a copolymer. A copolymer is a polymer derived from two (or more) monomers.

e.g. SBR, Nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate, etc.

There are four sub types copolymers

1. **Random Copolymer:** In these polymers, the two monomers may follow any order.
2. **Alternating Copolymer:** in these polymers, the two monomers arranged in alternating fashion.
3. **Block copolymer:** A block copolymer can be synthesized by controlled polymerization of one monomer followed by chain extension with different monomers.
4. **Graft copolymer:** A graft copolymers can be prepared by one kind of monomers in their main chain and another kind of monomers in their side chains.

- **Based on Mode of Polymerization**

a) **Addition Polymers:** The addition polymers are designed by the repeated addition of monomer molecules possessing double or triple bonds. e.g. polythene from ethane, polypropene from propene, Buna-S, Buna-N, etc.

b) **Condensation Polymers**: The condensation polymers are designed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units by the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. e.g. Polyamides, polyimides, polyazomethines, polyesters, polycarbonates, etc

- **Based on Molecular Forces or ultimate use of polymer**

The mechanical properties of polymers are ruled by intermolecular forces (van der Waals forces and hydrogen bonds) present in the polymer, these forces also bind the polymer chains. Under this category, the polymers are classified into the following groups on the basis of amount of intermolecular forces present in them, they are as below

a) **Elastomers:** These are rubber-like solids with elastic properties. In these elastomeric polymers, the polymer chains have random coiled structure, they are held together by the weakest intermolecular forces, so they are highly amorphous polymers. These weak binding forces allow the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber e.g. Polyisoprene, SBR, neoprene, etc

b) **Fibers:** Fibres are thread- like polymer possessing high tensile strength and high modulus. These characterizations are due to strong intermolecular forces like hydrogen bonding which results in close packing of chain impart crystalline structure to the polymer. e.g. Nylon 6, 6, terylene, Nylon 6, silk, etc.

c) **Liquid Resins:** Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins. e.g. epoxy adhesives, polysulphide sealants, polyvinyl acetate, etc.

d) **Plastics:** A polymer is shaped into hard and tough utility articles by the application of heat and pressure; it is used as a 'plastic'. The intermolecular forces between polymeric chains of plastic are intermediate between elastomers and fibers, so they are partly crystalline. e.g. polystyrene, PVC, polymethyl methacrylate, etc.

- **Based on Thermal behaviour of polymers:**

a) **Thermoplastic:** Many polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times, such polymers are termed 'thermoplastics'. These are the linear or slightly branched polymers capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction are in between elastomers and fibres. e.g. Polyethylene, PVC, nylon, polystyrene, sealing wax, etc.

b) **Thermosetting plastic:** These polymers undergo some chemical change on heating and convert themselves into an infusible mass. Such polymers are called 'thermosetting" polymers. These polymers are cross linked or heavily branched molecules, which on heating undergo wide cross linking in moulds and again become infusible and cannot be reshaped. e.g. bakelite, urea-formaldehyde resins, phenol-formaldehyde, melamine formaldehyde, etc.

1.2 High performance polymers

This type of polymer is one of the domain areas within polymer science. It has been renowned as a separate area within polymer chemistry for more than 60 years. Like many scientific faculty, it has received most of its impetus from the space program owing to the need for ablative systems, high temperature adhesives, coatings, heat- and flame-resistant fibers.

High performance polymers include all polymeric materials which can withstand thousands of hours at 230°C, hundreds of hours at 300°C, minutes at 540°C or seconds up to 760°C and have outstanding mechanical, optical, electrical, surface and rheological properties [6]. High performance polymers such as poly(ester-amide)s, poly(ether-amide)s, poly(ester-imide)s, poly(ether-azomethine)s and polyesters with higher thermal stability and better mechanical properties have been identified for a variety of applications, such as in optical and electronic devices, as engineering plastics for aerospace industries, and also as films or membranes [7-11]. The high regularity and high rigidity of the backbone of high performance polymers results in strong interchain interactions, low solubility and high melting points. Therefore, inspite of having excellent combination of properties, most of the high-performance polymers have some severe drawbacks, e.g. insolubility in common organic solvents, intractability and infusibility that make their processing difficult and often limit their utility in various advanced technological applications.

In order to improve processability of high performance polymers, several approaches have been used (Figure 1.1) which includes:

These structural features tender molecular dissymmetry; hinder close interchain packing and increase free volume resulting into improved solubility and processability of the polymer. Further, the improvement in processability should be carried out without scarifying the thermal stability [12].

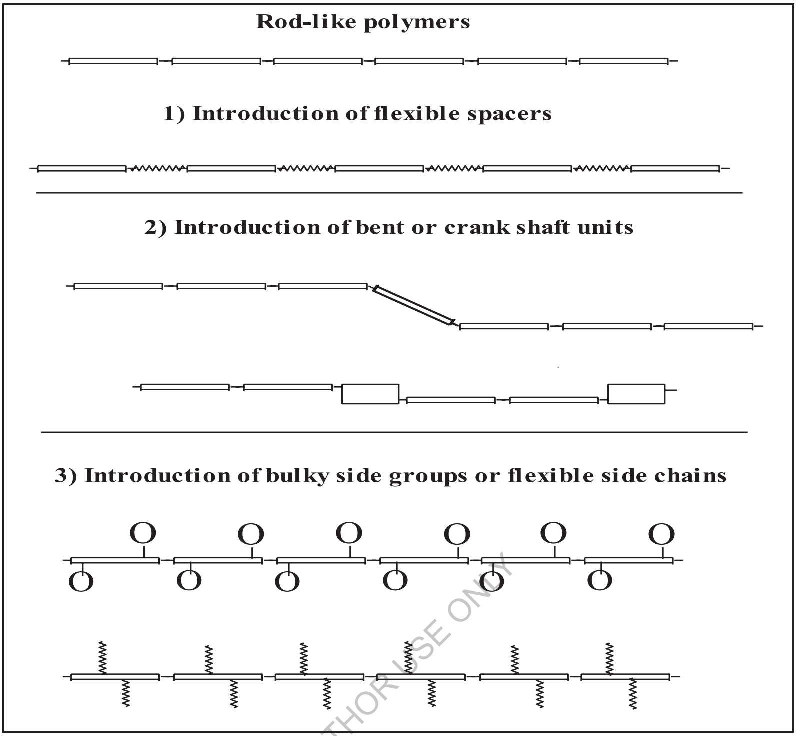


Fig 1.1. Macromolecular approaches for improving processability of high Performance polymers

1.2.1 Brief History of high performance polymers [HPP]

Prior to early 1500's, British pioneers exposed the ancient Mayan civilization in Central Asia, for the first time they set up application of polymers, as their children started playing with balls ready from local rubber trees. In 1839, Charles Goodyear produced the vulcanization method which converted the sticky latex of natural rubber to a useful elastomer for tire synthesis [13]. In 1847, Christian F. Schonbein reacted cellulose with nitric acid to obtain cellulose nitrate [14], which was used in 1860 as a first man made thermoplastic (celluloid) [15]. In 1907, Leo Baekeland produced bakelite (phenol formaldehyde) and its maximum heat resistivity made it a dazzling selection as an electric insulator [16]. In 1920, Staudinger concluded in his paper entitled

"Uber Polymerization", this paper indicated a decade of strong research for the development of modern polymer theory. In 1927, large scale production of vinyl chloride resins began, which is widely used nowadays to build plastic bottles, plumbing (PVC) pipes and tiles.

All through the 1930-38, Du Pont and his coworkers in USA had manufactured a variety of novel polymers including synthetic rubber, polystyrene and more exotic materials such as Teflon and nylon [17].

In 1938, Dow had manufactured for the first time numerous tones of polystyrene while polyethylene was made in 1941 by scientist at ICI in England [18]. After second world war, when many natural occurring materials, such as heavy rubber were in shortage then some exertion had been taken to develop innovative material, especially synthetic rubber. In 1950, Ziegler and Natta independently established a family of stereospecific transition metal catalysts that lead to the commercialization of polypropylene as a commodity plastic [19].

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

In 1960-1970 [20], the progress of high performance polymers that could participate constructively with more traditional materials, such as metals, for aerospace and automotive applications. The several polymers have been developed and more will be synthesized in future.

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

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

The longtime goals of the high temperature polymer chemists have been to achieve a material, which can exist for a long period in air at 500°C. In the beginning era of high performance polymers, the stabilities were in the range of 400°C to 500°C in air. Within six years the development of these polymers for thermal properties up to 600°C in air were realized. Up to that stage, poly(phenylene)s and poly(quinoxaline)s were of the highest thermal stability among all these types of polymers. Later on, many different heat-resistant polymer systems have been stated and some of these materials are now commercially available. The evolution of these types of polymers is outlined in **Table 1.2.**

By the mid-1960s true limitations in stability were suspected and the problem of tractability was readily marked. The research at that point began for modification of known systems to make them more soluble and processable materials. These structural alterations included reduction of phenylation of the backbone, crystallinity and introduction of flexible/bridging functional groups such as ether, alkylene, sulfone etc., co-polymerization and constructing random unalike backbone structure.

Table 1.2 List of high performance polymers (HPP) along with their year of reporting/commencement

Polymers	Year Reported/ Introduced	References
Poly(phenylene sulfide)s	1948	21
Poly(benzimidazole)s	1961	22
Polyimides	1962	23-25
Poly(quinoxaline)s	1964	26,27
Poly(amide-imide)s	1965	28
Poly(aryl-sulfone)s [Astrel*3600]	1967	29
Poly(phenyl quinoxaline)s	1967	30
Poly(imide)s containing hexafluoroisopropylidene group	1968	31
Bismaleimide resins	1970	32
Aromatic polyamides [PRD-49, Kevlar*]	1970	----
Norbornene-terminated polyimides(PMR-15)	1972	33
Ethenyl-terminated polyamides (Thermid*600)	1974	34
Poly(ether-imide)s (Ultem)	1974	35
Polyimide containing indane (Matrimid*)	1975	36
Liquid crystalline polyesters [Poly(4-benzoate) Ekonol*]	1976	37
Poly(ketoimide)s (LARC-TPI)	1976	38,39
Rigid rod like (PBT, PBI, PBO) Semi crystalline polyimides (LARC-CPI, New TPI)	1981 1987	40,41,42
Poly(arylsulfone)s (Radel*c)	1989	----

1.2.2 Factors influencing heat resistance property

Earlier work discovered numerous factors that contribute to the thermal stability of polymers. Some of these are rigid intra-chain structure, primary bond strength, secondary bonding forces, molecular weight, resonance stabilization, molecular weight distribution and stable end groups on the molecules. The chemical factors that influence thermal stability, mechanical properties and toughness of these polymers are as follows [43-46].

1.2.2.1 Primary bond strength

Primary bond strength is the single most significant factor which influences heat resistance. Bond dissociation energy [47, 48] of carbon-carbon single bond is 350 KJ/mol, that of carbon-carbon double bond is 610 KJ/mol and of aromatic systems it is even higher. As a result aromatic and heterocyclic rings are extensively used in the thermally stable polymers. The key requirements for high temperature resistant polymers are higher softening point and resistance to thermal oxidation. In terms of molecular structure these demands may be met by numerous ways. The higher bond strength in inorganic polymers could offer the potential for good high resistance property. Carbon-fluorine bonds have greater bond strength than carbon-hydrogen or carbon-carbon bonds; therefore fluoro polymers are extremely resistant to oxidative degradation. They also have superb resistance to chemical and solvent attack.

1.2.2.2 Secondary or Van der Waals bonding

The presence of these forces offers additional strength and thermal stability to the polymer. Dipole-dipole interactions and hydrogen bonding contribute towards molecular stability and affect the cohesive energy density, which impacts on the stiffness, Tg, melting point and solubility.

Resonance stabilization, mechanism of bond cleavage, rigid intra-chain structure, molecular symmetry (structural regularity), branching and cross-linking also affect the properties of a polymer. Physical properties of polymer are also influenced by atomic interaction between chain atoms. The flexibility of the chains, the ability of polymers to crystallize and the spacing of polar groups are of considerable importance.

The heat resistant polymers often contain polar groups e.g. –SO_2–, –CO–, etc. that participate in strong intermolecular association. Polymer containing electron-withdrawing group e.g. -SO_2-, -CO-, etc. as connecting groups are generally more stable than those containing electron-donating group like –O–. The substitution of aromatic or heterocyclic ring in the polymer backbone leads to rigid structure. The *p*-oriented aromatic polymers have lower solubility and processability compared to that of *m*-oriented aromatic polymers. Cross-linking increases heat resistance of a polymer and branching in a polymer tends to lower thermal stability.

1.2.2.3 Stability and processability of polymers

Most high temperature resistant polymers are composed mostly of aromatic or hetero-aromatic units. The chemical structure that makes a polymer thermally stable also makes it difficult to form into useful items because of limited solubility and moldability.

The high rigidity and regularity of the backbone of certain high performance polymers results in high melting points, high crystallinity, low solubility and strong chain-chain interaction. Thus processing of rod like polymers is often difficult. The research at present is to transform the known thermally stable polymers than finding new classes to improve thermal stability. Several approaches have been used to revise the structural unit of rod like polymers. They are:

1. Insertion of flexible spacers in the rigid units.
2. Insertion of “bent” or “crank shaft” units, along the aromatic backbone.
3. Affixing of bulky pendant groups or flexible side chains to aromatic backbone.
4. Copolymerization to form random or alternative copolymers.

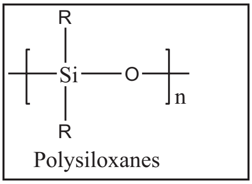
Thermal stability of polymers is related to crystallinity, high rigidity and cross-linking. To achieve good thermal stability, weak links to be avoided are mostly alicyclic, alkylene, nonaromatic, unsaturated hydrocarbons and –NH– linkage. Thus, there should be a satisfactory balance of thermal stability and solubility. Carboxylic acid derivatives (amide, imide), sulphones in the backbone of polymers are proven to be good attempts. The insertion of aromatic pendant group reports good solubility without negotiating the thermal stability.

The approach of novel engineering advanced polymer development covers a multitude of areas. Among these “High Performance Polymers” not only meet unusual requirements for long term durability at elevated temperature; they may also have distinctive and various characteristics such as insulating properties, conductivity, self – extinguishing, chemical resistance and selective gas barrier properties. They are in normal applications as films fibers, adhesives, elastomers and coatings as well as injection moldable materials, in enormous number of areas including medical, automobile, sophisticated high tech instruments, construction, agricultural and aero-space etc. Some of the industrially important classes of high performance and thermally stable classes of polymers are concisely discussed below.

1.3 Types of high performance polymers

1.3.1 Inorganic Polymers

The polymers containing elements other than carbon in backbone are known as inorganic polymers. Many exertions were dedicated to produce inorganic polymers [49-52]. Silicon elastomers are outstanding in retaining its elastic properties over the widest temperature range and mainly at the low temperatures. However, with the single exception of the silicon polymers *i.e.* Polysilioxanes, consisting of following repeating unit, none has attained commercial significance. Polysilioxanes often import poor stability to hydrolysis.


$$\left[-\underset{R}{\overset{R}{Si}}-O- \right]_n$$

Polysiloxanes

Silicons polymers with R- either methyl or mixed – phenyl groups have very low T_g values (about -100^{0}C). The high molecular weight silicon rubbers offer not only good high temperature resistance but also good low temperature flexibility. Cross-linked silicon has found minor use as glass reinforced thermosetting plastics for high temperature electric insulation purpose and other special applications.

1.3.2 Organic polymers

There have been ongoing strong efforts since the late 1950s to synthesize organic high temperature resistant polymers. The organic heat-resistant polymers possess the properties such as high stability to various environments (solvent, UV, chemical and oxygen), dimensional stability at higher temperature that match to other polymers at lower temperature and high mechanical strength and modulus. The motivation for heat-resistant polymers comes from the needs in such technological areas such as electronics and defense, advanced air and space-craft as well as consumer applications.

The main necessities for high-temperature polymers are high softening point and resistance to thermal oxidation. The most successful approach to the designing of high temperature resistant polymers, especially for the most important areas of applications has been to use features of polymer chain composed of phenyl rings i.e. of aromatic rings.

1.3.3 Fluoropolymers

The polymer of tetrafluoroethylene was discovered by R. J. Plunkeett [53]. Carbon-fluorine bond have higher bond strength than carbon-carbon and carbon – hydrogen bonds. Fluoropolymers are tremendously resistance to attack by the free radicals involved in oxidative degradation and hence to thermo-oxidative degradation. In addition they have excellent resistance to chemicals and solvent attack. e.g. Polytetrafluoroethylene [PTFE]

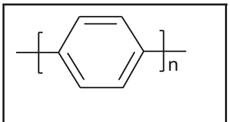
Fluoropolymers applications include mechanical (piston rings, seals, bearings), electrical (tapes, coaxial cable), antistick coating for cookware, chemical resistance parts (gaskets, pipe liners, tapes), self-lubricating parts and micro powders (used in plastics, links, lacquer, lubricants, furnishes). A unique application of Fluoropolymers is protection of Statue of Liberty against corrosion. The applications for fluoropolymers are specialty applications [54]; however they are restricted by their high cost.

1.3.4 Aromatic Polymers

The most successful approach to the design of high temperature resistant polymers, especially for the most important areas of application as plastic materials, has been to utilize the advantageous features of polymer chains composed of linked benzene rings *i.e.* of aromatic rings. Such polymers combine two main requirements for high temperature resistance. First, they have good oxidative resistance, since the C–H bonds of the benzene rings resist abstraction by the chain propagating free radicals compared with aliphatic C–H bond. It is roughly true that a polymer susceptibility to thermal oxidation correlates with its aliphatic C–H bond content. Second, the integration of the benzene ring structure into the polymer chain stiffens the chain and hence increases the T_g (and T_m if the polymer is crystalline). However the stiffening effect may be overdone.

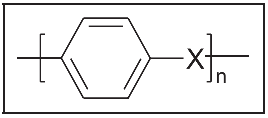
1.3.5 Polyphenylenes

The polymers consisting fully of benzene rings linked together *i.e.* poly-p-phenylene [55, 56], although excellently resistance to oxidation has a softening point of over 500°C and so it is not melt processable.



poly(p-phenylene)

This example demonstrate the need to attain a compromise between high softening point and adequate processability, preferably by conventional melt processing technique such as extrusion and injection molding. However, for polymers whose end use requires the highest softening points, special processing technique more similar to metallurgical technique may be needed. Therefore commercial polymers those attain the required compromise are mostly of this type;

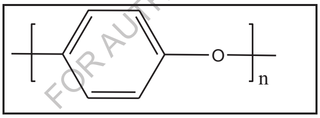


Where “X” is an atom or group of atoms, giving the polymer chain a certain degree of flexibility and hence melt processability. In most commercial polymers the benzene rings are linked through the *p*-position providing the most symmetrical type of structure and hence the best possibility for crystallization.

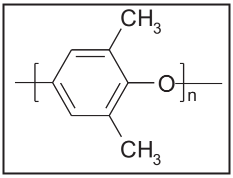
A great variety of flexibilising atoms or group is amide, ester, sulphone, keto, etc.

1.3.6 Polyethers

Ether links offer a very good choice of flexibilising group since – C – O – C – link is itself very flexible and is also highly resistance to thermal oxidation. The commercial polyphenylene oxide (PPO)



is based on the 2, 6-dimethyl substituted phenol as starting monomer, with a T_g of 208°C, it does not crystallize from the melt.



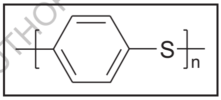
Poly (oxy-2, 6-dimethyl-1, 4-phenylene)

Aromatic polyether [57-59] is relatively new in the field of engineering plastics. The mechanical properties of PPO / polystyrene blends are significantly better than those of virgin polystyrene and hence such blends find increasing interest as engineering plastics [60, 61].

It became evident in the past two decades that aromatic polyethers is a versatile group of polymers that may be useful as resins for high performance composites, as thermostable engineering plastics, as basis material for the production of membranes and as high temperature adhesives [62,63]. A wide range of applications is found for modified poly(p-phenylene oxide); automotive (wheel covers, dashboard, trim, metalized grills), electrical (wiring splice devices, fuse boxes), consumer and business (computer housing, refrigerator door liners, keyboard frame) and liquid handling (valves, pipe, pumps), etc.

1.3.7 Polyphenylene sulfides

One of the important member of engineering resins is polyphenylene sulphide [64], which shows good thermal and thermo oxidative stability. It has the following repeating unit structure.



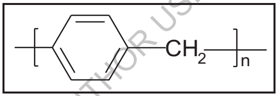
Poly (*p*-phenylene sulphide)

It may be used in air at temperature above 200°C for long periods. Poly(p-phenylene sulphide) [65, 66] is produced by the reaction of sodium sulphide with p-dichlorobenzene in a polar solvent. Polyphenylenes sulphide (PPS) is a highly crystalline polymer with T_m = 285°C and T_g = 85°C. It is evaluated for continuous service at 200-240°C, placing PPS between the polysulphones and the polyketones. It has inherent flame resistance, and its stability towards both organic and aqueous environment is excellent. Application of PPS includes industrial blends with fluorocarbon polymers, automotive and protective coatings.

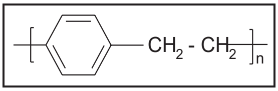
1.3.8 Aromatic-aliphatic hydrocarbon polymers

As high molecular weight polyphenylene is a highly inflexible material, so regardless of its excellent high temperature resistance to oxidation, it is not commercially useful. However low molecular weight branched polymers with mixed isomeric linkages (H-resin) have been used as soluble, flexible precursor polymers for fabrication of high temperature resistant composites with glass fibres of asbestos which forms cross-linked network on curing at high temperature (up to 250°C). Maximum use temperature in air is 215°C (continuous) or 350°C for short times.

Linked benzene rings through aliphatic methylene –(CH_2)— group is one approach of introducing chain flexibility and hence improving processability. However, the presence of aliphatic groups reduces resistance to thermal oxidation.



The simplest such polymer has not been synthesized. Polymers of the type poly (p-xylene) [67, 68] are valuable as electrically insulating coatings.

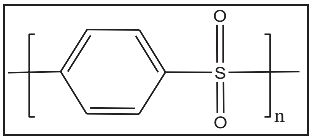


Poly(*p*-xylylene)s

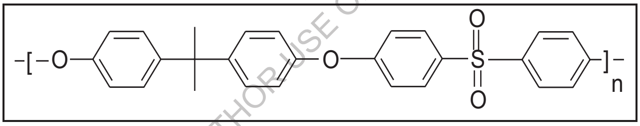
Other potential applications include coating of orthopedic parts (bone pins and joint prosthesis) to make them biocompatible and conversation of archival and artifact objects.

1.3.9 Polysulphones

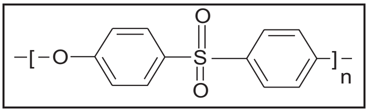
They are produced by nucleophilic aromatic substitution reaction between aromatic dihalides and diphenolate salts [69]. Poly-p-phenylene sulphone has the following repeating unit structure.



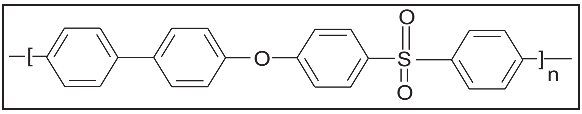
Another potential monomer that would not eliminate hydrogen chloride and would contribute to the aim of high thermal stability was 4, 4’-dichloro diphenyl sulphone. The electron withdrawing character of the sulphone group powerfully activated the chlorides towards displacement by nucleophiles such as phenoxide anion.



Poly(sulfone)s, PSF



Poly(ether sulfone)s, PESF



Poly(phenyl sulfone)s, PPSF

These polyether sulphones have T_g in the range of 150°C-250°C and are impassive to oxidation possessing short term thermo stabilities upto 450°C.

Polyarylethersulphones were stated in the patent literature as new materials prepared by novel polycondensation reaction during the early 1960’s. The effect of chain rigidity and polarity on T_g and T_m increase in either of these parameters leading to an increase in the transition temperature was well known. Integrating phenyl ring in polymer chain was noticeable method of increasing chain rigidity. However, the predictive power of knowledge available was limited by its qualitative nature and there was a major problem in predicting the softening points of aromatic polymers because the relationship between crystallisabillity and molecular structure were less well known for the polymers than those for their low molecular weight analogues.

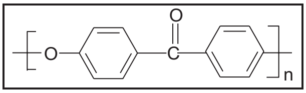
Thus, by 1960 there was enough information available to suggest that, in the search for new thermoplastics suitable for continuous use above 125°C, attention should be directed towards polymers consisting of linked aromatic rings. It can be now seen that the combination of flexible aryl ether bonds with polar aryl sulphone (or ketone) linkage provides an effective solution to this problem but the discovery of these combinations are mainly from the chemistry of the polycondensation processes investigated, rather than from properties versus structure predictions. In this environment, synthesis of novel aromatic polymers appeared to be a good topic for research as their attention was directed towards the aryl sulphone linkage because of its high polarity.

These polysulphones have found widespread use as injection molding materials when good dimensional stability at elevated temperature is required e.g. electrical components, including circuit’s boards, coil bobbins, connectors and relays applications operating at high temperature e.g. microwave ovens, fan heaters, hair driers, valves, pumps and lamp housing. The resistance of polysulphones to aqueous environment including bases, acids and oxidants are excellent. Their outdoor use is limited because of relatively low UV stability.

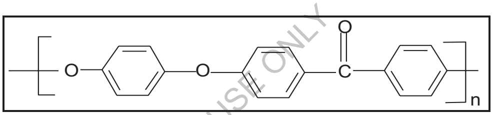
1.3.10 Polyether ketones and polyether ether ketones

Polyether ketone was reported independently by ICI and DuPont as novel material at about same time as the analogous polyether sulphone in the early 1960’s. Union Carbide was also interested in polyether ketones at this time and illustrated a bisphenol containing polyaryl ether ketone-sulphone and a polyaryl ether ketone.

The first preparation of completely aromatic polyether ketones was reported by Bonner [70, 71] of DuPont. Aromatic polyketones are the most recently developed type of aromatic polymer and probably offer the best high temperature resistance of any melt processable thermoplastic material. The arrival of high performance applications has increased the demand for these materials [72, 73]. Polyether ketone (PEEK) has been available since 1978 and has the following repeat unit structure.



Poly (ether ketone), PEK



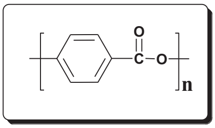
Poly(ether ether ketone), PEEK

Polyether ketones are partially crystalline. They have brilliant resistance to a wide range of aqueous and organic environment. The resistance to aqueous environment matches that of high temperature and aggressive environment, automotive (piston parts, bearings), aerospace (structural components), oil and chemical (pumps, compressor, valves plates) and electrical-electronic (cable insulation) application.

The application area for the polymer was an extruded insulation for performance cables and wires, injection molded parts, monofilament for industrial belts and filters, chemically resistant surface coating and as the matrix in cable fiber composites for the aerospace components. Special class of the photosensitive PEEK has been also reported.

1.3.11 Polyester

Several combinations of reactants and process conditions are potentially available to synthesize polyester [74]. The partly aromatic polyesters, poly(butylene terephthalate); PBT and poly(ethylene terephthalate); PET, are well established as plastics and fiber forming materials. However, they have limited heat resistance. The earliest marketable wholly aromatic polyester was Ekonol (polyhydroxy benzoic acid), which is crystalline and soften only above 500°C, therefore it can be processed by metallurgical technique such as sintering and hammering. It can be used as bearing material at temperatures up to 320°C.

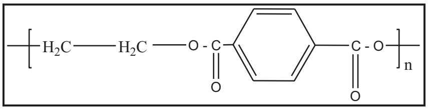


Polyester

Completely aliphatic polyesters are not of major industrial importance because of their low melting temperatures and poor hydrolytic stability. Low molecular weight aliphatic polyesters are used as a plasticizers and prepolymer reactants in the synthesis of polyurethanes.

1.3.12 Poly (ethylene terephthalate)

Glass strengthened injection moldable PET resins have become major engineering thermoplastics. PET was first synthesized by J. R. Winfield in England in the 1940's. PET was used as a fibre for clothing, film for packaging / insulation and in the bottles of beverages.

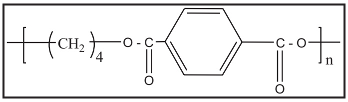


Poly(ethylene terephthalate)

Various factors retained PET accepted; the most important of these was that, PET did not crystallize completely in conventional water heated molds. First commercial engineering PET resins for injection molding were introduced by Akzo Chemie in Europe and Teisin in Japan. They used conventional nucleating agents such as talc. This did increase crystallization rate but would not allow full crystallization in water-heated molds.

1.3.13 Poly (butylene terephthalate)

It is linear condensation type of polymer based on terephthalic acid and 1, 4-butane diol. The more absolute name of PBT is poly(tetramethylene terephthalate), PTMT.



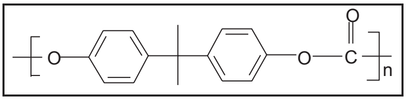
Poly(butylene terephthalate)

There is evidence of some interest in the materials, in the form of patents issued to ICI over the period 1957 to 1962, which deal with formation of PBT from both DMT/ 1,4 butane diol and terephthalic acid / 1,4 butane diol. PBT finds used in stretch fabrics and carpets. Other classes of polyesters of commercial importance are polycarbonate, unsaturated polyesters and liquid crystal polyester.

1.3.14 Polycarbonate

It is special class of polyesters derived from carbonic acid and diol. There are two major classes of poly(carbonate)s: aromatic and aliphatic. Aliphatic poly(carbonate)s have not found any noteworthy commercial use as thermoplastics. Most of the aliphatic poly(carbonate)s are semi-crystalline materials with low melting points, normally less than 120°C. Aromatic polycarbonates were first revealed by A. Einhorn in 1898. He reacted pyridine solution of hydroquinone, resorcinol and catechol with phosgene to produce polycarbonate. Four year later C. Bischoff and A. Von Hedenstrom synthesized and reported the same by using trans esterification and then the subject of aromatic polycarbonate was apparently forgotten. More than 50 years later Dr.

Herman Schnell at Bayer A. G. and Brunel at General Electric Corporation laboratory in Schenectady N. Y. independently synthesized aromatic polycarbonate based on bisphenol-A. Bisphenol polycarbonates have found broad application around the world as a premier “Engineering Plastics” due to their properties, which include outstanding dimensional stability, toughness, load bearing properties over a very broad temperature range [75-78], excellent electrical properties, resistance to burning, transparency, high impact strength and a Tg of 149°C etc.

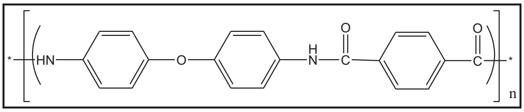


Bisphenol-A polycarbonate

1.3.15 Polyamides

Polyamides are polymers with repeated amide groups (-CO-NH-) as an integral part of the main polymer chain. The polyamides are generally divided into two groups.

a) Aliphatic polyamides (nylons), b) Aromatic polyamides (aramids).

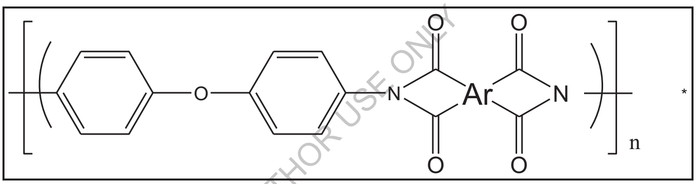


In 1974, the aliphatic and aromatic polyamides were given separate generic nomenclature by the U.S. Federal Trade Commission. The aliphatic polyamides are termed as nylons and aromatic polyamides are termed as aramids [79-81].

Historically, the chemistry of polyamides was first studied in 1862 by Harbordt and the first aliphatic polyamide was reported in 1899 by Gabriel and Mass, whereas high molecular weight polyamides were synthesized in 1933 by Carothers. Aromatic polyamides because of their special properties like polarity and hydrogen bonding are highly multipurpose and find a great variety of application as high performance polymers. Aramids are flame resistant, heat resistant, have high tensile strength, high Young's modulus, highly crystalline and some of the aramids show liquid crystal (lyotropic) behavior and used in the membrane, resin, films, fiber and plastic etc. [82-84].

1.3.16 Polyimides

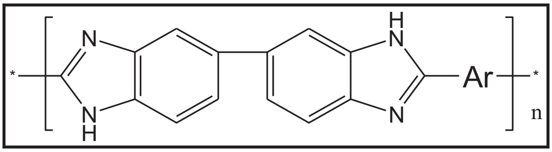
Aromatic polyimides are significant class of high performance polymers due to their excellent mechanical strength, electrical properties, thermo-oxidative stability and high radiation and solvent resistance. They are condensation polymers uniting the imide group CO-N-CO in their repeating units either as open chain or as rings and are generally derived from the reaction of organic diamines with organic tetracarboxylic acids or their dianhydrides [85-87].



Bogart and Reshow in 1908, obtained first polyimide, from 4-amino phthalic anhydride a relatively stable compound, which did not melt upon heating but evolves water at elevated temperature with the formation of a poly molecular imide. Edward and Robinson synthesized first aliphatic polyimides by melt fusion method from aliphatic diamines and tetra acids or diacids/diester [88].

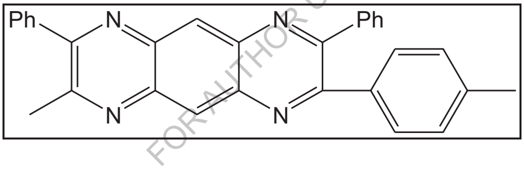
1.3.17 Poly(benzimidazole)s (PBI)

Poly(benzimidazoles) were first appealed in the US patent in 1959 and then published in a scientific report by Vogel and Marvel in 1961 with expectation that these polymers would have exceptional thermal and thermo-oxidative stability [89]. These polymers are a class of polymers, having excellent properties such as thermal stability, radioactive stability, flame resistance, mechanical and dielectrical strength and chemical inertness. Due to these properties polybenzimidazoles find applications in defense industries and aerospace.



1.3.18 Poly(quinoxaline)s (PQ)

Poly (quinoxaline)s are heterocyclic polymers, produced by the Friedlander reaction of a bis(o-aminoaromaticaldehyde/ ketones) with bis keto methylene reactant [90]. They can be also synthesized by polymerization of bis(o-diamine) and bis (o-keto aldehyde) reactants in m-Cresol [91]. These polymers have excellent oxidative, thermal stability, resistance to acids and bases, high Tg and high strength / modulus.



1.4 Scope and Objective

Aromatic poly(ether-amide)s, poly(ester-amide)s, etc. are classes of high performance polymers which exhibit excellent thermal, mechanical and electrical properties over a wide range of temperature [92]. However, these polyamides are processable only under extreme conditions which limit their application areas. Therefore, chemical/structural alteration of these high-performance polyamides for increasing the solubility and lowering the transition temperatures while maintaining thermal stability is of specific interest. Many studies have been directed to improve the processability of these polyamides by making use of structurally modified monomers [93].

The majority of these studies involved three main structural modifications to modify the properties; i) introduction of flexible side chains/ segments or cardo groups into/ along the polymer backbone, which reduces the chain stiffness, ii) use of 1,3-disubstituted instead of 1,4-disubstituted monomers or use of asymmetric monomers which lower the regularity and molecular ordering, and iii) introduction of bulky side substituent which help for the separation of polyamide chains and hinder the molecular packing and crystallization.

Among the various structural modification methods stated above, the appendance of flexible side chains along the polyamide backbone is a particularly interesting approach [94], since the peculiar structure of the main chain of such polyamide is not changed by the attachment of flexible side chains. It is reported that the use of monomers bearing pendent flexible groups significantly reduces strong molecular interactions of stiff-chain aromatic polyamides, producing an effective chain separation effect. In general, such pendent group not only improves solubility but also helps to lower the melting and glass transition temperatures *via* "internal plasticization" effect [95-97].

The aim of the present research work was to make use of the structural modifications mentioned above, to have a cumulative effect on the properties of the resulting polyamides. Thus, our synthetic research effort was focused towards designing monomers with features that disturb structural regularity and chain packing hence imparting improved processability to the polyamides.

The goal of the present research was to utilize cyclopentanone as a starting material to design and synthesize of various difunctional monomers such as aromatic diamines, diacids. Important considerations in designing monomers were: i) *meta*-linkage introduces "kinks" to the main chain which decrease the rigidity of the polyamide backbone and inhibit packing, thus reducing the interchain interactions leading to enhanced solubility [98], ii) the presence of cardo cyclopentane ring along with the polyamide backbone reduces strong molecular interactions of stiff-chain aromatic polyamides, producing an effective chain separation effect and consecutively aid in improved processability, iii) the presence of pendant methyl group on aromatic ring offers asymmetry to the polyamide backbone leading to constitutional isomerism, which could impart interesting properties to the derived polyamides [99].

The second objective of this work was to investigate the effect of incorporation of cardo cyclopentane ring on the polyamide properties, such as solubility and thermal stability.

Based on these objectives, the following specific problems were chosen for the presented work.

1. Synthesis of bisphenol containing cyclopentylidene cardo group starting from cyclopentanone and phenol or o-cresol.
2. Design and synthesis of difunctional monomers, *viz.,* aromatic diamines and diacids starting from above synthesized bisphenols.
3. Synthesis and characterization of poly(ether-amide)s, poly(ester-amide)s from above monomers containing pendant methyl groups or ester linkage and cardo groups with flexible ether linkages and study the effect of incorporation of these groups on structure- property relationship among polyamides.

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Polyamides are polymers with repeated amide (-CO-NH) groups as an integral part of the main polymer chain and they are the largest and most significant group of linear-acyclic nitrogen polymers. Polyamides are vital class of synthetic polymers widely used in industry as tire cord in tires of automobiles, as membrane materials, aircrafts, coatings, in circuit boards, foams, adhesives, packaging materials and biomedical aids. Such crucial applications of polyamides are possible as a result of the design of polymer properties tailored to utilize distinct functions. As polyamides are frequently prepared by condensation polymerization between diacids or derivatives and diamines, appropriate combination of these components regulates the unique and on demand properties of final products [1].

Polyamides occupy a noticeable position among the synthetic high performance polymers. The first synthetic polyamide, polybenzamide was achieved by Harbordt in 1862 [2]. The first commercially manufactured aromatic polyamide was poly(m-phenylene iso-phthalamide) (Nomex, Du Pont, 1967) [2, 4]. After some years, development of the preparation of poly(p-phenylene terephthalamide) led to the commercialization of the *para* product Kevlar (DuPont) in the early seventies [3,4].

Absolutely aromatic polyamides are considered to be high performance organic materials due to their excellent mechanical and thermal resistance. Their properties arise from aromatic structure and amide linkages, which result in rigid rod-like macromolecular chains that interact with each other *via* strong and highly directional hydrogen bonds. They are finding increasing demand for used as valuable replacements for metals or ceramics in currently used goods, or even as new materials in innovative technological applications [5]. However, high glass transition temperatures of the marketable aromatic polyamides, which lie above their decomposition temperatures and their poor solubility in common organic solvents give rise to processing difficulties and limit their applications [6]. Therefore, recent basic and applied research has focused on improving their processability and solubility in order to broaden the scope of the technological applications of these materials.

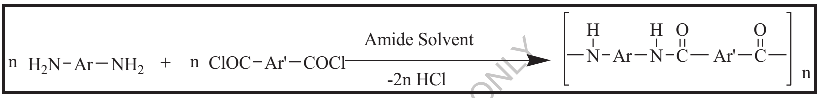
2.1 Synthetic methods for the preparation of aromatic polyamides

2.1.1 Low temperature polycondensation of a diamine and a diacid chloride

This process was developed by DuPont and has been used for the synthesis of high molecular weight polyamides. The step growth polycondensation of a diamine and a diacid chloride can be carried out in solution or at the interface of two solvents at room temperature.

2.1.1.1 Solution polycondensation of a diamine and a diacid chloride

Solution polycondensation involves a diamine and a diacid chloride reacting in an amide solvent such as DMAc, NMP, HMPA or tetramethylurea.



$$n\ H_2N-Ar-NH_2 + n\ ClOC-Ar'-COCl \xrightarrow[-2n\ HCl]{\text{Amide Solvent}} \left[-\overset{H}{N}-Ar-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-Ar'-\overset{O}{\overset{\|}{C}}- \right]_n$$

Scheme 2.1 Solution polycondensation of a diamine and a diacid chloride.

The amide solvent also acts as hydrogen chloride acid acceptor produced in the reaction. Other polar aprotic solvents such as DMSO and DMF cannot be used because they react significantly with acid chlorides. The solvent should allow supreme solubility/swellability of the polymer formed at the early stage of polycondensation, and the solvation properties of amide solvents can be typically increased by adding salts such as LiCl or $CaCl_2$ [7].

2.1.1.2 Interfacial polycondensation of a diamine and a diacid chloride

The step-growth polycondensation reaction can also be carried out in a two phase system at room temperature *via* interfacial polymerization. In this technique, the two fast reacting reagents are dissolved in a pair of immiscible liquids, one of which is preferably water [8]. The water phase usually contains the diamine and typically an inorganic base, the other phase contains the acid chloride in an organic solvent such as toluene, dichloromethane or hexane.

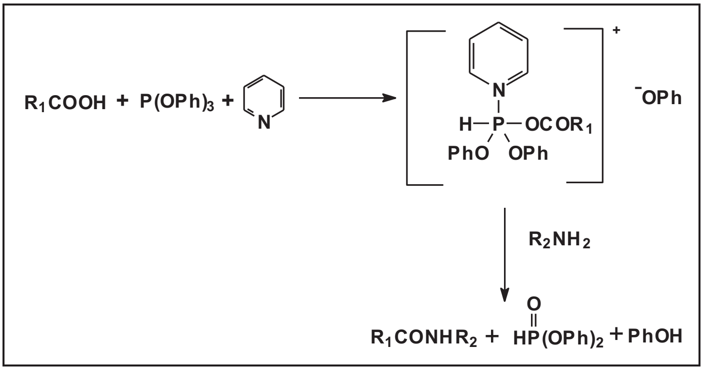
The two-phase system is stirred dynamically to obtain high molecular weight polymers.

Scheme 2.2 Interfacial polycondensation of diamine and diacid chloride.

The difference between conventional step-growth polymerization and interfacial polymerization is that, in the interfacial polymerization the monomer dispersing to the interface reacts only with the end of the polymer chain resulting in high molecular weight polymer. Since the temperature needed is low, the side reactions are reduced and also the polymers which are unstable at high temperatures can be synthesized.

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

This technique was developed by Yamazaki et al [9] which includes the direct polycondensation of dicarboxyllic acids and diamines to produce polyamides. This reaction comprises the formation of a complex of an acid with triphenylphosphite in NMP and pyridine, which additionally reacts with diamine to give the product.



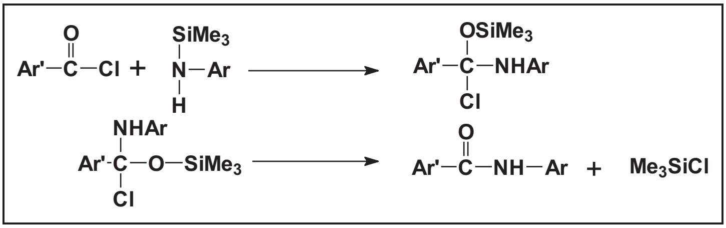
Scheme 2.3 Condensation reaction of acid and amine to form amide in the presence of triphenylphosphite.

LiCl or $CaCl_2$ was used along with NMP to increase the molecular weight of polymers. The role of LiCl or $CaCl_2$ is quite complicated. They can form complexes with pyridine which are more soluble than the salts alone and NMP with a more content of metal salt can solubilize polyamide formed in the reaction medium more efficiently leading to high molecular weight products. Many key factors can considerably influence the molecular weight of the final polymer such as, (i) concentration of monomers, (ii) solvent and amount of pyridine relative to the metal salt, (iii) reaction temperature and time, (iv) concentration of LiCl or $CaCl_2$ and (v) ratio of triphenylphosphite to monomer. The high-temperature solution polycondensation method was recently reformed by the introduction of microwave-assisted polycondensation. The conventional heating system, i.e., temperature controlled oil bath, is replaced by microwave radiation system, which decreases the reaction time from 4 h to approximately 2 min [10]. The polymers obtained by both processes have comparable inherent viscosities. Recent exertions have been directed to the greener advancement of polycondensation under low or high temperature solution methods which contains replacements of conventional solvents (DMAc, NMP and pyridine) by ionic liquids [11]. The ionic liquids have low vapor pressure, high thermal stability, have a high dielectric constant and are highly polar which makes them suitable to dissolve the aromatic polyamides.

2.1.3 Polycondensation of an activated diamine and a diacid

Step-growth polycondensation chemistry has been enhanced in the last two decades through the usage of activated monomers. The activation of monomers can be attained either by activation of the carboxylic acids, chiefly through organophosphorous reagents such as phenyl dichlorophosphite (PDCP) [12, 13] or activation of the diamines by their silylation [14]. Even though most of the efforts in the production of high molecular weight polyamides have been directed towards the activation of the diacids, there are some reports on the activation of diamine component by reacting it with trimethylsilyl chloride.

Actually, high molecular weight polyamides have been produced by low temperature polycondensation of an N-silylated aromatic diamine with aromatic diacid chloride [15-17]. The following nucleophilic addition-elimination two-step mechanism has been recommended for the acyl substitution of an acid chloride with an N-silylated amine



Scheme 2.4 Condensation reaction of N-silylated amine and acid chloride

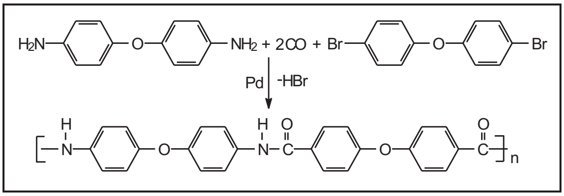
Lozano et.al [18] has reported the formation of silylated diamines *in situ* by adding trimethylchlorosilane to the diamine solution that, on addition of diacid chloride gives polyamides. This method is especially useful for the preparation of polyamides from aromatic diamines having low reactivity.

2.1.4 Polycondensation of diisocyanates and dicarboxylic acids

Another favorable route for the preparation of aromatic polyamides has been established by Simioneseu et al and Onder et al [19] 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 [20]. A commercial scale manufacturing of aromatic polyamides from 1, 3-phenylene diisocyanate and isophthalic acid in the presence of a catalyst has been reported [21]. Polyamides have also been synthesized by the reaction of aromatic diisocyanates with aromatic hydrocarbons in the presence of Friedel-Crafts catalyst [22].

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

Polyamides can also be prepared by palladium-catalyzed carbonylative coupling of diamines and dihalides [23].



Scheme 2.5 Transition metal catalyzed carbonylative coupling of aromatic diamines and dihalides

2.2 Structure-property relationship in aromatic polyamides

Aromatic polyamides have crucial properties like, high strength, high thermo oxidative properties, low solubility in common organic solvent, high melting point; very good flame resistance, good chemical and electrical resistance and high moisture regain properties. These polymers are problematic to process into desired shape because of their low solubility in common organic solvent. Due to their high glass transition temperature (T_g) and high melt temperatures (T_m), there is restriction on their processability. The polymers with rigid chains are more intractable [24, 25]. Numerous attempts which have been made to reduce the T_g and increase the solubility of polyamides without affecting the thermo-mechanical properties are listed below.

2.2.1 Solubility and thermal stability

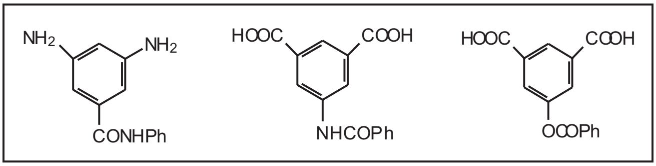
Several attempts and number of strategies have been made to enhance the solubility of polyamides such as (1) insertion of flexible bonds in the backbone (2) insertion of bulky pendent group in the diamine or diacid monomer and (3) usage of non-coplanar structures and (4) the usage of heterocyclic monomers [26].

2.2.2 Halogen substituents

The solubility of polyamides enhanced when the number of halogen substituents are increased. The effect of various halogen substituents on polymer properties is well known [27]. The integration of halogen substituents along the polymer backbone leads to flame resistant polymers. The thermostability of halogen substituted polyamides drops in the order H > F > Cl > Br. This order is related to the bond dissociation energy. Increase of halogen content usually leads to a decrease in decomposition temperature. Fluorinated polyamides have shown excellent film forming properties, mechanical properties, enhanced solubility, improved melt flow, flame resistance and chemical resistance. Low reactivity of tetrafluoro terephthaloyl chloride and tetrafluoro isophthaloyl chloride was attributed to steric hindrance of the nearby fluorene atoms [28]. The reaction of these halogenated acid chlorides can be carried out with N-silylated diamines as they are far more reactive than the analogous nonsubstituted diamines [15, 16].

2.2.3 Other substituents

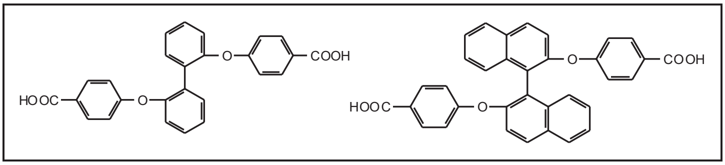
Chaudhari et al. [29] in their study of thermo stability of aromatic polyamides have introduced several polar groups into the polymer e.g. -COOH, -NO$_2$, -SO$_3$H, -OH. They reported that, the thermostability reduced in the following order -NO$_2$ > -COOH, and -OH > -SO$_3$H. Utilization of isophthalic acid containing –NHCOPh, and –OCOPh groups and usage of m-phenylene diamine containing –CONHPh group is also reported [30-32] to impart solubility in highly polar solvents and some are soluble or swellable in m-cresol



Substituted monomers for polyamide synthesis

2.2.4 Pendant alkyl/aryl group containing polyamides.

The pendant groups were inserted in the main chain [33-38], as an effective means of increasing solubility with retaining of good thermal stability [39-44]. Cimecioglu and Weiss [45] synthesized polyisophthlamides using 5-benzamidoisophthalic acid by direct polyamidation, leads to soluble polymers without sacrificing thermal properties. Polyamides founded on substituted bulky monomers containing 3, 3-substituted binaphthyl and biphenyl groups have also been reported [46].



Monomers containing benzene rings for polyamide synthesis

Biphenyl-2,2’-diyl and 1,1’-binaphthyl-2,2-diyl having aramids can be produced by reacting diacid chlorides of 2,2’-bis(p-carboxy phenoxy)biphenyl and 2,2’-bis(p-carboxy phenoxy)-1,1’-binaphthyl with aromatic diamines by low-temperature solution polymerization [47]. They had outstanding solubility and high Tg. Phenylated heterocyclic diamine such as 2, 5-bis(4-aminophenyl)-3, 4-diphenylthiophene and diacid chlorides have been utilized to prepare polyamides with higher solubility and retaining thermal stability [48-74].

2.2.5 Polyamides containing flexible linkages.

Insertion of flexible and polar linkages into the polymer backbone is one of the approaches to enhance solubility without considerable loss of thermal stability. Aromatic polyamides containing sulfone, sulfide, and ketone groups have been prepared. Direct polycondensation of bis (p-phenylthio) dibenzoic acid, 4, 4’-sulphonyl bis(p-phenylthio) dibenzoic acid and 4,4’-[carbonyl bis (p-phenylthio) dibenzoic acid with several aromatic diamines has been reported by Joseph et al [59]. Now a day’s one of the utmost common approaches to enhance solubility with retaining thermal properties is, the insertion of flexible bonds in the polymer backbone along with the incorporation of bulky pendent or cardo groups along the main chain.

- **Approaches to improve processability of polyamides.**

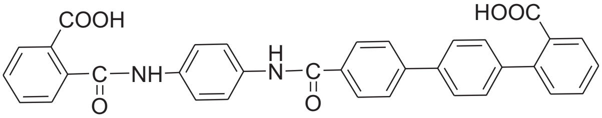
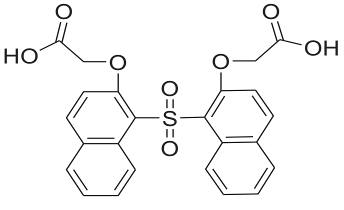
i. Introduction of cardo or pendant aliphatic group along the polymer backbones.
ii. Insertion of flexible linkages such as ether, sulfone ether, sulphone, siloxane, carbonyl, aliphatic linkages in polymer back bones.
iii. N-alkylation's or N-arylation of the amide groups to decrease interchain hydrogen bonding.
iv. Random co-polymerization with small amounts of ortho and meta substituted aromatic rings to disrupt chain conformation.
v. Usage of bulky asymmetrical heterocyclic monomers.

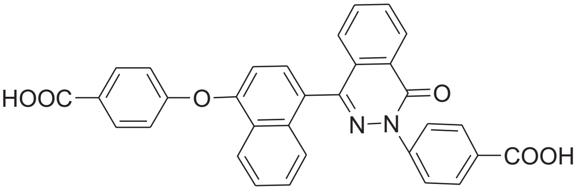
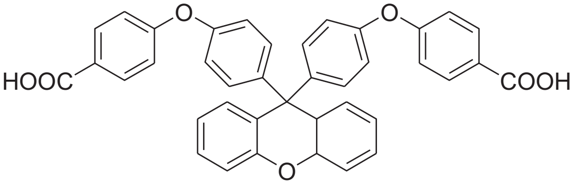
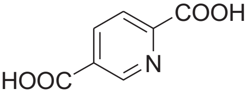
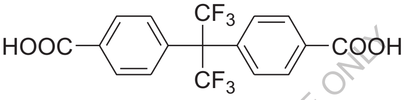
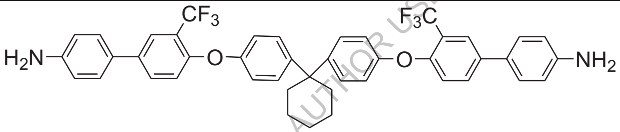
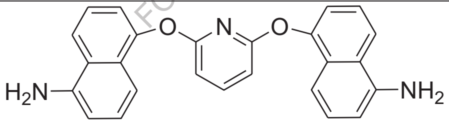
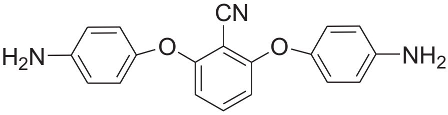
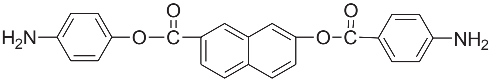
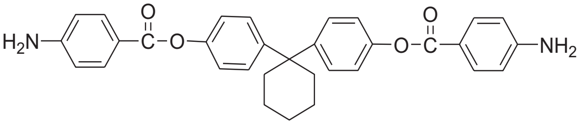
2.3 Literature Survey

The presence of ether moieties in the polymer back bone enhanced solubility, processability and hydrolytic stability [75]. Dulbnora et.al [76] prepared polyamide containing paraoxyphenyline groups in the main chain and revealed that, the solubility of polymers was improved with increasing the number of "oxy" groups in the polymer chain. The polyamide containing sulphone, carbonyl groups in the polymer chain have been reported. These polymers showed good mechanical and thermal properties, better solubility and low T_g [77-79]. Similarly insertion of sulphone ether linkages in the polymer backbone, imparts better solubility, good thermal stability, superior chain flexibility and excellent mechanical and thermal properties. Insertion of aliphatic units in the polymer back bone improved the solubility of polymer. Shrinivasan et al [80] and Mahajan et al [81] synthesized polyamides with flexible aliphatic units in polymer back-bone. Lenk et al [82] produced polyamides containing ether as well as aliphatic linkage in polymer backbone. These polymers were amorphous and revealed better solubility. The existence of pendant groups in the polyamide chain improves the solubility in organic solvents comparative to the analogous unsubstituted polyamides. Preston et al [83, 84] synthesized aromatic polyamides containing pendant carboxylic acid linkages through solution and interfacial polymerization. Imai et al [85, 86] produced the polyamides using bulky pendant phenyl group in diamine and/or dicarboxylic acid monomers. These polyamides were eagerly soluble in organic solvent. It is known that T_g enhances by the introduction of stiff rod like structure along the polymer backbone. On the other hand kinked structure such as meta linkages decreases the T_g values. Guey Sheng Liou [87] synthesized soluble polyamides having high T_g by inserting bulky and rigid structure into the polymer backbone and flexible ester group into main chain. Fluorine containing polyamides exhibited good solubility in organic solvents, as compared with polyamides containing other halogen. Polymers containing di and tri fluoroalkyl groups displayed good solubility and thermal properties [88, 89]. Some heterocyclic groups like 5-(2 benzimidazoyl) [90], benzothiazole [91, 92] benzoxazole etc. [93] have also been inserted into the polymer backbone to progress the properties of the resulting polyamides. These polyamides had better solubility in polar solvent and showed improved hydrophilicity, low T_g and good thermal stability.

The representative examples of this kind of diamines and diacids having flexible ether or ester linkages with bulky groups for the synthesis of polyamides are given in **Table 2.1.**

Table 2.1 List of the selected diacids and diamines containing flexible chains reported for synthesis of polyamides

Sr. No.	Diacids or Diamines	Reference
1.		**229**
2.		**230**

3.		**231**
4.		**232**
5.		**233**
6.		**234**
7.		**235**
8.		**236**
9.		**237**
10.		**238**
11.		**239**

Based on above structure-property relationship and literature survey over polyamide, we successfully tried to insert cardo group with flexible ether or ester and aliphatic linkages into the diacid and diamine monomer and produced new polyamides having improved properties.

2.4 Applications of polyamides

Aromatic polyamides (aramids) are a high temperature resistance engineering polymers which have good chemical resistance, thermal stability and mechanical properties [98]. Aromatic polyamides are unaffected to alkali and have better hydrolytic stability as compared to nylons and polyesters. 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 several types of salts from water [94]. Many polyamides having pendant alkyl groups have been prepared to enhance the selectivity and permeability of the resulting membranes [95-96]. Polyamides are well-known for reverse osmosis membranes but less for gas separation [97]. Aromatic polyamides are easily turned into hollow fibers for high performance gas separation components.

Polyamides containing pendant alkyl groups [98-100] have been used as liquid crystal alignment layers. Polyamides have also found application as light emmiting polymers [101]. Hsiao et al [101] have studied polyamide films based on 4, 4’-dicarboxy-4’’-N-carbazoyltriphenyl amine and different aromatic diamines. These films exhibited multicolor electrochromic behaviour from original pale yellow to green and then to blue colors when numerous different potentials were applied.

‘Nomex’ fibers are used as tyre cord in car cases and as belts in biased belted and radial belted tyres. They are also used as parachutes, cables, body armor in rigid re-enforced plastics. Aromatic polyamides exhibit high dielectric strength and high volume resistivity. At elevated temperatures they maintain these properties and possess high potential to be used as high temperature dielectrics particularly in motors and transformers [102]. Aromatic polyamide fibers possess flame retardence hence they are used as industrial protective clothing, protective shields and welder clothing.

Chapter-2A:Synthesis and Characterization of Poly(ether-amide)s based on Methyl Substituted diamine Monomer by Yamazaki's Phosphorylation method.

Aromatic polyamides are gorgeous high performance polymers due to their excellent mechanical strength and high thermal stability [103-107]. However, their high softening or melting temperatures and poor solubility in organic solvents due to high crystallinity and high rigidity of the polymer backbone limit their processability and applications [108,109]. Numerous approaches have been outlined to enhance the solubility and processability of aromatic polyamides with retaining of their high thermal stability. These approaches include integration of non-coplanar groups in the main chain [110-113], molecular asymmetry [114-125], the use of *meta*-oriented monomers [126,127], flexible linkages [128-133], and bulky pendent [134-157] or cardo groups [158-163]. These alterations work by breaking chain symmetry and regularity and by terminating hydrogen bonding, usually leading to better solubility and processability.

The objective of the present work was to synthesize a series of poly(ether-amide)s which contains cardo cyclopentane ring and pendent methyl group and to investigate the effect of the insertion of cardo cyclopentane ring and pendent methyl group on the polymer properties such as solubility and thermal behavior. Thus, a series of poly(ether-amide)s was produced by solution polycondensation of 1, 1-bis [4- (4-amino phenoxy)- 3-methyl phenyl] cyclopentane with commercially available diacids, *viz.*, 4,4'-Oxybis(benzoic acid); 4,4'-Hexafluoroisopropylidene bis(benzoic acid); 4,4'-Sulfonyl dibenzoic acid and Biphenyl 4,4' dicarboxyllic acid. The synthesized polyamides were characterized by inherent viscosity measurements, solubility tests, FT-IR spectroscopy, X-ray diffraction pattern, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies.

Here we have synthesized new series of methyl substituted poly(ether-amide)s from new methyl substituted diamine with commercially available diacids.

2A.1 Experimental

2A.1.1 Materials

All the solvents / chemicals were purified before use by following the standard procedures.

- N, N'- Dimethylacetamide was refluxed over barium oxide for 4h, the liquid was decanted in a separate round bottom flask and distilled at reduced pressure over calcium hydride and stored over Linde type 4 Å Molecular sieves.
- K_2CO_3 was dried under vacuum at 150°C for 6h.
- O-Cresol, cyclopentanone purchased from Spectrochem and used as received.
- 10% Pd/C, 3-mercaptopropanoic acid, triphenyl phosphate, 4, 4'-Oxybis(benzoic acid), 4, 4'-Hexafluoroisopropylidene bis(benzoic acid), 4,4'-Sulfonyl dibenzoic acid and Biphenyl 4, 4' dicarboxyllic acid were purchased from Sigma Aldrich (USA) and used as received.
- 4-Chloro nitrobenzene purchased from Spectrochem (India) and used as received.
- Pyridine was refluxed with solid potassium hydroxide pellets, fractionally distilled and stored over Linde type 4 Å Molecular sieves.
- N-Methyl-2 pyrrolidone (NMP) was dried by azeotropic removal of water with benzene for 6 h, distilled under reduced pressure and stored over Linde type 4 Å Molecular sieves.

2A.1.2 Synthesis of methyl substituted diether-diamine monomer

2A.1.2.1 Synthesis of 1, 1-bis(4-hydroxy 3-methyl phenyl) cyclopentane (BHMPC)

In a 250 mL three necked round bottom flask equipped with HCl gas deep tube, reflux condenser and magnetic stirrer were placed 64.80 g (0.60 mol) of o-cresol and 8.4 g (0.1 mol) of cyclopentanone and 0.2 mL 3-mercaptopropanoic acid. To this reaction mixture dry HCl gas was bubbled at room temperature. The reaction mixture becomes solid in 2 h. The solid reaction mixture was dissolved in ethyl acetate (600 mL) and neutralized by washing with aq. $NaHCO_3$ solution 3 X 200 mL, followed by washing with distilled water 2 X 200 mL. The organic layer was dried over magnesium sulfate, decanted and distilled off to obtain viscous liquid. Then upon addition of pet ether in viscous liquid, solid product was separated. The solid product was washed with water and dried under vaccum. Finally the bisphenol was reprecipitated through methanol-water mixture.

Yield: 15.10 g (65 %)		M.P.:140°C

2A.1.2.2 Synthesis of 1, 1-bis[4-(4-nitro phenoxy)-3-methyl phenyl] cyclopentane (BMNPC)

In a 500 mL three neck round bottom flask equipped with calcium chloride guard tube, thermowell, nitrogen gas inlet and magnetic stirrer were placed 11.28 g (0.04 mol) 1, 1-bis (4-hydroxy 3-methyl phenyl) cyclopentane (BHMPC) and 12.56 g (0.08 mol) 4- chloro nitrobenzene in 60 mL N, N-dimethyl formamide (DMF), then 11.04 g (0.08 mol) of anhydrous K_2CO_3 was added. The resulting reaction mixture was refluxed for 8 h. Then allowed to cool at room temperature and water was added in reaction mixture to precipitate the product. The product was isolated by filtration, washed with water then washed with ethyl acetate and finally dried under vacuum.

Yield: 22.86 g (98%),

M.P.: 270°C.

IR: 3062 cm^{-1} (Aromatic –CH stretch), 2959, 2870 cm^{-1} (Aliphatic –CH stretch) 1505, 1346 cm^{-1} (-NO_2 stretching), 1256, 1178 cm^{-1} (C-O-C stretching).

^{1}H NMR (400MHz, DMSO-*d6*), δ (ppm): 8.13 (d, 4H), 7.31 (d, 4H), 7.12 (d, 4H), 6.87 (s, 2H), 2.31(s, 6H), 2.08 (m, 4H), 1.60 (m, 4H).

2A.1.2.3 Synthesis of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC)

In a 250 mL single neck round bottom flask equipped with calcium chloride guard tube and magnetic stirrer were placed 13.10 g (0.025 mol) of the 1, 1-bis [4- (4-nitro 3-methyl phenoxy) phenyl] cyclopentane (BMNPC) and 0.284 g of 10% Pd/C and 13.5 g hydrazine hydrate in 100 mL 75:25 mixture of ethanol and N, N'-dimethyl acetamide. The resulting reaction mixture was kept at refluxed temperature for 10 h. The progress of reaction was monitored by TLC. At the end reaction mixture was filtered while hot to remove the catalyst. The obtained filtrate was poured into 500 mL of water under vigorous stirring to give a light yellow product. Finally product was filtered, washed with ethanol and dried. BAMPC recrystallized from DMAc-water system.

Yield: 9.86 g (85 %) M.P.: 160°C.

IR: 3464, 3377 cm^{-1} (-NH$_2$ stretching), 3010, 2957, 2869, 1276, 1165 cm^{-1}

^{1}H NMR (400MHz, CDCl$_3$), δ (ppm): 7.28 (s, 2H), 7.11 (d, 2H), 7.02 (d, 2H), 6.78 (s 4H), 3.35 (s, 4H), 6.68 (s, 4H), 2.25(s, 10H), 1.70(m, 4H).

^{13}C NMR (100MHz, CDCl$_3$), δ (ppm): 153.93, 149.80, 143.28, 141.84, 129.79, 127.84, 125.26, 119.77, 116.75, 116.27, 54.64, 38.94, 23.02, 16.55.

2A.1.3 Synthesis of Homo poly(ether-amide)s from 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0. 464 g (0.001mol) 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC), 0.258g (1mmol) 4,4'-dicarboxydiphenyl ether(ODCA), 0.115g lithium chloride [5 wt % based on solvent N-methyl pyrrolidone (NMP) and pyridine mixture] and 0.744g (0.63mL, 2.4mmol) triphenyl phosphite (TPP), 0.5mL pyridine and 2mL NMP. The mixture was stirred well and temperature was slowly raised to 100°C over a period of 30 min. The mixture was heated at 100°C for 3h under nitrogen. After cooling, the resulting viscous solution was poured into rapidly stirred 200 mL of methanol. The precipitated polymer (HPA-1) was filtered, washed with methanol and dried. The polymer was purified by dissolving in N, N-dimethylformamide (DMF) and reprecipitating in methanol. It was filtered, washed with methanol and dried under vacuum at 100°C for 6 h. The yield of polymer HPA-1 was 99% and the viscosity in DMF was 0.45 dL/g.

The other poly(ether-amide)s HPA -2 to HPA -4 were synthesized with different diacids by similar procedure.

IR Spectrum

HPA-1: 3300 (N-H stretch), 2970, 2877, 1648 (C=O), 1596, 1223, 1164, 756, cm^{-1}

HPA-2: 3429(N-H stretch), 2954, 2850, 1647(C=O), 1607, 1225, 1165,750 cm^{-1}

HPA-4: 3311(N-H stretch), 2968, 2865, 1660 (C=O), 1606, 1226, 1207 (C-F stretch), 1173,748 cm^{-1}

2A.2 Results and Discussion

Aromatic polyamides have received attention concerning to the production of high performance materials due to their outstanding chemical resistance, thermal stability, mechanical and electrical properties. However their applications are limited because of their poor solubility in organic solvents and tremendously high glass transition temperatures that make them very hard to be processed by spin coating or thermoforming methods. Abundant effort has been made to create structurally improved aromatic polymers having enhanced solubility and processability with retention of their high thermal stability. It is well-known that the solubility of polymers is often improved when flexible bonds such as [-O-, CH_2-, -SO_2-, -$C(CF_3)_2$], bulky pendent groups (such as t-butyl, methyl, adamantyl, etc.) are used along the polymer backbone. If the moiety is cautiously chosen, it is possible to enhance solubility without sacrifycing thermal and mechanical properties to any great extent.

In this article, synthesis and characterization of four new poly(ether-amide)s containing cyclopentylidene moieties and pendant methyl group in the main chain was reported from the polycondensation reaction of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane with commercially available diacids, *viz.*, 4,4'-Oxybis(benzoic acid), 4,4'-Hexafluoroisopropylidene bis(benzoic acid), 4,4'-Sulfonyl dibenzoic acid and Biphenyl 4,4' dicarboxyllic acid by using N-methyl-2-pyrrolidone (NMP), triphenylphosphite and pyridine as condensing agents. These polymers have aliphatic cyclopentylidene moiety, pendant methyl substitution and ether linkage in the main chain for improving solubility in organic solvents compared to aromatic polyamides.

Synthesis of Monomer

2A.2.1 Synthesis of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

In the first step, cyclopentanone was reacted with o-cresol by using HCl gas in the presence of 3-mercapto propanoic acid as catalyst to obtain the bisphenol (BHMPC). The bisphenol followed by reacts with 4-chloronitrobenzene in presence of anhydrous K_2CO_3 to yield intermediate dinitro compound *viz.*, 1, 1-bis [4-(4-nitro phenoxy)-3-methyl phenyl] cyclopentane (BMNPC). Pure BMNPC was characterized by FT-IR, ^{1}H-NMR spectroscopy.

Scheme 2A.1 outlines the route for the synthesis of diamines containing preformed ether linkages.

FT-IR spectrum of BMNPC **(Fig 2A.1)** exhibited characteristic absorption bands at 1505 cm^{-1} (asymmetric -NO_2 stretching) and 1346 cm^{-1} (symmetric -NO_2 stretching). The band at 3062 and 2959 cm^{-1} were assigned to aromatic –CH stretch and aliphatic –CH stretch respectively. The band at 1255 and 1178 exhibits C-O-C stretching which indicates presence of ether linkages in di-nitro compound.

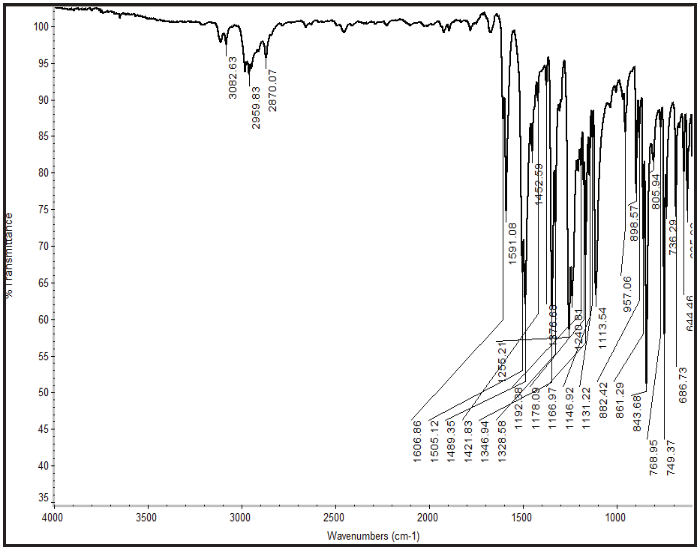
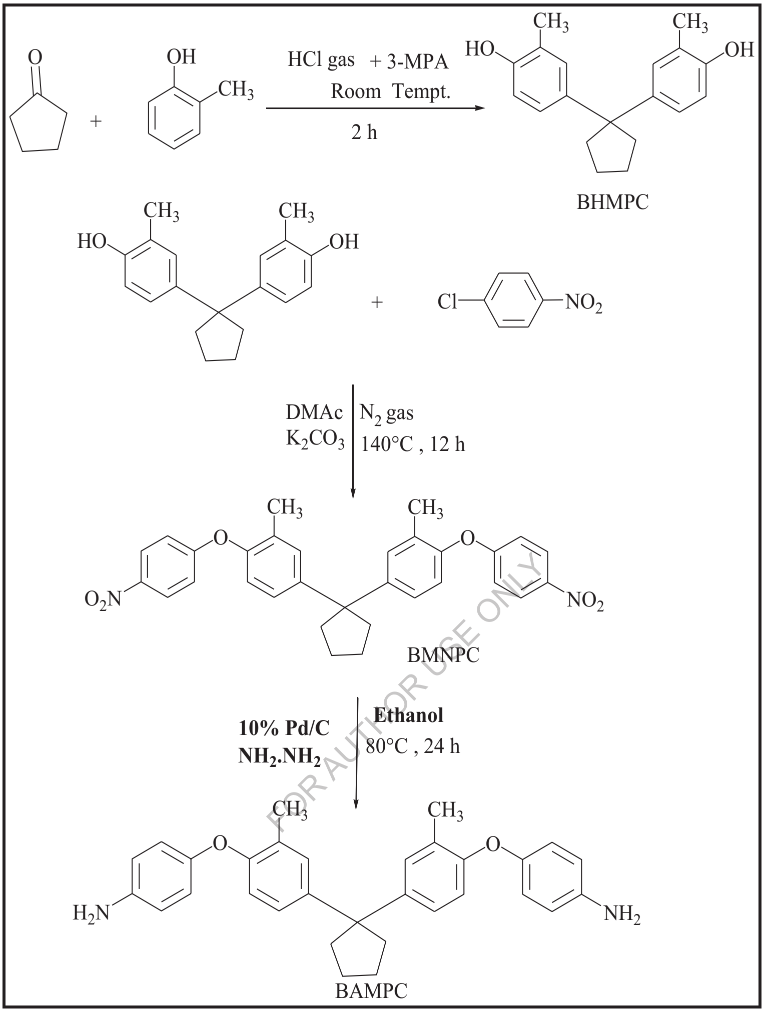


Fig 2A.1 FT-IR spectrum of 1, 1-bis [4- (4-nitro phenoxy)-3-methyl phenyl] cyclopentane

^{1}H-NMR spectrum of BMNPC is depicted in **Fig 2A.2.** The aromatic protons ‘h’ and ‘g’ appeared in the range 8.13 δ, ppm and 7.31 δ, ppm as doublet and which is corresponding to aromatic protons of phenyl ring attached to nitro group. The aromatic proton ‘c’ , ‘d’ and ‘e’ appeared in the range 7.12 δ, ppm and 6.87 δ, ppm as singlet and doublet respectively which is corresponding to aromatic protons of phenyl ring attached to cyclopentane ring. The proton ‘f’ flanked by two methyl groups displayed a peak at 2.08 δ, ppm as singlet and the aliphatic protons ‘a’ and ‘b’ appeared as two multiplete at 1.60 and 2.31 δ, ppm, respectively.

In the next step, BMNPC was reduced to the diamine *viz.*, 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) by catalytic hydrogenation using hydrazine hydrate and Pd-C (10 wt.%). The crude diamine was purified by recrystallization from DMAc-water and was characterized by FT-IR, ^{1}H-NMR, ^{13}CNMR and Mass spectroscopy.



Scheme 2A.1 Synthesis of 1,1-bis[4-(4-amino phenoxy)- 3-methyl phenyl]cyclopentane

FT-IR spectrum of BAMPC (**Fig 2A.3)** exhibited N-H stretching absorption bands at 3464 (asymmetric N-H stretching) and 3377 cm-1 (symmetric N-H stretching) and C-O-C stretching at 1223 cm^{-1} and 1122 cm^{-1}. Band at 3010 cm^{-1} is due to aromatic C-H stretching and band at 2957 and 2869 cm^{-1} is due to aliphatic C-H stretching of cyclopentane moiety.

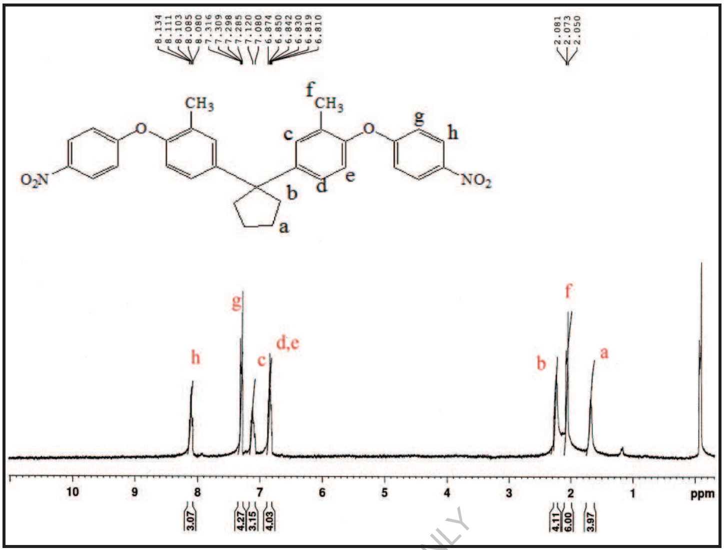


Fig 2A.2 ^{1}H NMR spectrum of 1, 1-bis[4- (4-nitro phenoxy)-3-methyl phenyl] cyclopentane

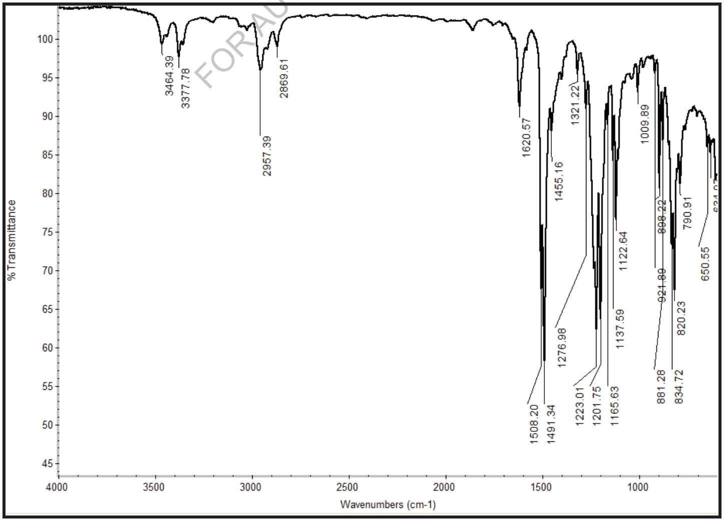


Fig 2A.3 FT-IR spectrum of 1, 1-bis [4- (4-amino phenoxy)- 3-methyl phenyl] cyclopentane

^{1}H-NMR spectrum of 1, 1-bis[4-(4-aminophenoxy)-3-methyl phenyl]cyclopentane (BAMPC) is represented in **Fig 2A.4**.

The aliphatic protons ‘a’ and ‘b’ were observed for methylene group of cyclopentylidene ring at 1.70 and 2.25 δ, ppm. The aliphatic protons ‘f’ at 2.25 δ, ppm overlapped with proton ‘b’ and it is corresponding to methyl group attached to aromatic ring. The aromatic protons‘d’ and ‘e’ displayed peaks at 6.78 and 6.68 δ, ppm, appered as doublet respectively. The aromatic proton ‘g’and ‘i’ appeared as a doublet at 7.02 δ, ppm and 7.28 δ, ppm corresponding to phenyl ring attached to cyclopentylidene ring.The proton ‘h’ appeared as a singlet at 7.11 δ, ppm. The signal at 3.35 δ, ppm is due to $-NH_2$ protons.

^{13}C-NMR spectrum of 1, 1 -bis [3- methyl- 4- (4-amino phenoxy) phenyl]cyclopentane (BAMPC) alongwith assignments is presented in **Fig 2A.5**. ^{13}C NMR spectrum showed fourteen NMR signals to 14 types of different carbons atoms. The NMR signals appeared at 127.84, 125.26, 119.77, 116.75, 116.27 δ; corresponding to aromatic CH carbons. The tertiary carbons showed signals at 153.93, 149.80, 143.28 ($C-NH_2$), 141.84, 129.79 δ, and 54.64 δ whereas CH_2 carbon gave NMR signals at 38.94, 23.02 δ confirming aliphatic cyclopentylidene ring. The carbon showed signal 16.55 δ confirming methyl group attached to aromatic ring.

DEPT spectrum (Fig-2A.6) of BAMPC also confirms the structure of amino compound, all the quaternary carbons are absent in the spectrum and the peaks of CH and CH_3 carbons are upper sides at 129.79, 125.26, 119.80, 116.71, 116.27 δ and 16.58 respectively. The peaks of CH_2 appeared at down side at 38.93, 23.0 δ.

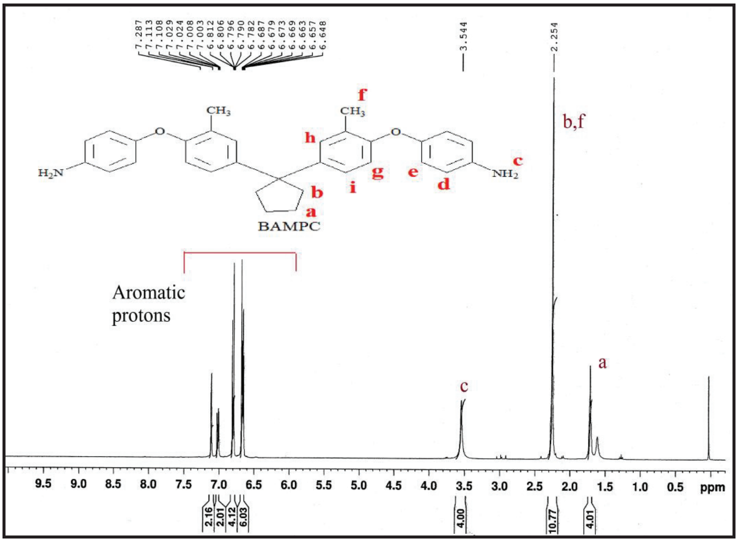


Fig 2A.4 ^{1}H NMR spectrum of 1, 1-bis [4- (4-amino phenoxy)- 3-methyl phenyl] cyclopentane

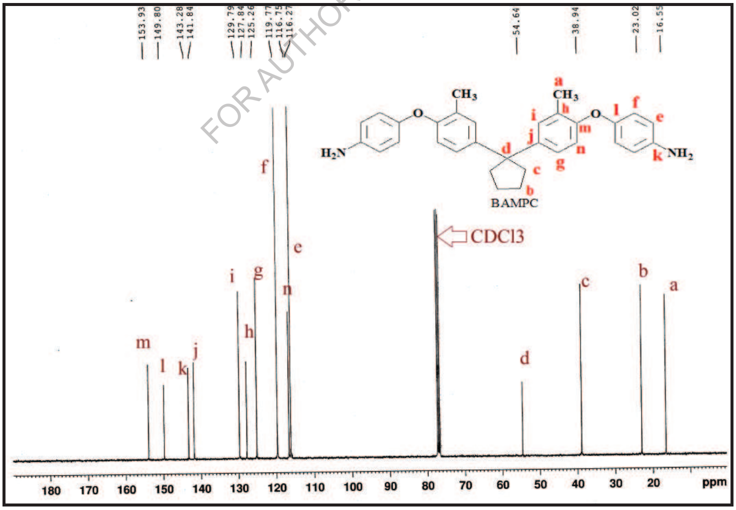


Fig 2A.5 ^{13}C NMR spectrum of 1, 1-bis [4- (4-amino phenoxy) - 3-methyl phenyl] cyclopentane

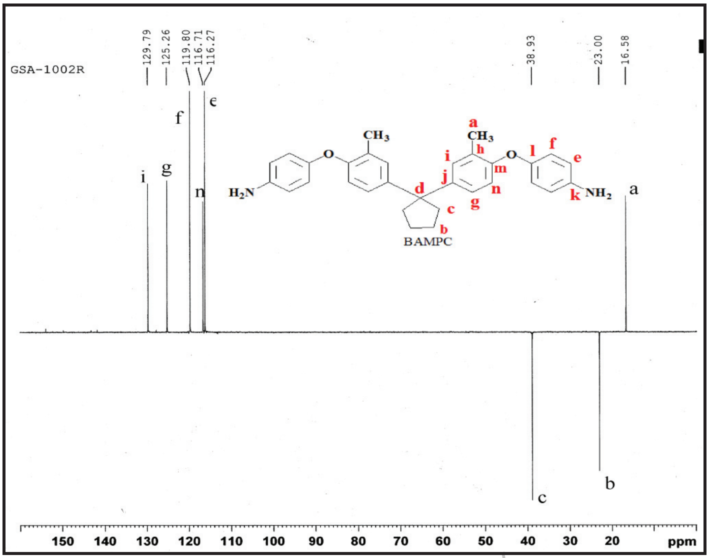


Fig 2A.6 DEPT-135 spectrum of 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane

The mass spectrum of (Fig-2A.7) BAMPC showed molecular ion peak at m/e 465 corresponding to molecular weight of BAMPC.

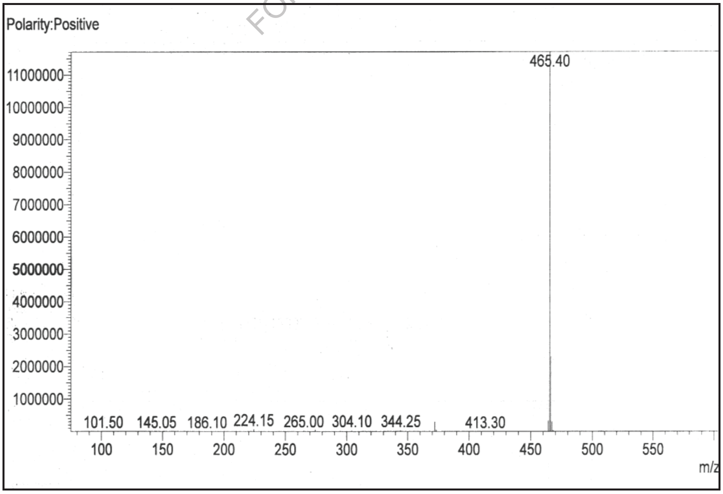


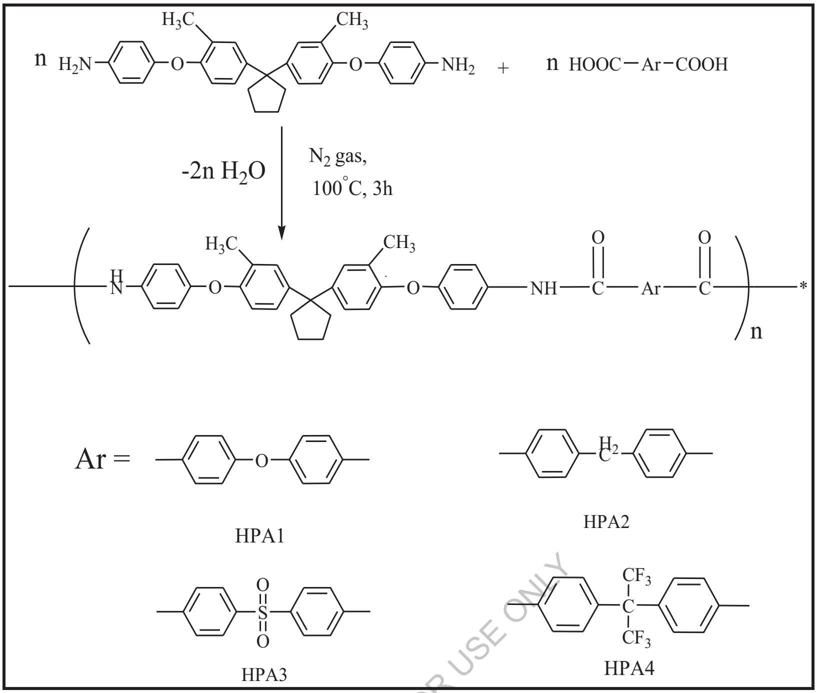
Fig 2A.7 Mass spectrum of 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane

Synthesis of Polymer

2A.2.2 Synthesis of poly(ether-amide)s from 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

As outlined in **Scheme 2A.2**, a series of new aromatic polyamides was synthesized by Yamazaki’s direct phosphorylation polycondensation of 1, 1-bis[4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane with various aromatic diacids in NMP containing lithium chloride using triphenyl phosphite and pyridine as condensing agents.

The direct polycondensation technique reported by Yamazaki et al is a well-accepted and very valuable laboratory method for the synthesis of polyamides [164-166]. This method includes the one-pot polycondensation of aromatic diamines with aromatic diacids in the presence of an aryl phosphite such as triphenyl phosphite and an organic base such as pyridine. The addition of inorganic salts such as LiCl increases the solubility of polymer and maximizes attainable molecular weights. The advantage of this technique is that, it avoids the use of moisture-sensitive diacid chlorides. The polycondensation reactions were carried out at 100°C for 3h. The polymerizations were homogeneous throughout the reaction and afforded viscous polymer solutions. The results of polymerization are summarized in **Table 2A.1**.



Scheme 2A.2 Synthesis of polyether-amides from 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane

Table 2A.1 Yield and Viscosity of Poly (ether-amide)s

Polymer	Monomers		Yield %	Inherent Viscosity dL/g [a]
	Diamine	Diacids		
HPA-01	BAMPC	ODCA	99	0.45
HPA-02	BAMPC	BPDCA	99	0.41
HPA-03	BAMPC	SDCA	95	0.50
HPA-04	BAMPC	6-FDCA	99	0.46

[a] Inherent viscosities were measured at a concentration of 0.5% (W/V) in DMF at 30°C

Inherent viscosities of polyamides were in the range 0.41-0.50 dL/g indicating the formation of medium to reasonably high molecular weight polymers. Tough, transparent and flexible films of polyamides could be cast from their DMF solutions.

Structural characterization

The formation of polyamides was confirmed by FT-IR spectroscopy. **Fig-2A.8** depicts FT-IR spectrum of polyamide HPA-1 derived from 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl]cyclopentane and 4,4’-Oxybis(benzoic acid). Polyamide formation was characterized by the –NH stretching frequency as a broad band around 3300 cm^{-1}. Due to the hydrogen bonding, the >C=O stretching vibration band shifted to lower wave number and appeared at 1648 cm^{-1}.

The polymer HPA-4 (Fig-2A.9) showed similar absorption bands, which are slightly shifted to lower frequency side, viz. at 3311 (N-H stretching), 1492 (N-H bending), 1660 cm^{-1} (amide C=O stretching).

Disappearance of peaks of –COOH & -NH_2 and appearance of amide carbonyl & -NH peaks confirms the formation of polyamides.

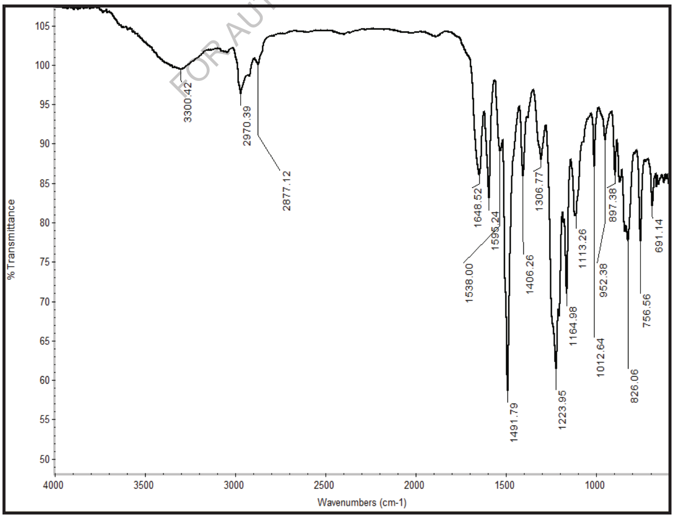


Fig 2A.8 FT-IR spectrum of HPA-1

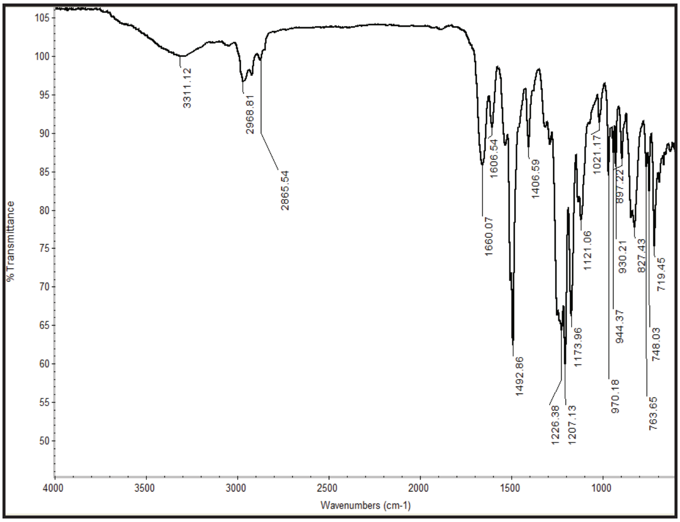


Fig 2A.9 FT-IR spectrum of HPA-4

2A.2.3 Properties of poly(ether-amide)

Solubility of Polyamides

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

Table 2A.2 Solubility Behavior of Poly (ether-amide)s

Polymer	**Solvents**								
	DMF	DMAc	DMSO	NMP	m-Cresol	THF	$CHCl_3$	DCM	C.H_2SO_4
HPA-01	+	+	+	+	+	+	-	-	+
HPA-02	+	+	-	+	+	+	-	-	+
HPA-03	+	+	+	+	+	+	-	-	+
HPA-04	+	+	-	+	-	+	-	-	+

+ : Soluble; - : Insoluble on heating; ± : Sparingly soluble

Polyamides were soluble in DMF, DMAc, DMSO, NMP, m-cresol and H_2SO_4 either at room temperature or upon heating. Whereas reference polyamides derived from rigid diacids like biphenyl-4, 4'dicarboxylic acid or terephthalic acid with 1,3-phenylene diamine were reported to be insoluble in the above solvents [167-169]. The improved solubility of polyamides containing cardo cyclopentylidene ring and pendant methyl group compared with that of reference polymers could be attributed to the presence of cyclopentane ring and methyl group. The cardo cyclopentylidene ring and pendant methyl group along the polymer backbone greatly reduce strong molecular interactions of stiff chain aromatic polymers producing an effective chain separation effect which prevents their tight chain packing and increases the free volume. The disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvent which leads to improvement in solubility.

Thermal properties

Thermal behaviour of polymers was evaluated by means of dynamic thermogravimetry and differential scanning calorimetry. **Table 2A.3** incorporate the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), temperature for 10 % Wt. loss (T_{10}) and residual weight at 900°C.

Table 2A.3 Physical properties of Poly (ether-amide)s

Polymer	**Thermal Behaviour** [b]			
	T_i °C	T_d °C	Residual Wt % at 900°C	Tg °C
HPA-1	297	448	16	225
HPA-2	285	401	25	240
HPA-3	285	472	33	245
HPA-4	283	457	29	196

[b] Temperature at which onset of decomposition was recorded by TG at a heating rate of 10°C /min.

Tg- Glass transition temperature determined at second heating by DSC at a heating rate of 10°C /min

T_d – Temperature of 10% decomposition

T_i – Initial decomposition temperature.

Thermal stability of polyamides was determined by thermogravimetric analysis (TGA) at a heating rate of 10°C/min under nitrogen atmosphere. TG curves of polyamides are shown in **Fig 2A.10**.

The 10% decomposition (T_d) values obtained from TG curves for polyamides were in the range 401-472°C

indicating their good thermal stability, which could obviously be attributed to the structure of diamine and diacid monomers. Along the series of polyamide maximum T_d value obtained for HPA-3 that is due to structure of diacid. The weight residue of polyamides when heated to 900°C in nitrogen was in the range 16-33%.

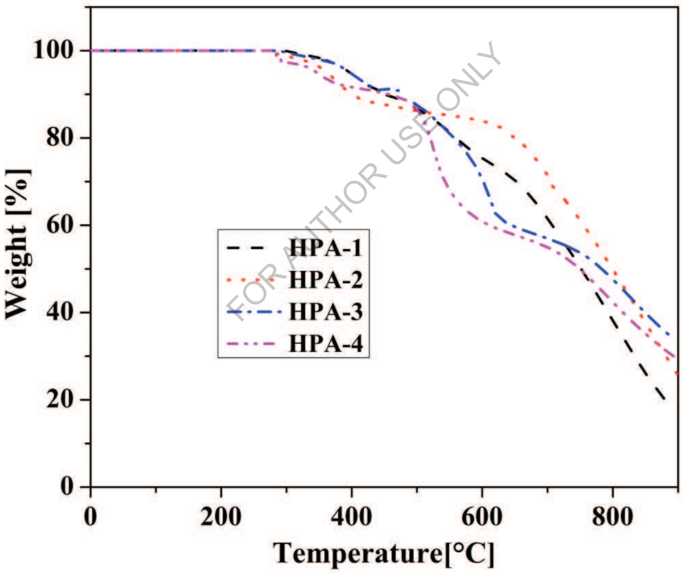


Fig 2A.10 TGA curve of Polyamides HPA-1 to HPA-4.

Glass transition (T_g) temperature of the polyamides was evaluated by differential scanning calorimetery (DSC). Tg values were obtained from second heating scans of polyamide samples at a heating rate of 10°C/min. DSC curves are reproduced in **Fig 2A.11** and Tg values are given in Table 2A.3.

T_g of polyamides containing cardo cyclopentylidene moiety were in the range 196°C-245°C. The increasing order of T_g corresponds to increase in the rigidity of the diacid. The polyamide HPA-4 shows lowest T_g value (196°C) due to trifluoromethyl substituents of diaicid monomer which hinder the chain packing and increase the free volume. The HPA-3 exhibited highest T_g value (245°C) among the series of polyamides due to strcture of diacid. These results are reasonable and can be attributed to the fact that cardo cyclopentylidene moiety and pendant methyl groups along the polymer backbone, which is acting as an internal plasticizer, increases free volume and thereby increases segmental mobility, thus resulting in a reduction in the T_g. A large difference in Tg and decomposition temperature of polyamides offers a broad processing window.

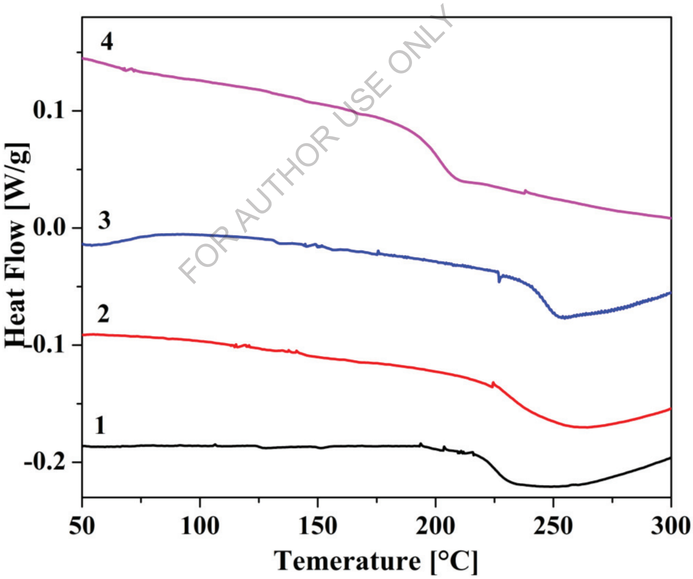


Fig 2A.11 DSC curve of Polyamides HPA-1 to HPA-4.

X-Ray diffractograms of polyamides derived from 1, 1-bis [4-(4-amino 3-methyl phenoxy) phenyl] cyclopentane and aromatic diacids are shown in **Fig 2A.12**.

X-Ray diffractograms of all polymers exhibited a broad halo in the wide angle region (at about 2θ ≈ 20°) indicating that all the polymers were amorphous in nature. This result could be explained in terms of the presence of the pendent methyl groups and cardo cyclopentylidene moiety in the polymer backbone which hindered packing of the polymer chains and decreased the intermolecular forces, subsequently causing a decrease in crystallinity. This behaviour was well supported by solubility of polymers.

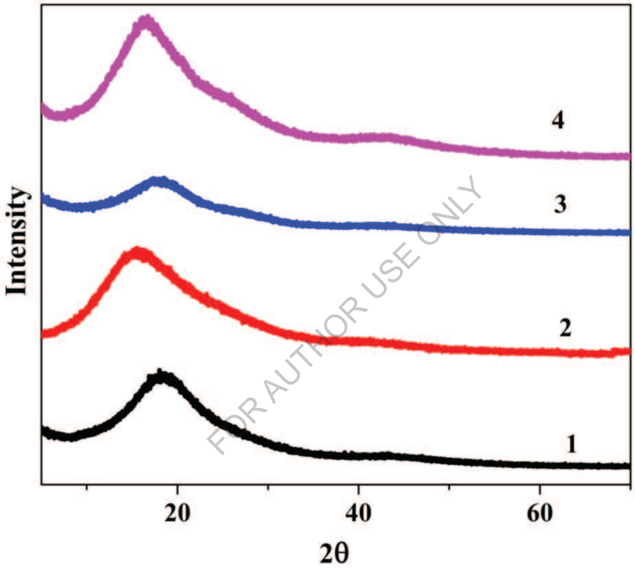


Fig 2A.12 XRD curve of Poly(ether-amide)s HPA-1 to HPA-4

2A.3 Summary and Conclusions

Based on results presented, following summary and conclusions have been drawn.

- Novel monomer; 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC), was synthesized and characterized by physical constant, IR, NMR and mass spectral techniques.

- A series of new polyamides (HPA-1 to HPA-4) containing pendent methyl group and cardo cyclopentylidene moiety was synthesized by the direct polycondensation of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane and aromatic diacids.
- Inherent viscosities of new polyamides were in the range of 0.41-0.50 dL/g indicating formation of medium to high molecular weight polymers.
- Polyamides were found to be soluble in DMF, DMAc, DMSO, NMP, and *m*-cresol at room temperature or upon heating. This indicates that the incorporation of pendent flexible methyl group, ether linkage and cardo cyclopentylidene moiety leads to a significant improvement in solubility of polyamides.
- Tough, transparent and flexible films of the polyamides could be cast from DMAc solution.
- Wide angle X-ray diffraction patterns indicated that polyamides containing pendent Methyl group and cardo cyclopentylidene were amorphous in nature.
- The T_d values for polyamides were in the range 401-472°C indicating good thermal stability of polyamides.
- The T_g values of polyamides were in the range 196-245°C. The depression in T_g values of polyamides could be attributed to the presence of cardo cyclopentylidene moiety, pendant methyl groups as well as commercial diacids used in polymerization.
- A large difference in T_g and decomposition temperature of polyamides offers a broad processing window for this new series of polyamides.

Chapter-2B:Synthesis and Characterization of Co-Poly(ether-amide)s based on Methyl Substituted Diamine Monomers by low temperature polycondensation method.

In recent years various efforts have been focused to improve the processability and solubility of polyamides by chemical alteration of their structure. These structural reformations can be brought about by either producing new diamines or by synthesizing new diacids which finally make the backbone of the polymer. Earlier studies have reported that integration of cardo groups such as cyclododecylidene [170,171], adamantine [172,173], tricyclo [5.2.1.0], decane [174,175], *tert*-butylcyclohexylidene [176] into the backbone of polyamides results in polymers with improved solubility with retaining high thermal stability. The synthesis and characterization of co-poly(ether-amide)s starting from newly prepared cardo diamine monomer namely 1, 1-bis[4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) and commercial IPC/TPC is reported in the present work.

2B.1 Experimental

2B.1.1 Materials

- Isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) were purchased from Sigma Aldrich and used as received.
- Lithium carbonate dried under vaccum at 150°C for 6 h.

2B.1.2 Synthesis of methyl substituted diether-diamine

The same monomer Diether-diamine i.e. 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane synthesized in 2A.1.2 was utilized for the synthesis of Co-poly(ether-amide)s.

2B.1.3 Synthesis of Co-poly(ether-amide)s from 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

In a 100 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet, a calcium chloride guard tube, and a thermowell were placed 0.464 g (0.001mol) 1, 1-bis[4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) and 3 mL dry DMAc were added to the flask. The mixture was stirred under nitrogen atmosphere till the dissolution was complete. The reaction mixture was cooled to -15°C with the help of ice-salt mixture. Then 0.203 g (0.001 mol) Terephthaloyl chloride was added in two lots and kept under stirring for 2 h at 0°C and 12 h at room temperature. The reaction mixture was neutralized with 0.075 g (0.00104 mol) lithium carbonate and heated at 80°C, for 20 min. It was then degassed under vacuum and the polymer was precipitated by pouring viscous polymer solution into excess of rapidly stirred methanol. The precipitated polymer was filtered, washed with water and finally with methanol. It was dried at 80°C under vacuum for 6 h. The yield of polymer (CPA-1) was 99% and inherent viscosity of polymer was 0.83 dL/ g.

The other copoly(ether-amide)s CPA-2 to CPA-5 were synthesized by utilizing similar procedure, where in a mixture of different mol % proportion of (TPC) and (IPC) were polycondensed with BAMPC.

IR Spectrum

CPA 1: 3297 (N-H stretch), 2919, 2860, 1666 (C=O), 1606, 1206, 1182, 720 cm^{-1}

CPA 3: 3297 (N-H stretch), 2970, 2865, 1649(C=O), 1602, 1225, 1182,722 cm^{-1}

CPA 5: 3306 (N-H stretch), 2919, 2865, 1660 (C=O), 1603, 1207, 1182, 722 cm^{-1}

2B.2 Results and Discussion

Aromatic polyamides have marketable value, because fibers and films of these polymers not only possess excellent physical properties at room temperature but maintain their strength and excellent response to loading at elevated temperatures for long period of time. Most of these polyamides are synthesized from aromatic diamines and aromatic diacid chlorides by low temperature solution polycondensation method. Many of the thermally stable polymers are challenging to process because of their limited solubility. Several attempts have been made to modify the aromatic polyamides in order to obtain superior solubility and thermal stability.

In the present work, diamine containing cyclopentylidene moiety, viz. 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl]cyclopentane (BAMPC), containing pendant methyl substituent, cardo cyclopentylidene ring and ether linkage; have been prepared and used as building blocks for synthesis of homo and co-polyamides with TPC/IPC.

2B.2.1 Synthesis of 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane

The novel bis (ether-amine) viz, 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) was produced starting from cyclopentanone in numerous steps (**Scheme 2A.1**) as reported in **chapter 2A**.

1, 1-bis (4-hydroxy 3-methyl phenyl) cyclopentane was obtained as described in **chapter 2A**. The 1, 1-bis [4-(4-nitro phenoxy)-3-methyl phenyl]cyclopentane (BMNPC) was synthesized by condensation of 1, 1-bis(4-hydroxy 3-methyl phenyl) cyclopentane with 4- chloro nitrobenzene. The structure of (BMNPC) was confirmed by IR, ^{1}H NMR spectra.

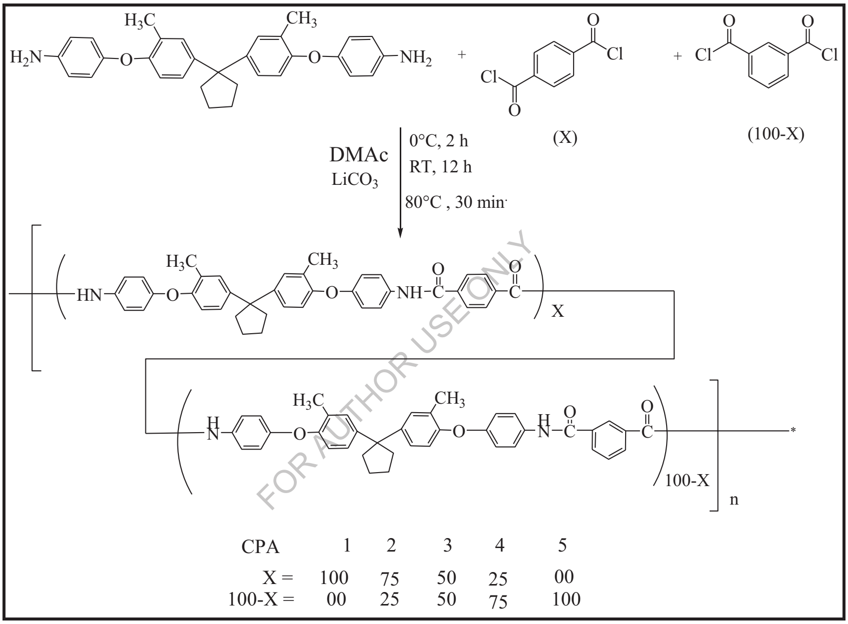
1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) was prepared by catalytic hydrogenation of the bis (ether-nitro) compound BMNPC by using hydrogen Pd/C catalyzed reduction. The structure of new bis(ether-amine) (BAMPC) was confirmed by IR, ^{1}H NMR, ^{13}C NMR and Mass spectra.

2B.2.2 Synthesis of Co-poly(ether-amide)s from 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

Copoly(ether-amide)s containing cardo cyclopentylidene moiety and methyl groups were synthesized by low temperature solution polycondensation reaction of 1, 1-bis[4-(4-amino phenoxy)- 3-methyl phenyl] cyclopentane and IPC and/or

TPC in DMAc at room temperature (**Scheme 2B.1).** The IPC/TPC feed ratios varied from 25% to 100%. The resulting polymers were precipitated by pouring the viscous solutions in methanol.

The yield and viscosities of copoly(ether-amide)s are presented in **Table 2B.1.** All the polymers were obtained in good yields (98 to 99 %). The inherent viscosities of polymers were in the range of 0.81 to 0.84 dL/g; indicating the formation of high molecular weight of polymers.



CPA	1	2	3	4	5
X =	100	75	50	25	00
100-X =	00	25	50	75	100

Scheme 2B.1 Synthesis of poly (ether-amide)s from 1, 1-bis [4- (4-amino phenoxy)- 3-methyl phenyl] cyclopentane

Structural Characterization

Copolyamides were characterized by FT-IR. A representative FT-IR spectrum of polyamide CPA-1 based on 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane and TPC is shown in **Fig 2B.1**. FT-IR spectrum of polyamide showed –NH stretching frequency as a broad band at 3297 cm^{-1}. The amide-I band, associated with stretching vibration of the carbonyl group, appeared at 1666 cm^{-1}. The amide-II band, ascribed to the coupling of the –N-H bending appeared at 1491 cm^{-1}.

Table 2B.1 Yield and Viscosity of Co-poly(ether-amide)s

Polymer	**Monomers**			**Yield %**	**Inherent Viscosity** dL/g [a]
	Diamine (BAMPC) **mol %**	**TPC mol%**	**IPC mol %**		
CPA-1	100	100	0	99	0.83
CPA-2	100	75	25	98	0.84
CPA-3	100	50	50	99	0.82
CPA-4	100	25	75	99	0.83
CPA-5	100	0	100	99	0.81

[a] Inherent viscosities were measured at a concentration of 0.5 % (W/V) in **DMF** at 30°C

The polymer CPA-3 (**Fig 2B.2**) showed similar absorption bands at 3297 (N-H stretching), 1501 (N-H bending), 1649 cm^{-1} (amide C=O stretching).

FT-IR spectrum of polyamide CPA-5 based on 1, 1-bis [3-methyl-4-(4-amino phenoxy)phenyl] cyclopentane and IPC is shown in **Fig 2B.3**. FT-IR spectrum of polyamide showed –NH stretching frequency as a broad band at 3306 cm^{-1}. The amide-I band, associated with stretching vibration of the carbonyl group, appeared at 1660 cm^{-1}. The amide-II band, ascribed to the coupling of the –N-H bending appeared at 1536 cm^{-1}.

All other poly (ether-amide)s CPA-1, CPA-3 and CPA-5 also exhibited strong characteristics absorption bands at around 1225 and 1182 cm^{-1} (asymmetrical and symmetrical C – O –C stretching, due to the ether group.

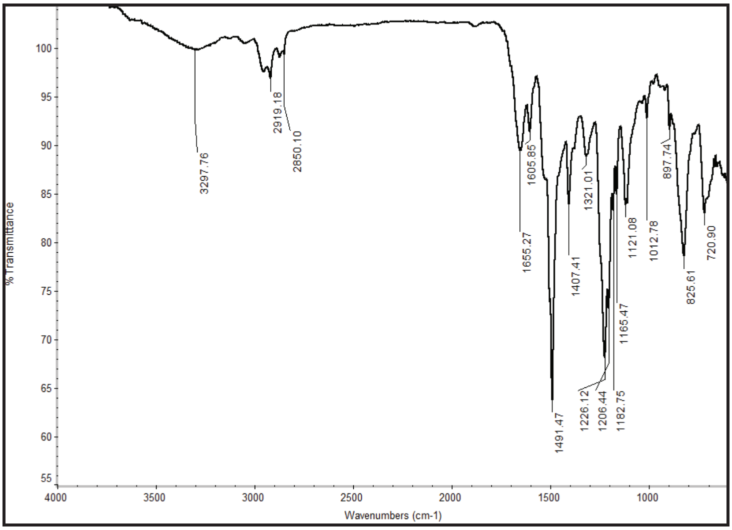


Fig 2B.1 FT-IR spectrum of CPA-1

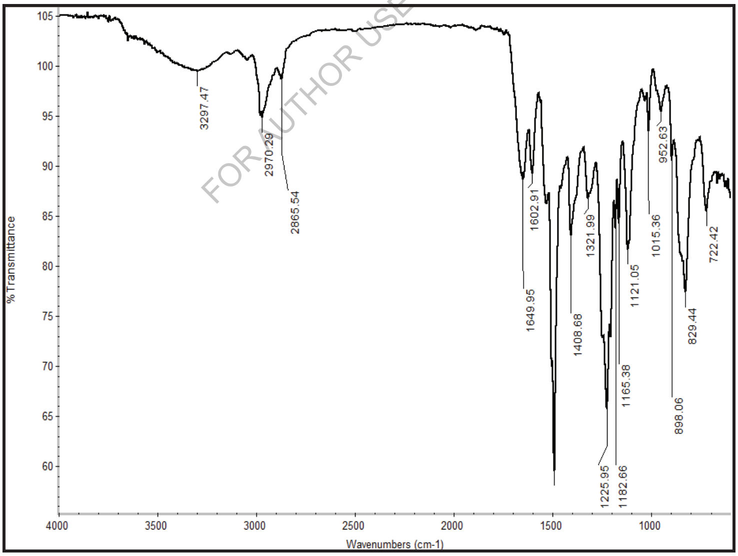


Fig 2B.2 FT-IR spectrum of CPA-3

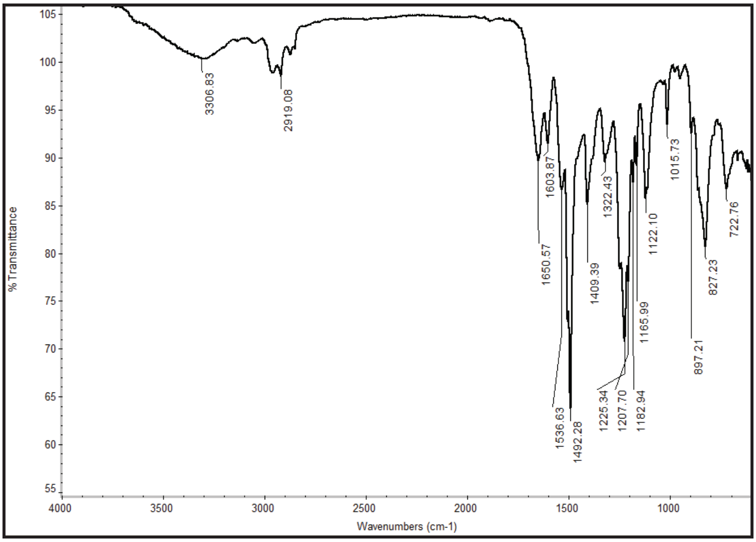


Fig 2B.3 FT-IR spectrum of CPA-5

2B.2.3. Properties of poly(ether-amide)

Solubility of polyamides

Solubility of polyamides was tested in several organic solvents at 3 wt % (w/v) concentration and the data is summarized in **Table 2B.2**.

Table 2B.2 Solubility behavior of Poly(ether-amide)s

Polymer	Solvents							
	DMF	DMAc	DMSO	NMP	Pyridine	THF	DCM	C.H_2SO_4
CPA-1	+	+	+	+	+	-	-	+
CPA-2	+	+	+	+	+	-	-	+
CPA-3	+	+	+	+	+	-	-	+
CPA-4	+	+	+	+	-	-	-	+
CPA-5	+	+	+	+	-	-	-	+

+ : Soluble ; - : Insoluble on heating; ± : Sparingly soluble

Copolyamides were found to be soluble in DMF, DMAc, DMSO, NMP, pyridine and conc. H_2SO_4 at room temperature and they were insoluble in DCM and THF. It is exceptionally reported that polyamide derived from BAMPC with TPC is soluble in pyridine at room temperature but polyamides from BAMPC with IPC is insoluble in pyridine. These results indicated that incorporation of cardo cyclopentylidene moiety and pendant methyl group has disturbed closed packing of polymer chains.

Thus better solubility of these copoly(ether-amide)s; as expected; can be attributed to the introduction of cardo cyclopentylidene moiety, flexible ether linkage and pendant methyl group in the polymer backbone.

Thermal properties of polyamides

Thermal behaviour of polymers was evaluated by means of dynamic thermogravimetry and differential scanning calorimetry. **Table 2B.3** incorporate the thermal data such as glass transition temperature (T_g), temperature for 10 % Wt. loss (T_d) and residual weight at 900°C.

Table 2B.3 Physical properties of Poly(ether-amide)s

Polymer	**Thermal behaviour**[b]			
	T_i °C	**T_d °C**	**Residual Wt % at 900°C**	**Tg °C**
CPA-1	310	439	13	197
CPA-2	305	444	15	192
CPA-3	300	450	25	192
CPA-4	300	458	16	190
CPA-5	298	418	8	189

[b] Temperature at which onset of decomposition was recorded by TG at **a** heating rate of 10°C /min.

Tg- Glass transition temperature determined at second heating by DSC at a heating rate of 10°C /min

T_d – Temperature of 10 % decomposition

T_i- Initial decomposition temperature

Thermal stability of polyamides was determined by thermogravimetric analysis (TGA) at heating rate of 10°C /min under nitrogen atmosphere. TG curves of polyamides are shown in **Fig 2B.4**

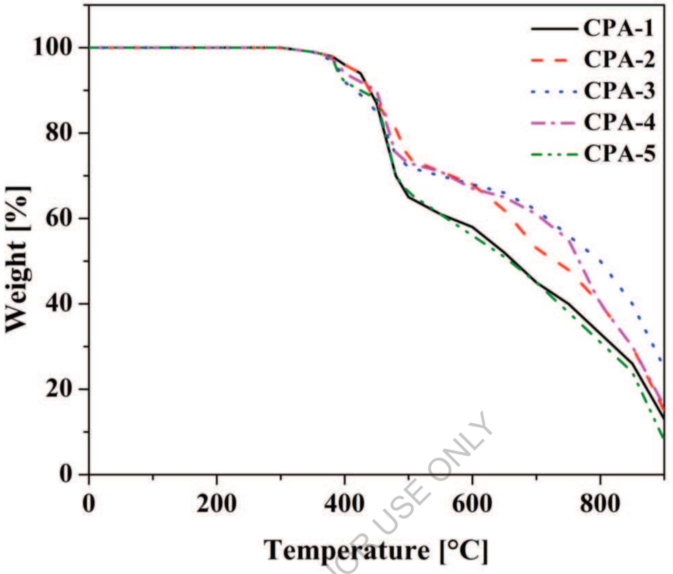


Fig 2B.4 TGA curve of Poly(ether-amide)s CPA-1 to CPA-5.

The T_d values obtained from TG curves for polyamides were in the range 418-458°C indicating their good thermal stability. The initial decoposition range were in the range of 298-310°C. The weight residue of polyamides when heated to 900°C in nitrogen was in the range of 8-28%. This good thermal stability of polymers can be attributed to structure of new diamine and diacid chloride monomer.

DSC curves of poly (ether-amide)s from BAMPC are shown in **Fig 2B.5.**

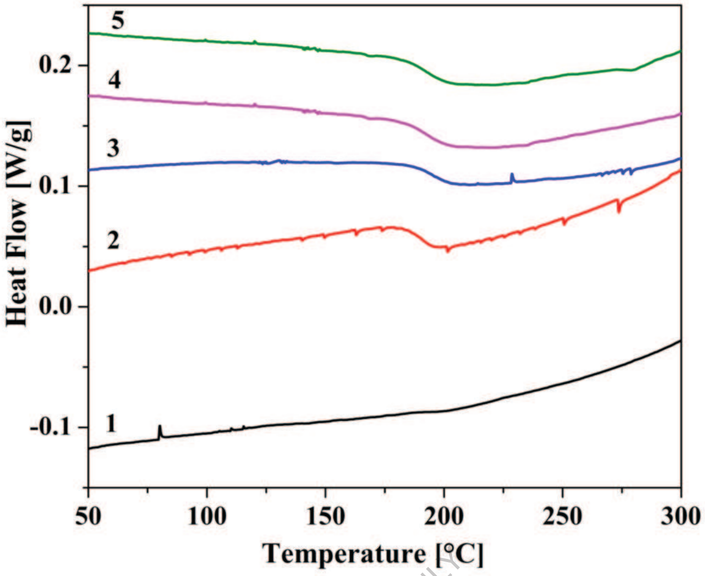


Fig 2B.5 DSC curve of Poly(ether-amide)s CPA-1 to CPA-5.

The glass transition temperatures of the copoly(ether-amide)s are in the range of 189°C to 197°C. The DSC curves for all the polymers showed similar trend with nearly same values for T_g. The polyamide CPA-1 showed higher T_g value due to para catenation of TPC. The polyamide CPA-5 showed lower T_g value, it is attributed to meta catenation of IPC.

Wide-angle X-ray diffraction (WAXD) patterns of polyamides containing cardo cyclopentylidene groups are shown in **Fig 2B.6.** Copoly(ether-amide)s exhibited a broad halo over the range 2θ ≈10-20°, indicating their amorphous to partially crystalline in nature. Polyamide (CPA-1) derived from BAMPC with TPC observed to be partially crystalline in nature in contrast to from IPC (CPA-5). Apparently, the introduction of cardo cyclopentylidene moiety, ether linkage and pendant methyl groups in polyamide, interferes with the dense chain packing, thus resulting in their amorphous nature.

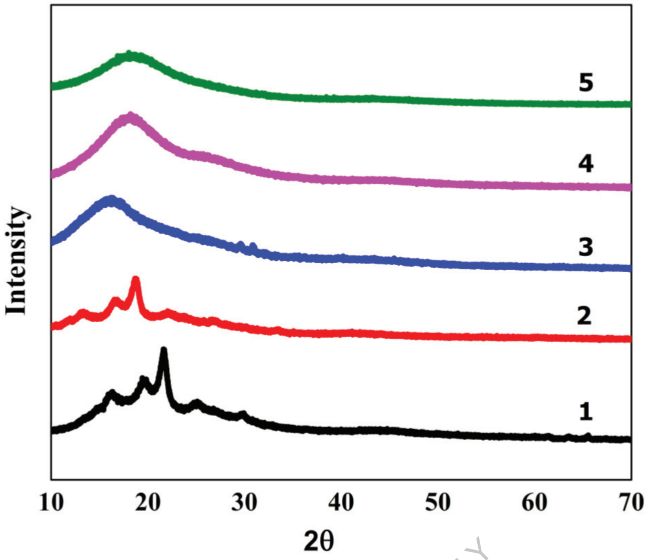


Fig 2B.6 XRD curve of Co-poly(ether-amide)s CPA-1 to CPA-5

2B.3 Summary and Conclusions

- By using low temperature solution polymerization novel bis (ether-amine); BAMPC was polymerized with IPC and / or TPC in different mol proportion in DMAc solvent to synthesize the new series of co-poly(ether-amide)s CPA1 to CPA-5.
- Inherent viscosities of these polyamides were in the range of 0.81 to 0.84 dL/g indicating built-up of moderately high molecular weights.
- Solubility of poly(ether-amide)s was tested in different solvents. All the polymers were soluble in polar aprotic solvents viz. DMF, DMSO, DMAc, NMP etc. These polymers also dissolved in pyridine and hot m-cresol. Polymers had better solubility because of random, nonorder arrangement and less crystalline (i.e. more amorphous) nature. This has been attributed to the flexibility of the system caused by the increased mobility of the molecular segments when amorphous polymers interact with solvent. Incorporation of BAMPC increased the solubility remarkably. Thus the approach of

incorporation of BAMPC was more effective for improving the solubility of polymers in organic solvents; because it gave ether and methyl containing cardo cyclopentylidene moiety.

- The glass transition temperature of poly (ether-amide)s (189°C to 197°C) can allow processing of polymer above 197°C.
- Thermal stability of poly(ether-amide)s was evaluated by dynamic thermogravimetric analysis under nitrogen atmosphere, and all polymers showed 10% weight loss in between 418°C to 458°C.
- X-ray diffraction pattern of polymers suggested that introduction of cardo cyclopentane group, pendant methyl group, ether linkage and copolymerization (involving TPC, IPC; para-para and meta-meta catenation) may have disrupted the chain regularity and packing leading to amorphous nature. The above observation also support solubility properties of the polymers investigated.

Chapter-2C:Synthesis and Characterization of Copoly(ester-amide)s Based on Diester-Diamine Monomer

Aromatic polyamides (aramids) have excellent mechanical strength and high temperature resistance. However their infusibility and restricted solubility in organic solvents limits applications [177-181], hence, many efforts have been made with the goal of designing the chemical structure of the stiff aromatic back bone with some aliphatic or heterocyclic linkages to obtain aramids that are processable by conventional techniques [182,183]. Attempts in this area include introducing flexible linkages, m, m'-linkages and bulky pendant groups into polymer chain, non-coplanar conformation, which leads to a decrease in crystallinity [184-186]. These changes lower the melting temperature and lead to soluble and amorphous polymers which may open applications in the areas of gas separation membranes, engineering, films, coatings, plastics, polymer blends, and composites [187,188]. Studies have been focused on inserting both ester and bulky pendant groups along the aramids backbone to minimize the compromise between the processability and useful properties of aramids. The introduction of ester linkages is known to enhance the processability and toughness of aromatic polymers without a significant reduction in thermal stability [189-192]. Furthermore, the integration of cardo group can decrease hydrogen bonding and inter chain interactions in polyamides and generally disturb the co-planarity of aromatic units to reduce packing density and crystallinity [193-196]. This should improve solubility [197,198].

In present investigation a new meta oriented cardo aromatic diamine containing cyclopentylidene moiety, 1, 1-bis (3-aminobenzoyloxy phenyl)cyclopentane; m-BAPCP, (III) was synthesized and characterized by spectral techniques. A series of poly(ester- amide)s was synthesized from (III) by low temperature solution polycondensation method with different mol proportion of IPC and TPC. The polymers were characterized by measurement of FT-IR spectra, solubility, inherent viscosity, differential scanning calorimetry

(DSC), thermogravimetric analysis (TGA) and X-ray diffraction pattern so as to study the effect of insertion of cardo cyclopentylidene moiety and ester linkage as well as structure of aromatic diacid chloride into polymer backbone. It has been demonstrated that integration of both ester and cyclopentylidene cardo units into the polymer backbone is a successful route to increase the solubility of aramids while retaining high thermal stability.

2C.1 Experimental

2C.1.1 Materials

- Phenol, 4-nitrobenzoic acid, glacial acetic acid, Conc. hydrochloric acid were purchased from S.D. fine chemicals and used as received.

2C.1.2 Synthesis of Diester-Diamine monomer

2C.1.2.1 Synthesis of m- nitrobenzoyl chloride (MNBC).

In a 100 ml round bottom flask equipped with reflux condenser and calcium chloride guard tube, 20 g (0.12 mol) of m- nitrobenzoic acid (MNBA) and 35 mL (0.48 mol) thionyl chloride were placed. The mixture was stirred with magnetic stirrer, and 4 mL of dimethyl formamide were added. The reaction mixture was heated at 80°C for 5h to get clear solution. The excess of thionyl chloride was removed by distillation and traces of thionyl chloride were removed azeotropically using dry benzene. The residue was dissolved in dry hexane and filtered rapidly under nitrogen, and filtrate was subjected to distillation to remove hexane. The residual acid chloride (PNBC) was purified by vacuum distillation and distillate was recrystallized from dry hexane.

Yield: 81 %

M.P.: 74-76°C (Lit. 75°C).

2C.1.2.2 Synthesis of 1, 1-bis (4-hydroxy phenyl) cyclopentane (BHPP) (I)

In a 500 mL round bottom flask equipped with a thermowell, a condenser and a magnetic stirrer were placed 141 g (1.5mol) of phenol and 21 g (0.25 mol) of cyclopentanone. To this solution 100 mL of conc. 36 % HCl and 50 mL of glacial acetic acid were added. Resulting reaction mixture was stirred for 8 h at 45°**C** and kept overnight at room temperature. Then pink color product was isolated by filtration and washed with hot water till it is free from phenol and acid. A crude bisphenol (I) was purified by dissolving in minimum quantity of 2 M NaOH at room temperature and the resulting solution was filtered to remove the gummy product. The filtrate was acidified with conc. HCl to yield the precipitate. The precipitated product was filtered, washed with water till free from acid and dried. Finally the crude bisphenol, was reprecipitated from methanol-water mixture to get faint pink shining crystals.

Yield: 28.6 g (45.03 %)

M.P.: 168-170°C

IR: 3582, 3387, 3299, 2967, 2865, 1633, 1592, 1449, 1373, 1251, 1178, 1083, 835, 735, 681 cm^{-1}

2C.1.2.3 Synthesis of 1, 1-bis(3-nitrobenzoyloxy phenyl) cyclopentane (BNPC) (II)

1, 1- bis (4-hydroxy phenyl)cyclopentane (BHPP) (10.16 g, 0.04 mol) was dissolved in 120 mL dry N, N- dimethyl acetamide (DMAc); and triethyl amine (12 mL, 0.088 mol) were mixed in a 500 mL three neck round bottom flask equipped with a calcium chloride guard tube, a condenser, a thermowell and a magnetic stirrer. The resulting reaction mixture was cooled to 5**°C** and a solution of 3-nitrobenzoyl chloride (15.6 g; 0.084 mol) in DMAc (40 mL) was added dropwisely over a period of about 1 h. After complete addition, the reaction mixture was stirred at room temperature for 1 h and at 80°C for 8 h. The reaction mixture was then poured into 600 mL water. The precipitate was collected by filtration, washed thoroughly with water, methanol and dried. The product was light yellowish in colour.

Yield: 19.90 g (90 %)

M.P.: 186-188**°C**.

IR: 1742 cm-1 (C=O stretching); 1548, 1324 cm-1 (-NO_2 stretching) and 1284, 1170 cm-1 (C-O-C stretching).

^{1}H NMR (400MHz, DMSO-*d6*), δ (ppm): 9.04 (s, 2H), 8.54 (s, 2H), 8.52 (dd, 2H), 7.77 (dd, 2H), 7.28 (d, 4H), 7.18 (d, 4H), 2.36(m, 4H), 1.80(m, 4H).

2C.1.2.4 Synthesis of 1, 1-bis(3-aminobenzoyloxy phenyl) cyclopentane (BABPC) (III)

A mixture of 13.80 g (0.025 mol) of the bis(ester-nitro) BNPC compound and 0.284 g of 10% Pd/C in 150 mL of DMAc was stirred at room temperature under a 4 kg/cm^2 hydrogen pressure. The progress of reaction was supervised by TLC. The time required for complete conversion of dinitro to diamine was about 30 h. The solution was filtered to remove the catalyst, and the obtained filtrate was poured into 700 mL of stirred water to give a light green product, m-BABPC. Finally the bis (ester-amine) (m-BABPC) was recrystallized from DMF-methanol mixture, filtered washed with methanol and dried.

Yield: 9.6 g (78 %)

M.P.: 264-266°C.

IR: 3450 cm^{-1} (N-H stretching), 3360, 2960(C-H Stretching), 1728 cm^{-1} (C=O stretching), and 1292, 1168 cm-1 (C-O-C stretching).

^{1}H NMR (400MHz, DMSO-d_6), δ (ppm): 7.59 (d, *J* = 8.9Hz, 2H), 7.49 (d, *J* =8.6Hz, 2H), 7.46 (s, 2H), 7.24 (d, *J* = 7.6Hz, 4H), 7.06 (t, *J* = 7.8Hz, 4H), 6.96 (d, *J* = 7.8Hz, 2H), 5.12 (s, NH$_2$, 4H), 2.30(m,4H), 1.68(m,4H)

^{13}C NMR (100MHz, DMSO-d_6), δ (ppm): 165.47, 152.61, 148.88, 146.08, 129.95, 128.95, 127.96, 121.46, 119.64, 118.05, 115.31, 55.14, 38.65, 22.82

2C.1.3 Synthesis of poly(ester-amide)s from 1, 1-bis(3-aminobenzoyloxy phenyl) Cyclopentane

In a 100 mL three necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet, a calcium chloride guard tube, and a thermowell were placed 0.492 g (0.001mol) 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (m-BABPC) and 3 mL dry DMAc was added to the flask. The mixture was stirred under nitrogen atmosphere till the dissolution was complete. The reaction mixture was cooled to -15**°C** with the help of ice -salt mixture. The

0.203 g (0.001mol) Terephthaloyl chloride was added in two lots with continuous stirring for 2 h at 0°**C**. Then the mixture was stirred for 12 h at room temperature; and neutralized with 0.075 g (0.00104 mol) lithium carbonate and heated at 80°**C**, for 20 min. It was then degassed under vacuum and the polymer was precipitated by adding reaction mixture to excess of rapidly stirred methanol. The precipitated polymer was filtered, washed with water and finally with methanol. It was dried at 80°**C** under vacuum for 6 h. The yield of polymer (PEA-1) was 100 % and inherent viscosity of polymer was 0.46 dL / g. The other poly (ester-amide)s PEA-2 to PEA -5 were produced by utilizing similar procedure, where in a mixture of different mol % proportion of (TPC) and (IPC) were polycondensed with (m-BABPC).

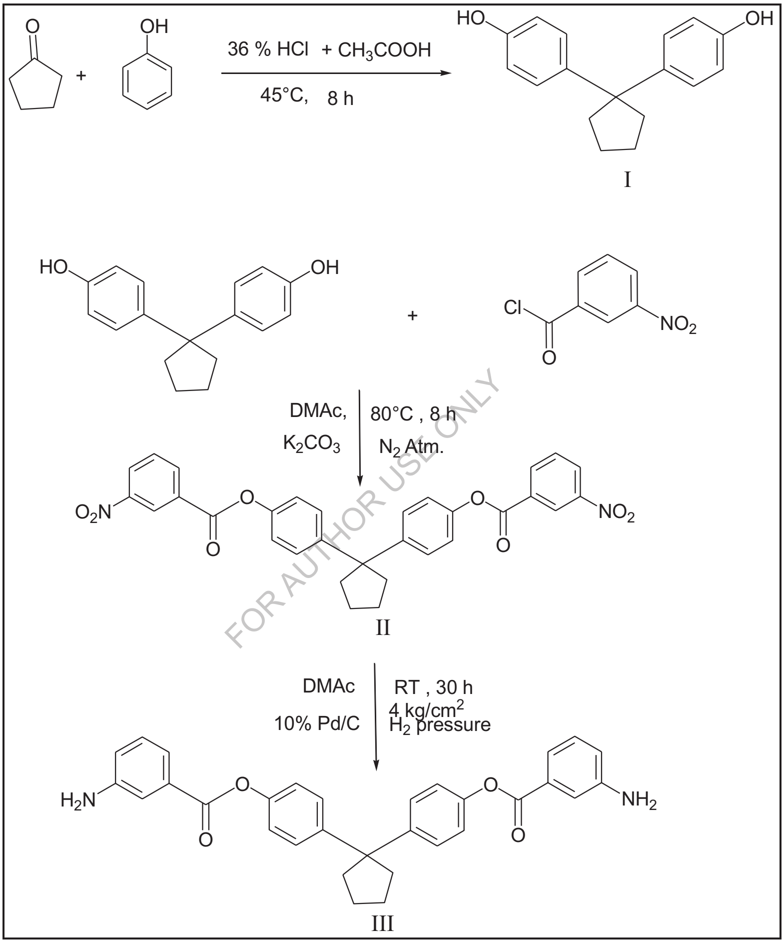
2C.2 Results and Discussion

Diamines are valuable building blocks for the synthesis of high performance polymers including polyamides and their co-polymers. To extend the effectiveness of these high performance polymers it has been a long desired goal to design and prepare diamines, which produce soluble and processable polyamides without too much sacrificing thermal stability. Also, co-polymerization is an effective approach to improve the solubility of the polyamides [199-201]. Even though most soluble polymers have been prepared by combinations of the structural modifications, it does appear that a flexible or kinked linkage is a necessary requirement for solubility. Co-polymers having ether and ester linkages lead to flexibility of the polyamides without negotiating thermal stability.

The main objective of this study was focused on improving the solubility of the new polyamides through the design and synthesis of new diamine. Therefore, for the preparation of a flexible diamine with built-in ester group, a series of reactions was performed.

2C.2.1 Synthesis of 1, 1-bis(3- aminobenzoyloxy phenyl) cyclopentane

The novel diester-diamine, 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (III) (m-BABPC) was synthesized from phenol and cyclopentanone in several steps. (**Scheme 2C.1**)



Scheme 2C.1 Synthesis of 1, 1-bis(3- aminobenzoyloxy phenyl) cyclopentane (III)

1, 1-bis (4-hydroxy phenyl) cyclopentane (I) was synthesized by reacting phenol with cyclopentanone in presence of acid catalyst. The m- nitrobenzoyl chloride (MNBC) was synthesized from m- nitrobenzoic acid (MNBA) and thionyl chloride.

1, 1-bis (3- nitrobenzoyloxy phenyl) cyclopentane (BNPC) (II) was prepared by condensation of BHPP with two moles of m- nitrobenzoyl chloride. Structure of novel BNPC was confirmed by IR, ^{1}H NMR spectra.

The infrared spectrum of (II) exhibited characteristic absorptions at 1742 carbonyl (>C=O) stretching; 1548, 1324 nitro ($-NO_2$) stretching and 1284, 1170 cm^{-1} ether (C-O-C) stretching (**Fig 2C.1**).The absorption band at 867 cm^{-1} and 702 cm^{-1} is due to meta substitution to aromatic ring.

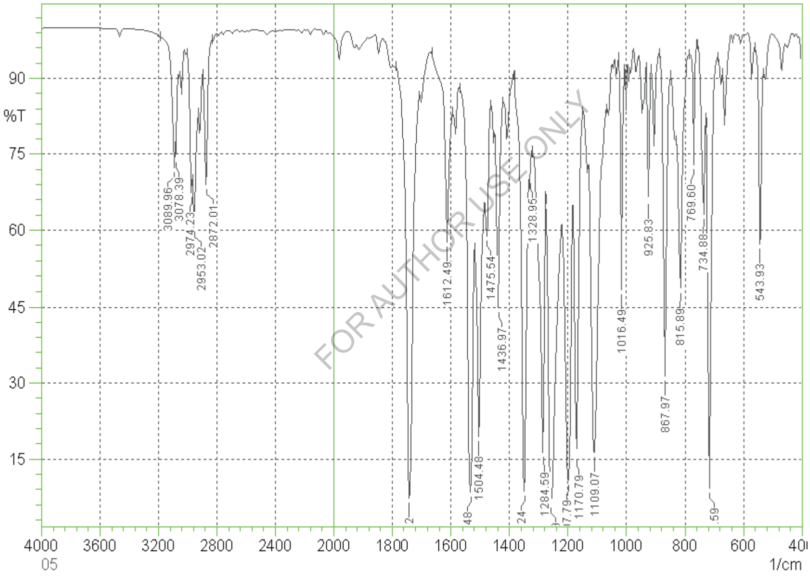


Fig 2C.1 FT-IR of 1, 1-bis (3- nitrobenzoyloxy phenyl) cyclopentane (II)

^{1}H NMR spectrum (**Fig 2C.2**) of (II) showed singlet at 9.04; 9.02; doublet at 8.54; 8.52; doublet of doublet at 7.77; 7.75; 7.63 δ corresponding to aromatic protons of phenyl ring attached to nitro group and at 7.48; 7.28; 7.18; 7.16 δ for aromatic proton of phenyl ring with cyclopentylidene moiety. Peaks at 2.36 and 1.80 δ correspond to aliphatic proton of cyclopentylidene moiety.

Bis (ester-nitro) compound (II) on catalytic (Pd/C) hydrogenation yielded 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (III) (m-BABPC). The structure of bis (ester-amine) (III) was confirmed by IR, ^{1}H NMR, ^{13}C NMR, DEPT-135 spectra.

FT-IR spectrum of m-bis(ester-amine) (III) (**Fig 2C.3**) exhibited the characteristic absorptions band at 1728 cm^{-1} (C=O stretching). Absorption bands at 3440-3360 cm^{-1} (N-H stretching) and 1220, 1168 cm^{-1} (C-O-C stretching) were seen. Band at 3010 cm^{-1} is due to aromatic C-H stretching and band at 2939 cm^{-1} is due to aliphatic C-H stretching of cyclopentane moiety. The absorption band at 866 cm^{-1} and 748 cm^{-1} due to meta substitution to aromatic ring.

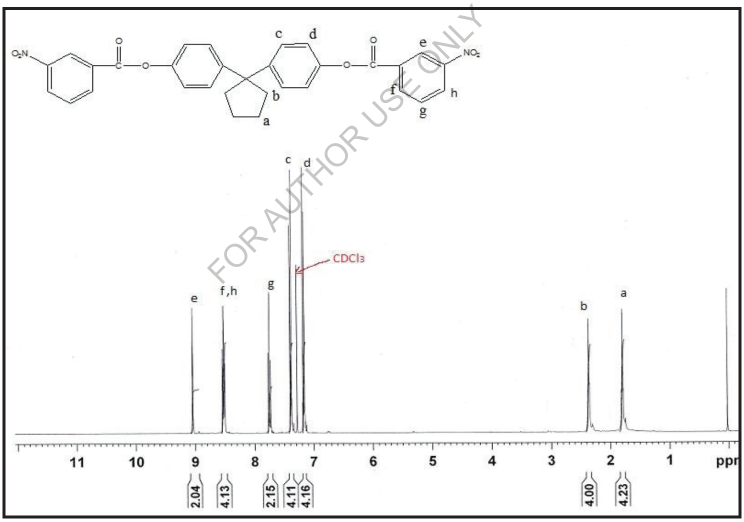


Fig 2C.2 ^{1}H NMR of 1, 1-bis (3- nitrobenzoyloxy phenyl) cyclopentane (II)

Proton NMR spectrum (**Fig 2C.4**) of (III) showed aromatic proton signals at 7.59; 7.49; 7.24; 7.06; 6.86 δ as expected with desired integration and splitting pattern. The amino group signal appeared at 5.12 δ. Peaks at 2.30 and 1.68 δ correspond to methylene protons of cyclopentylidene moiety.

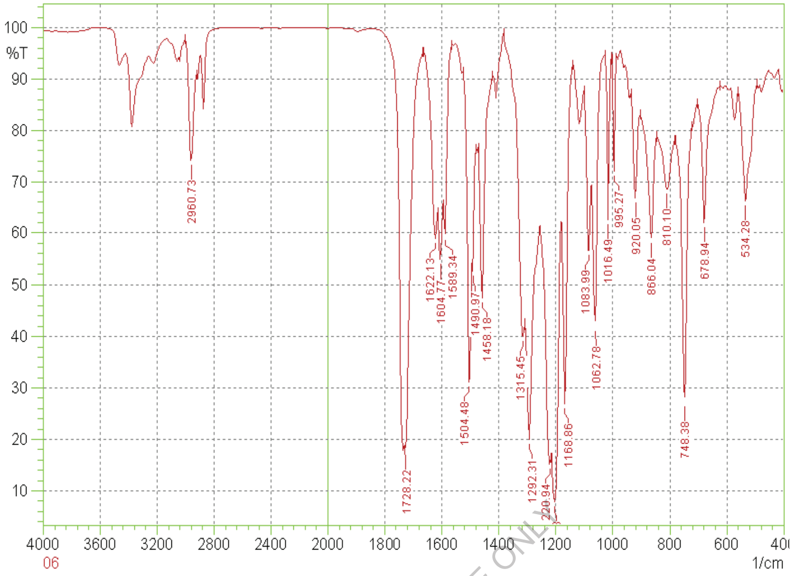


Fig 2C.3 FT-IR spectrum of 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (III)

^{13}C NMR spectrum (**Fig 2C.5**) of (III) showed fourteen NMR signals to 14 types of different carbons atoms. The NMR signals of carbonyl carbon appeared at 165.47 δ; whereas tertiary carbons showed signals at 152.61 (C-NH_2); 148.88, 146.08, 129.95 and 55.14 δ. The CH carbons appeared at 128.95, 127.99, 121.23, 119.64, 118.05, 115.31 δ, whereas CH_2 carbon gave NMR signals at 38.65, and 22.82 δ confirming the formation of amino compound.

DEPT-135 spectrum of bis (ester – amine) also confirms the structure of (III), all the quaternary carbons were absent in the spectrum and the peaks of CH carbons appeared as upside (positive signals) at 129.34, 127.97, 121.47, 114.39 δ and CH_2 appeared as down side (negative signals) at 38.65 and 22.82 δ.(Fig-2C.6)

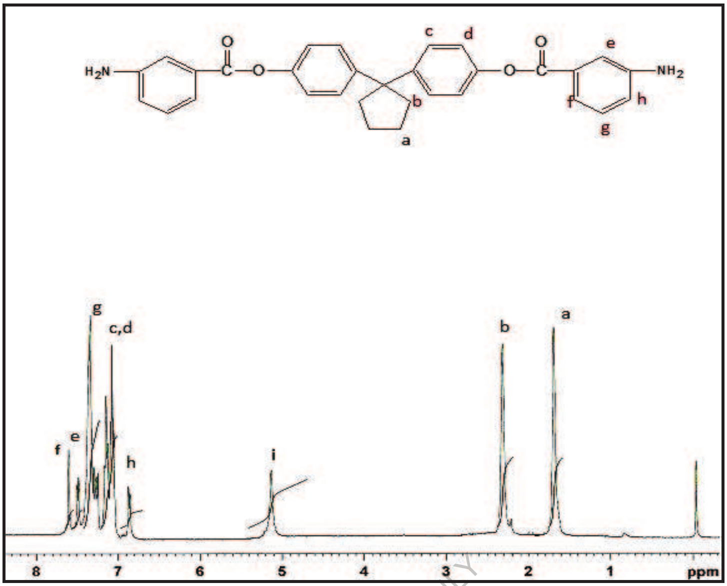


Fig 2C.4 ^{1}H NMR of 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (III)

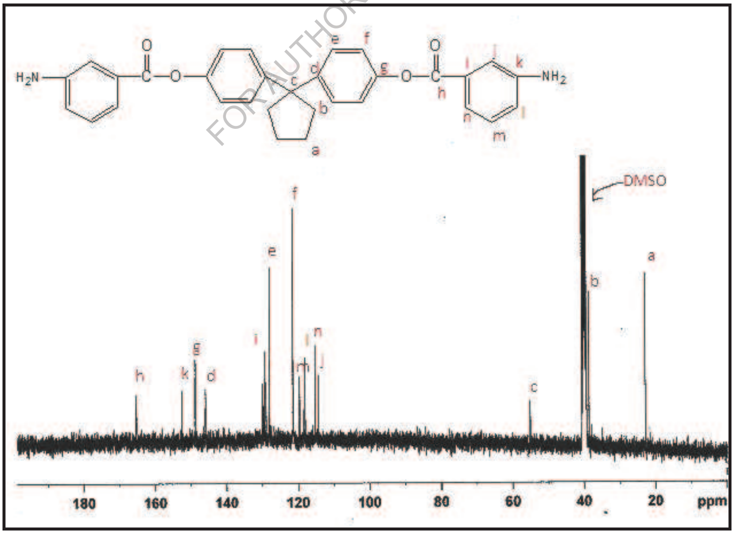


Fig 2C.5 ^{13}C NMR of 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (III)

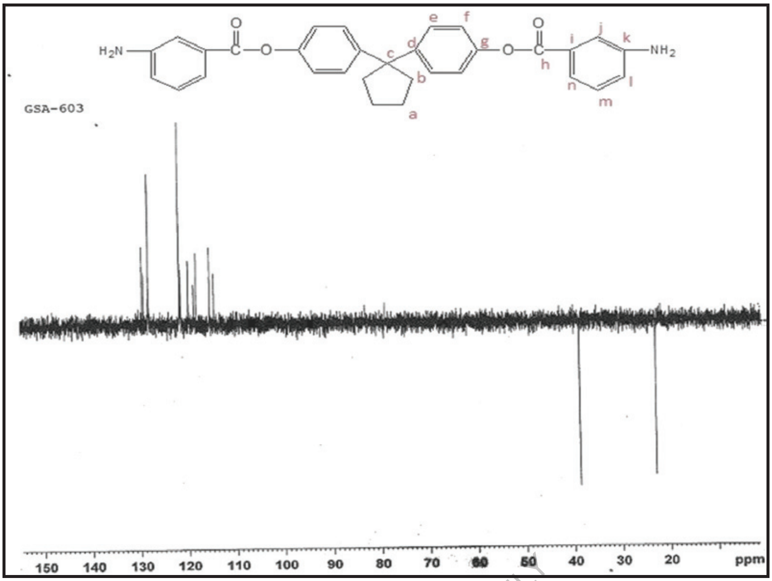


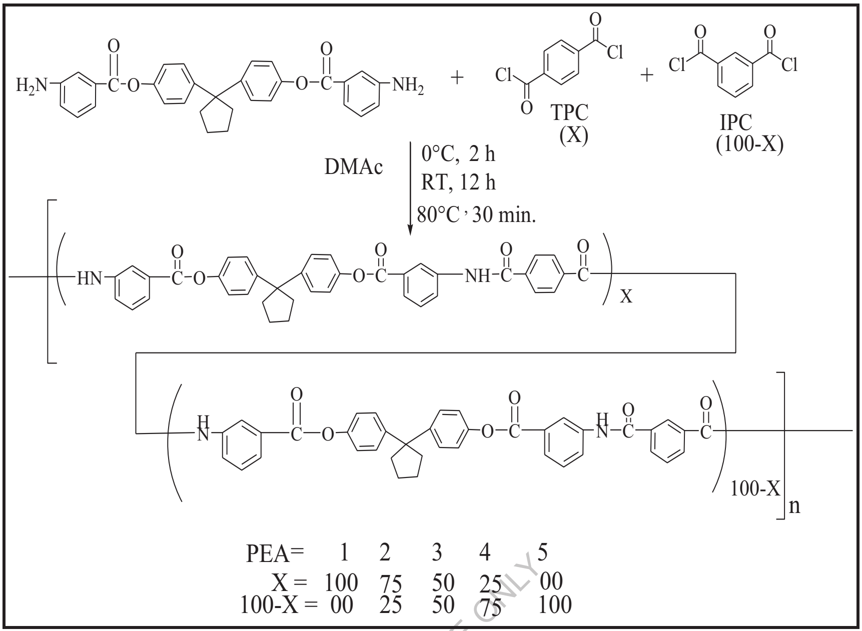
Fig 2C.6 DEPT-135 of 1, 1-bis (3- aminobenzoyloxy phenyl) cyclopentane (III)

2C.2.2 Synthesis of polyester-amides from 1, 1-bis(3-aminobenzoyloxy phenyl) cyclopentane

Aromatic poly (ester-amide)s were synthesized (**Scheme 2C.2**) by condensation of (m-BABPC), (III) with IPC and / or TPC in different mol proportion by low temperature solution polymerization in DMAc. The polymerization preceded smoothly giving viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in methanol.

2C.2.3 Properties of poly(ester-amide)

The Mol %, yield and viscosity data of poly (ester-amide)s from (m-BABPC), (III) are presented in **Table 2C.1.** All the polymers were obtained in good yields (98 to 100 %). The inherent viscosities of polymers were in the range of 0.30 to 0.46 dL/g; indicating the formation of moderate to reasonably high molecular weight polymers.



Scheme 2C.2 Synthesis of Poly(ester-amide)s (PEA-1 to PEA-5)

Table 2C.1 Yield and Viscosity of Poly(ester-amide)s[b]

Polymer	Monomers			Yield %	Inherent Viscosity dL/g [a]
	Diamine BABCP mol %	TPC mol %	IPC mol%		
PEA-1	100	100	0	100	0.46
PEA-2	100	75	25	99	0.32
PEA-3	100	50	50	98	0.36
PEA-4	100	25	75	99	0.33
PEA-5	100	0	100	100	0.30

[a] Inherent viscosities were measured at a concentration of 0.5 % (W/V) in **NMP** at 30°C

[b] Polymerization was carried out with 1 mmol of m-BABPC (III) and 1 mmol of TPC and / or IPC.

Structural Characterization

The structural features of the poly (ester-amide)s were characterized by FT-IR spectroscopy. The infrared spectrum of polymer PEA-1 showed characteristics absorption at 3320 cm-1 (N-H stretching), 1502 cm-1 (N-H bending), 1670 cm-1 (amide C=O stretching). Absorption band at 864 cm^{-1} and 748 cm^{-1} indicates meta catenation (**Fig 2C.7**).

The polymer PEA-2 showed similar absorption bands, which are slightly shifted to lower frequency side, viz. at 3343 (N-H stretching), 1502 (N-H bending), 1650 cm-1 (amide C=O stretching). Absorption band at 862 cm^{-1} and 747 cm^{-1} indicates meta catenation (**Fig 2C.8**).

The polymer PEA-5 showed similar absorption bands, which are slightly shifted to lower frequency side, viz. at 3310 (N-H stretching), 1504 (N-H bending), 1660 cm-1 (amide C=O stretching). Absorption band at 864 cm^{-1} and 750 cm^{-1} indicates meta catenation (**Fig 2C.9**).

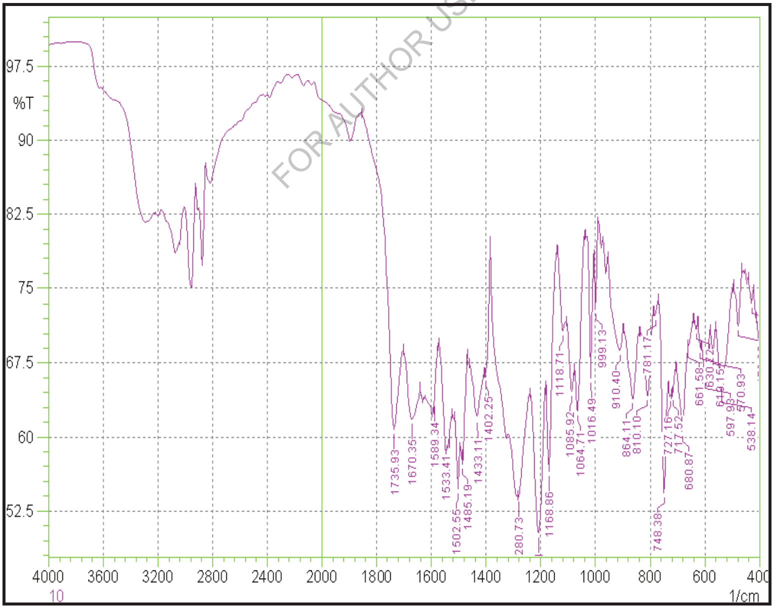


Fig 2C.7 FT-IR spectrum of PEA-1

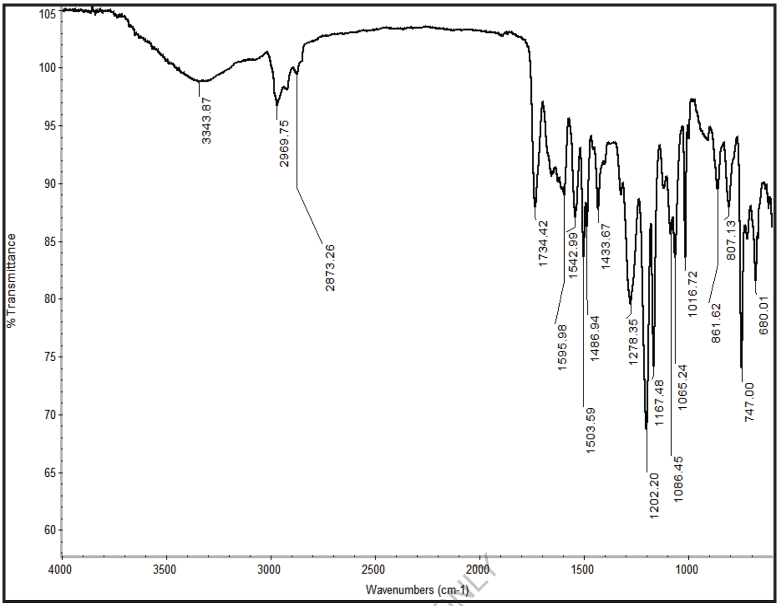


Fig 2C.8 FT-IR spectrum of PEA-2

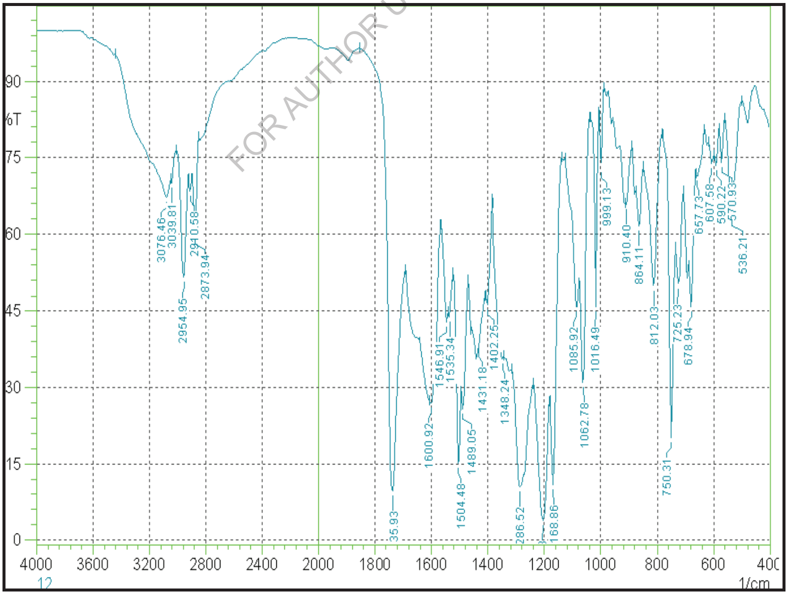


Fig 2C.9 FT-IR spectrum of PEA-5

Solubilty properties

Solubility characteristics of poly(ester-amide)s is tabulated in **Table 2C.2**. The solubility of polymers was determined in different common organic solvents.

Table 2C.2 Solubility Behavior of Poly(ester-amide)s

Polymer	Solubility							
	DMF	DMAc	DMSO	NMP	Pyridine	$CHCl_3$	DCM	$C.H_2SO_4$
PEA-1	±	±	±	+	+	-	-	+
PEA-2	±	±	±	+	+	-	-	+
PEA-3	+	+	+	+	+	-	-	+
PEA-4	±	±	±	+	+	-	-	+
PEA-5	±	±	±	+	+	-	-	+

+: Soluble ; -: Insoluble on heating; ±: Sparingly soluble

It is observed that poly(ester-amide)s synthesized from (m-BABPC) (III), exhibited partial solubility in various polar aprotic solvents such as N-methylpyrrolidone (NMP), Pyridine, dimethyl sulphoxide (DMSO), N, N-dimethylacetamide (DMAc), N, N-dimethyl formamide (DMF). These poly (ester-amide)s also dissolved in pyridine, and Conc. H_2SO_4 etc. The Polymer PEA-5 have better solubility in all above solvents whereas PEA-1, PEA-2, PEA-3 and PEA-4 shows better solubility in NMP and Pyridine as well as these polymers shows partial solubility in dimethyl sulphoxide (DMSO), N, N-dimethylacetamide (DMAc), N, N-dimethyl formamide (DMF). Among all the polymers PEA-3 has better solubility; it may be due to more random arrangement occurred by equal composition of IPC and TPC. All the polymers were also insoluble in DCM, $CHCl_3$. Thus better solubility of these poly (ester-amide)s as expected; can be attributed to the introduction of cardo cyclopentylidene moiety, flexible ester linkage in the polymer backbone, meta catenation of novel monomer and copolymerization resulted in amorphous nature of polymers.

Thermal properties

Thermal behaviour of polymers was evaluated by means of Thermogravimetry and differential scanning calorimetry.

Table 2C.3 incorporate the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), 10 % Wt. loss temperature (T_d) and residual weight at 900°**C**

Table 2C.3 Thermal properties of Poly(ester-amide)s

Polymer	**Thermal Behaviour**[b]			
	T_i °C	**T_d °C**	**Residual Wt % at 900°C**	**T_g °C**
PEA-1	245	425	44	222
PEA-2	205	355	35	214
PEA-3	215	315	40	202
PEA-4	205	375	47	200
PEA-5	215	365	35	196

[b] Temperature at which onset of decomposition was recorded by TG at a heating rate of 10°C /min.

Tg - Glass transition temperature determined at second heating by DSC at a heating rate of 10°C /min

T_d - Temperature of 10% decomposition

T_i - Initial decomposition temperature.

The thermal stability of the polyamides was studied by thermogravimetric analysis **(Fig 2C.10) at** a heating rate of 10°**C**/min in nitrogen atmosphere. The initial decomposition temperature (T_i), temperature at which 10 % weight loss (T_d), and char yields at 900°**C** were determined from the original thermograms. T_i and T_d values range between 205°**C** to 245°**C** and 315°**C** to 425°**C** respectively. Residual wt. % loss at 900°**C** was in the range of 35 to 47 %. Effect of meta and para catenation was clearly visible along the series of polymer as the composition of TPC increases stability increases.

The DSC curves shown in **Fig 2C.11** represent the T_g of polyamides synthesized from novel diamine m-BABPC. The glass transition temperatures of these polyamides are in the range of 196°**C** to 222°**C**.

The glass transition temperatures (T_g) of the polymers PEA-1, showed higher value 222°C as it is derived from terephthaloyl chloride (TPC) which has para catenation and it attributes to form rigid chain but polymer PEA-5 indicated relatively lower T_g values due to meta catenation of isophthaloyl chloride (IPC). The polymers showed T_g in the range 196 -222°C. This decrease in T_g value can be explained on the basis of use of new monomer containing meta catenation, ester linkage as well as cyclopentylidene cardo moiety which disturbs chain regularity and close packing.

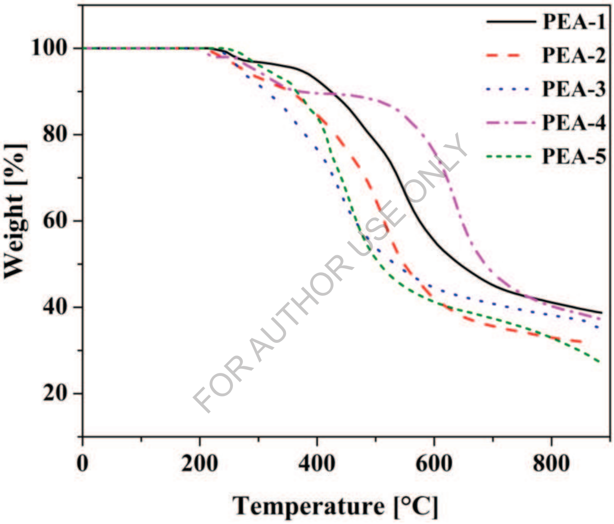


Fig 2C.10 TGA of Poly(ester-amide)s PEA-1 to PEA-5

XRD Studies

All the poly(ester-amide)s were structurally characterized by wide-angle X-Ray diffraction (WAXD) studies (**Fig 2C.12**). It is observed that all the polymers exhibit semicrystalline to amorphous nature. More enhancements in amorphous nature of polymer PEA-3 additionally may be attributed due to the random placement of monomers, caused by combination of two monomers (TPC and IPC) in copolymerization with novel monomer containing meta linkage, which reduces the orderly arrangement of polymer chains resulting in reduced crystallinity and leading to amorphous nature. This behaviour is supported by solubility, wherein PEA-3 is soluble in all polar aprotic solvents and remaining polymers sparingly soluble in DMF, DMAc, DMSO, etc.

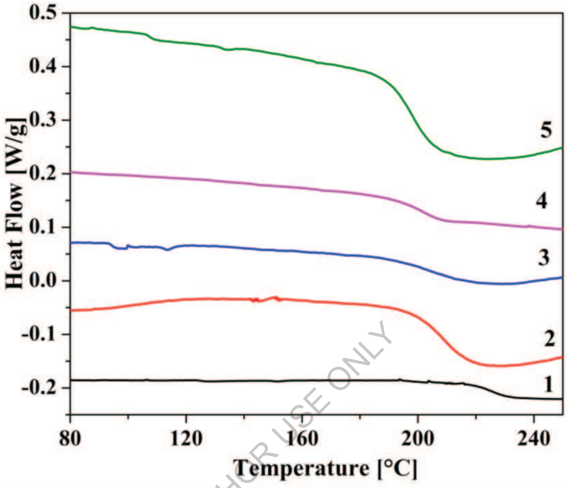


Fig 2C.11 DSC of Poly(ester-amide)s PEA-1 to PEA-5

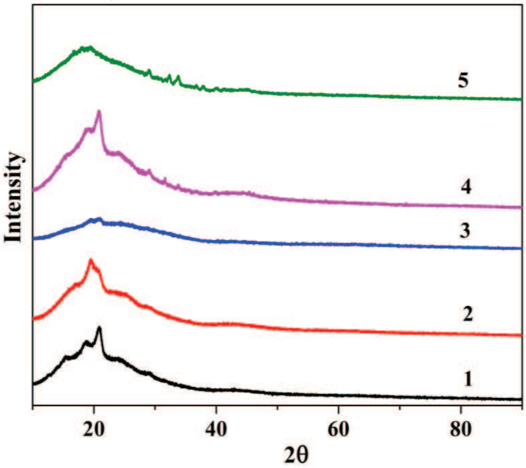


Fig 2C.12 XRD of Poly (ester-amide)s PEA-1 to PEA-5

2C.3 Summary and Conclusions

- Novel monomer; 1, 1-bis (3-aminobenzoyloxy phenyl) cyclopentane (m-BABPC), was synthesized and characterized by physical constant, IR, NMR and mass spectral techniques.
- Using low temperature solution polymerization novel bis (ester – amine); m-BABPC was polymerized with IPC and / or TPC in different mol proportion in DMAc solvent.
- Inherent Viscosity values were in the range of 0.25 to 0.46 dL/g indicating built-up of moderately high molecular weights.
- Solubility of poly (ester-amide)s was tested in different solvents. All the polymers were soluble in polar aprotic solvents viz. NMP and pyridine. These polymers also partially dissolved in DMF, DMAc and DMSO. Polymers had moderate solubility because of random, nonorder arrangement and less crystalline (i.e. more amorphous) nature. Thus better solubility of these poly (ester-amide)s as expected; can be attributed to the introduction of cardo cyclopentylidene moiety, flexible ester linkage in the polymer backbone, crank structure of novel monomer and copolymerization resulted in semicrystalline to amorphous nature of polymer
- The glass transition temperature of poly (ester-amide)s were in the range of 196 -222°C.
- Thermal stability of poly(ester-amide)s was evaluated by dynamic thermogravimetric analysis under nitrogen atmosphere, and all polymers showed 10% weight loss between 315**°C** to 425**°C**. This high thermal stability is characteristic of aromatic poly (ester-amide)s.
- X-ray diffraction pattern of polymers suggested that introduction of pendant cyclopentylidene group and ester linkage and copolymerization (involving TPC, IPC; para-para and meta-meta catenation) may have disrupted the chain regularity and packing leading to amorphous nature. The above observation also support solubility properties of the polymers investigated.

Chapter-2D: Synthesis and characterizations of Poly(ether-amide)s based on Diacid Monomers

Aromatic polyamides attract much attention because of their chemical and thermal resistances as well as their high strength and high modulus in fiber form. However these materials suffer very poor processability due to their inadequate solubility, tremendously high glass transition temperatures and infusibility caused by the high crystallinity and rigidity of polymer backbones and that make them very difficult to be processed by spin coating or thermoforming methods [202,203]. Much exertion has been made to produce structurally modified aromatic polymers having improved solubility and processability with retention of their high thermal stability. It is known that the solubility of polymers is frequently increased when flexible bonds such as [-O-, -CH_2-, -SO_2-, -$C(CF_3)_2$-], bulky pendent groups (such as t-butyl, adamantyl and naphtyl), large pendent groups or polar constituents such as heterocyclic segments are integrated into the polymer backbone which alters crystallinity and intermolecular interactions [204-206]. If the cardo or pendant moiety is carefully chosen, it is possible to increase solubility without affecting mechanical and thermal properties to any greater extent [207-215]. In the literature study we observed that synthesis of different polyamides containing pendant or cardo moieties such as cyclohexylidene, t-butyl, adamantly, naphtyl as well as insertion of flexible bonds such as O-, -CH_2-, -SO_2-, -$C(CF_3)_2$- in the main chain with enhanced solubility and thermal properties [216-239].

In this article, synthesis and characterization of six new polyamides SPA-1 to SPA-6 containing cyclopentylidene moieties in the main chain is reported from the Yamazaki's phosphorylative polycondensation reaction of 1,1-bis[4-(4-carboxy methylene phenoxy) phenyl]cyclopentane (BCMPP) and 4,4'-diamino diphenyl ether (SPA-1); 4,4'-diamino diphenyl methane (SPA-2); 4,4'-diamino diphenyl sulfone (SPA-4); 1,4-phenylene diamine (SPA-3); 1,1-bis(4(4'-aminophenoxy)phenyl)cyclopentane (SPA-5) and 1,3-bis(4-amino phenoxy)benzene (SPA-6) by using N-methyl-2-pyrrolidone (NMP), triphenylphosphite and pyridine as condensing agents. These polymers have a cyclopentylidene ring as cardo moiety and –O-, -CH_2- flexible bonds in the main chain for enhancing solubility in organic solvents without much sacrificing thermal stability. Therefore synthesis of soluble and processable polyamides has been a major research interest. It is highly desirable that these polymers be soluble in some specific organic solvents to facilitate processing, however they should retain resistance to common solvents during their use. We have reported the series of new poly(ether-amide)s from newly synthesized diacid.

2D.1 Experimental

2D.1.1 Materials

- All the reagents such as 4, 4'-Oxydianiline; 4, 4'- methylenedianiline; 4, 4'-Sulfonyl dianiline, triphenyl phosphate were purchased from Sigma Aldrich and used as received.
- The p-Phenylene diamine was purified by recrystallization in ethanol.
- The monomers 1, 3-bis(4-aminophenoxy) benzene (BAPB) and 1, 1'-bis(4(4-aminophenoxy)phenyl)cyclopentane (BAPC) were recrystallized from ethanol.
- 4-fluoronitrobenzene were purchased from Spectrochem and used as received.
- N, N'-dimethylformamide (DMF) refluxed over P_2O_5, decanted and purified by vaccum distillation. Commercially available Sulphur was also purified by refluxing with calcium oxide for 30 min and reprcipitated with 1:1 HCl.

2D.1.2 Synthesis of Diether-Diacid monomer

2D.1.2.1 Synthesis of 1, 1-bis(4-hydroxy phenyl) cyclopentane (I)

Bisphenol (I) was synthesized as per the procedure reported in Chapter 2C.1.2.2

2D.1.2.2 Synthesis of 1, 1-bis [4- (4-acetyl phenoxy) phenyl]cyclopentane(II)

In a 500 mL three neck round bottom flask equipped with calcium chloride guard tube, thermowell, N_2 gas inlet and magnetic stirrer, were placed 12.7 g bisphenol (I) (0.05 mol) and 13.814 g 4- fluoroacetophenone (0.1 mol) in 125 mL N,N-dimethyl acetamide (DMAc), then 13.821 g of anhydrous K_2CO_3 was added. The resulting reaction mixture was refluxed for 12 h, then allowed to cool at room temperature and water was added precipitate the product. The product was isolated by filtration, washed with water and finally dried under vacuum. The crude product was purified by recrystallization from methanol.

Yield: 21.7 g (88.97 %)

M.P.: 90-92°C.

IR: 2972, 2868, 1985, 1591, 1497, 1452, 1355, 1321, 1243, 1169, 1159, 1107, 1012, 957, 880, 848, 828, 768, 712 cm^{-1}

2D.1.2.3 Synthesis of 1, 1-bis[4-(4-thioacetomorpholide phenoxy)phenyl] cyclopentane (III)

In a 100 mL round bottom flask equipped with reflux condenser and magnetic stirrer were placed 9.8 g (0.02 mol) of diketone (II); 1.84 g (0.06 mol) of sulphur and 5.227 g (0.06 mol) of morpholine (5.2 mL). The resulting reaction mixture was stirred initially under gentle reflux until the evolution of hydrogen sulphide subsides and more vigorously at 140°C for 14 h. The reaction mixture was allowed to cool and then 90 mL ethanol was added to obtain buff colored product which was filtered, washed with excess of ethanol and dried.

Yield: 11.0 g (79.47 %)

M.P.: 90°C.

IR: 2930, 2861, 1684, 1494, 1453, 1240, 1169, 1160, 1029, 1013, 957, 879, 868, 849, 839 cm^{-1}.

2D.1.2.4 Synthesis of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) (IV)

In a 500 mL round bottom flask equipped with reflux condenser, magnetic stirrer were placed 10.38 g (0.015 mol) of (III) and 200 mL ethanolic 10% NaOH solution, the reaction mixture was kept for reflux under stirring for 14 h. Then the most of ethanol was distilled out under reduced pressure. To the residual product 200 mL hot water was added and filtered. The filtrate was acidified by 1:1 HCl. The precipitated product was filtered, washed thoroughly with hot water and dried. Then product was dissolved in Sodium bicarbonate solution and reprecipitated from 1:1 HCl. Filtered product and washed thoroughly with water, dried under vaccum.

Yield: 7.0 g (89.39 %)

M.P.: 110-114°C.

IR: 3500-3260, 2959, 2873, 1707, 1593, 1500, 1408, 1240, 1170, 878, 826, 540 cm^{-1}.

^{1}H NMR (DMSO, δ): 7.27-6.83 δ (m, 16H), 3.5 δ (s, 4H), 2.23δ (4H,), 1.62 δ (4H).

^{13}C NMR (DMSO, δ): 173,156,154,143,131,129,128,119,117,54,40,38,22 δ.

2D.1.3 Synthesis of poly(ether-amide)s from 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0.522 g (1mmol) 1,1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP); (IV), 0.200 g (1 mmol) 4,4'-diaminodiphenyl ether (ODA), 0.115g lithium chloride [5 wt % based on solvent N-methyl pyrrolidone (NMP) and pyridine mixture] and 0.744g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 mL pyridine and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100°C over a period of 30 min. The reaction mixture was heated at 100°C for 3h under nitrogen. After cooling the resulting polymer viscous solution was poured into rapidly stirred 200 mL of methanol. The precipitated polymer (SPA-1) was filtered, washed with methanol and dried. The polymer was purified by dissolving in N, N-dimethylacetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol and dried under vacuum at 100°C for 6 h. The yield was 100% and the inherent viscosity of polymer in DMAc was 0.20 dL/g.

The polyamides SPA-2 to SPA-6 were produced with varying diamines by similar procedure.

IR Spectrum

SPA-1: 3269, 3194, 3035, 2954, 2916, 2873, 1658, 1532, 1490, 1235, 1170, 1014, 875, 831, 756, 692, 557 cm^{-1}

SPA-4: 3290, 3005, 2953, 2840, 1674, 1591, 1400, 1309, 1250, 1149, 1107, 875, 835, 758, 690, 553 cm^{-1}

SPA-5: 3309, 2980, 2919, 2865, 1669, 1601, 1543, 1405, 1300, 1183, 1013, 962, 875, 796, 692, 668 cm^{-1}

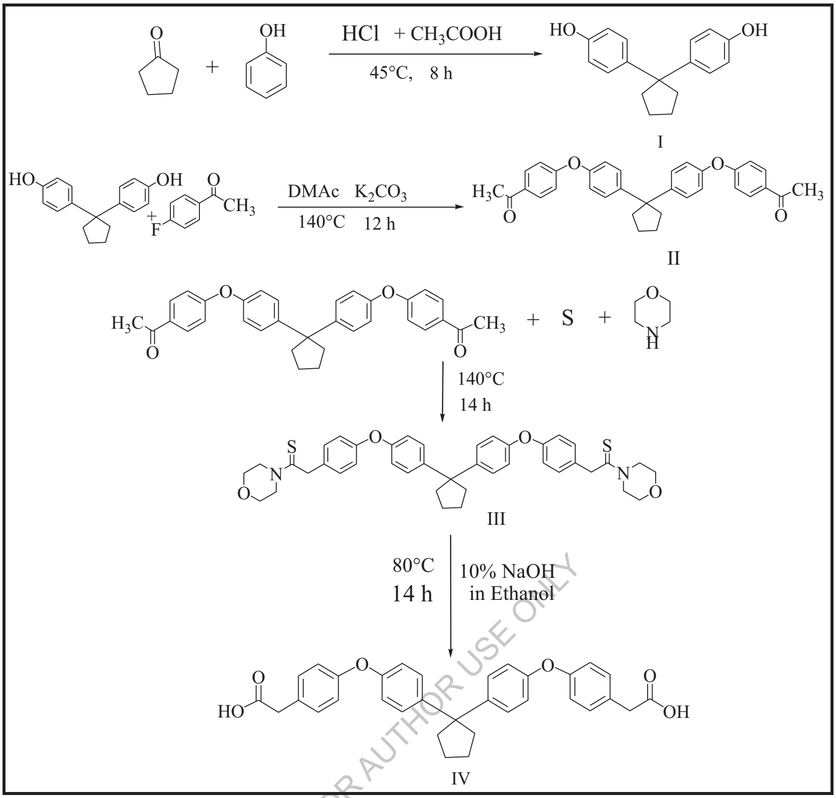
2D.2 Results and Discussion

The main objective of this study was focused on enhancing the solubility of the novel polyamides through the design and synthesis of new diacid monomer. Hence, for the preparation of a flexible diacid with built-in methylene linkage, cardo moiety and ether group, a Willigerodt-Kindler reaction was performed. Therefore in the present work, diacids containing cyclopentylidene moiety, viz. 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) have been synthesized and used as building blocks for preparing poly(ether-amide)s.

2D.2.1 Synthesis of 1, 1-bis [4-(4-carboxy methylene phenoxy) phenyl] cyclopentane

The novel dicarboxylic acid, 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) was prepared from phenol and cyclopentanone in several steps.(**Scheme. 2D.1**)

The 1, 1-bis(4-hydroxy phenyl) cyclopentane (I) was prepared by reacting phenol with cyclopentanone in presence of acid catalyst. The 1, 1-bis[4-(4-acetyl phenoxy)phenyl] cyclopentane (II) was obtained by reaction of (I) with 4-fluoroacetophenone and potassium carbonate in DMAc. Structure of (II) was confirmed by infrared spectroscopy.



Scheme 2D.1 Synthesis of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (IV)

The infrared spectrum of II (**Fig 2D.1**) showed medium strong absorption bands at 2972 and 2868 cm^{-1} showing the presence of aliphatic C-H stretching corresponding to the in phase and out phase vibration of cyclopentane ring and methylene groups. IR also shows absorption for aromatic C-H stretch near 3030 cm^{-1}. Spectrum also shows absorption near 1497 due to C-H bending vibration. Absorption at 1685 cm^{-1} of carbonyl (C=O) stretching adsorption indicated acetyl carbonyl moiety.

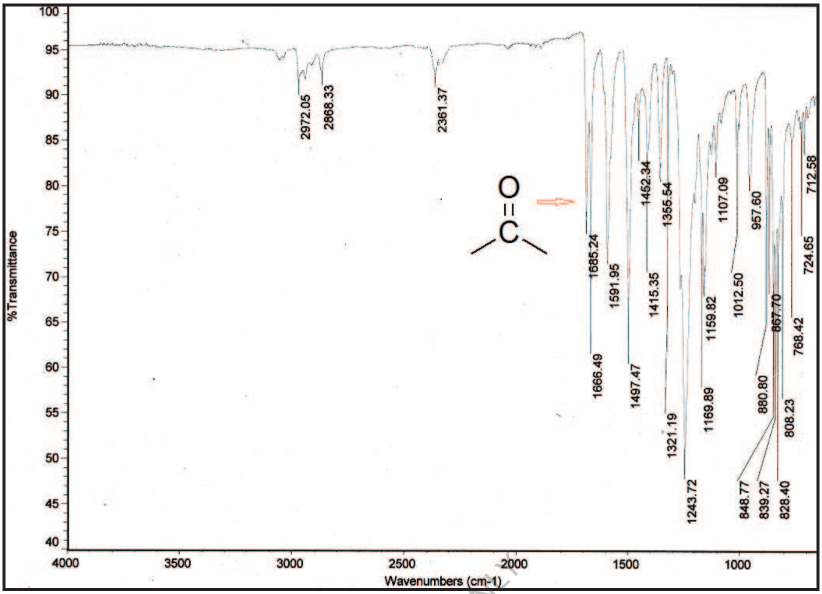


Fig 2D.1 FT-IR spectrum of 1, 1-bis [4- (4-acetyl phenoxy) phenyl] cyclopentane (II)

The 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl]cyclopentane (IV) was obtained by the Conrad Willgerodt reaction with Kindler variation.

The formation of intermediate thiomorpholide derivative (III) was confirmed by infrared spectroscopy. The infrared spectrum of III (**Fig 2D.2**) showed medium strong absorption bands at 2930 and 2861 cm^{-1}, due to the presence of aliphatic C-H stretching corresponding to the in phase and out phase vibration of cyclopentane unit and methylene group. Spectrum also shows absorption near 1497 cm^{-1} due to C-H bending vibration. The appearance of absorption at 1240 cm^{-1} (C=S) confirm formation of thiomorpholide.

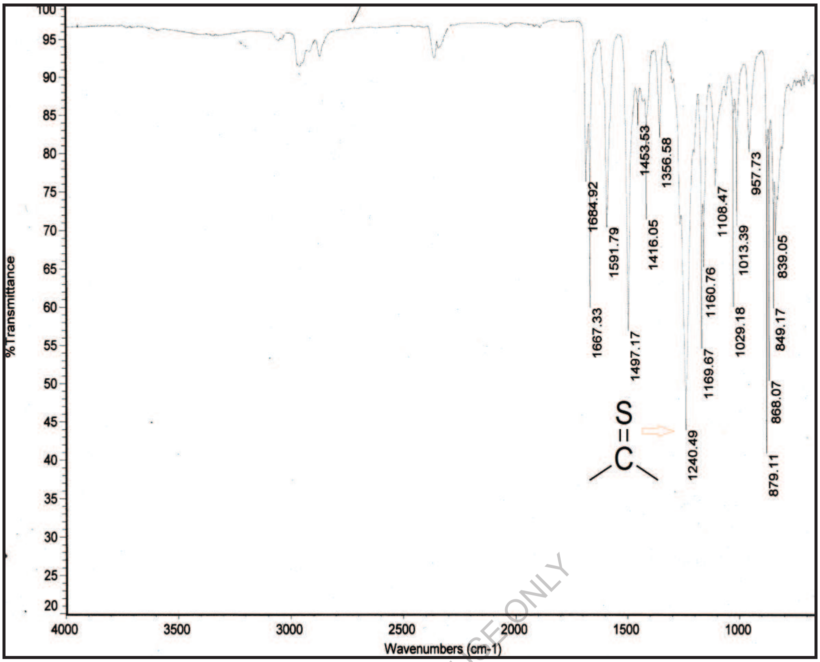


Fig 2D.2 FT-IR spectrum of 1, 1-bis [4- (4- thioacetomorpholide phenoxy) phenyl] cyclopentane (III)

Thiomorpholide derivative on alkaline hydrolysis yielded the 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV). The structure of IV was confirmed by IR, NMR (^{1}H and ^{13}C) and Mass spectrometry.

The infrared spectrum of IV (**Fig 2D.3**) showed absorption bands at 3500-3260 cm^{-1} (-OH stretching) and 1707 cm^{-1} (C=O) indicating the presence of carboxyl group. Infra- red spectrum also showed the absorption bands at 2959 and 2873 cm^{-1} corresponding to the in plane and out of plane stretching vibrations of the (-CH$_2$-) of the methylene group and cyclopentane unit.

The proton NMR spectrum (**Fig 2D.4**) of IV showed the NMR singlet at 3.50 δ corresponding to methylene (2H) group of –CH$_2$COOH. The signals in the range of 7.27 to 6.83 δ of (16H) are attributed to the aromatic protons of phenylene rings whereas signal at 2.23 and 1.61 δ are assigned to cyclopentane proton.

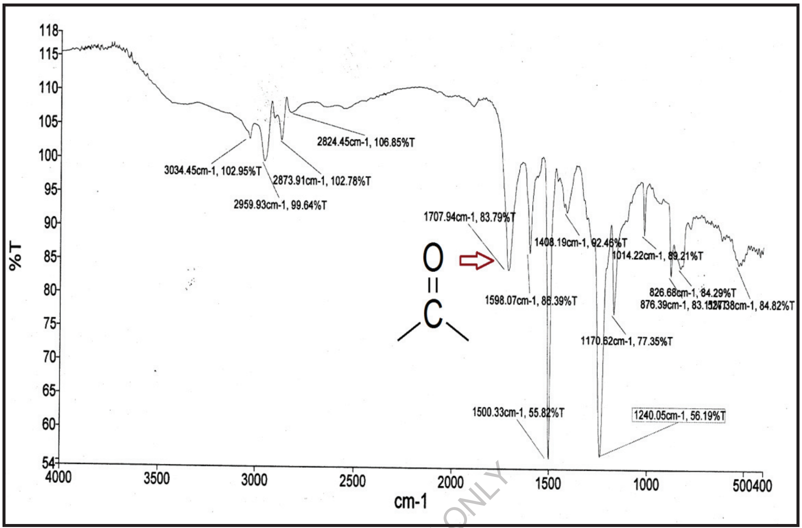


Fig 2D.3 FT-IR spectrum of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (IV)

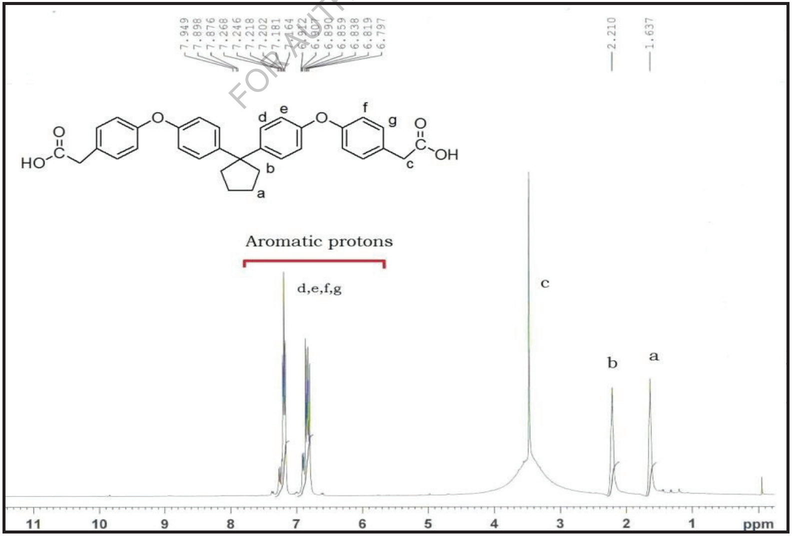


Fig 2D.4 ^{1}H NMR of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) (IV)

^{13}C NMR spectrum (**Fig 2D.5**) of (V) showed thirteen NMR signals corresponding thirteen types of different carbons of which carbonyl carbon appeared at 173.24 δ for (C=O); whereas tertiary carbons showed signals at 156.01; 154.80, 143.74, 128.57 and 54.88 δ. The CH carbons appeared at 131.79, 129.79, 118.30 and 117.22 δ, whereas CH_2 carbon gave NMR signals at 40.53, 38.76, 22.86 δ confirms the formation of diacid (V) monomer.

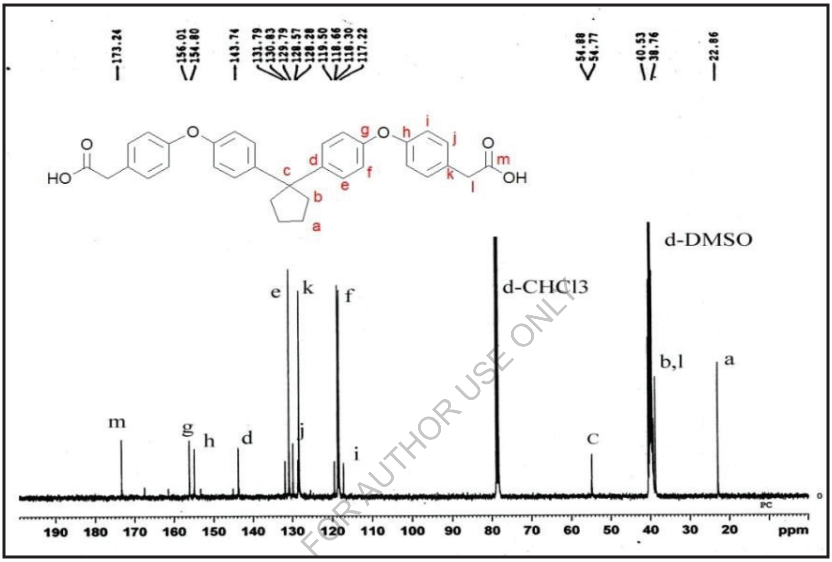


Fig 2D.5 ^{13}C NMR of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) (IV)

The DEPT spectrum (**Fig 2D.6**) of (IV) also confirms the diacid monomer wherein all the quaternary carbons are absent in the spectrum and the peaks of CH carbons are upper sides at 131.80, 128.58, 119.52, 118.65,118.30 δ and CH_2 appeared at down side at 40.52, 38.74, 22.85 δ.

The mass spectrum of (**Fig 2D.7**) (IV) showed molecular ion peak at m/e 521 corresponding to molecular weight of BAMPC.

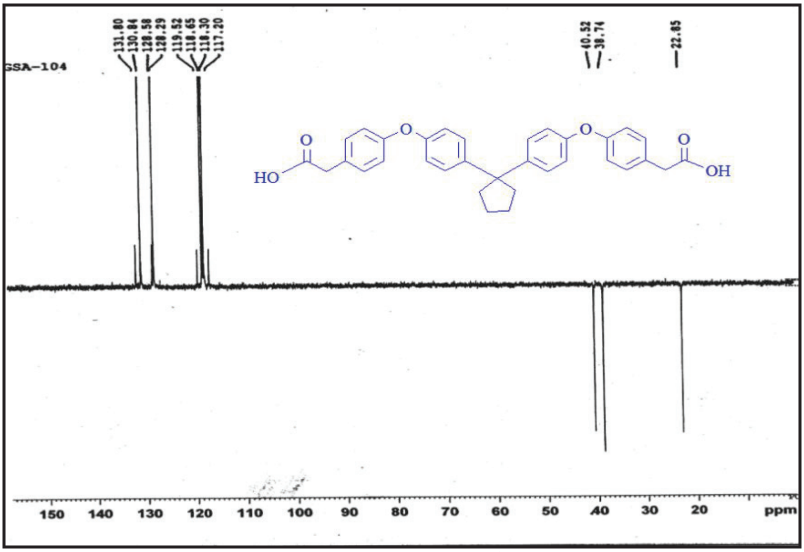


Fig 2D.6 DEPT of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) (IV)

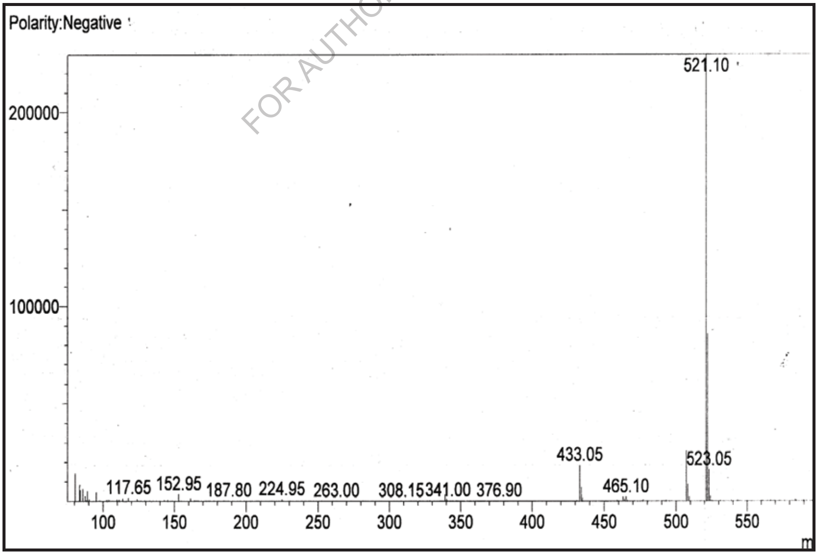
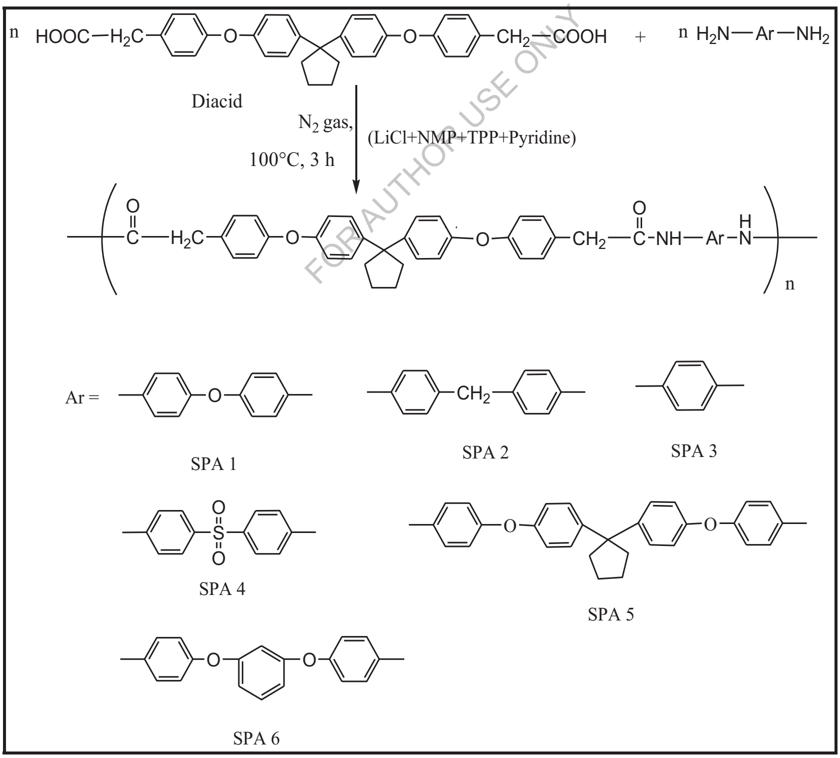


Fig 2D.7 Mass Spectrum of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) (IV)

2D.2.2 Synthesis of poly (ether-amide)s

The poly(ether-amide)s were produced by Yamazaki's phosphorylation method[128]. Series of poly (ether-amide)s were prepared from the stoichiometric quantities of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl]cyclopentane (IV) and numerous aromatic diamines by direct polycondensation method (**Scheme. 2D.2**). Triphenyl phosphite was used as the condensing agent, where in the mixture of NMP and pyridine (4.1 by volume) containing 8 wt. % anhydrous lithium chloride was employed as solvent. The polymerization was carried out at 100°C for 3 h. The different aromatic diamines used are shown below. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in methanol.



Scheme 2D.2 Synthesis of Poly(ether-amide)s

The yield and viscosity of polyamides synthesized from 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) are presented in **Table 2D.1.** All the polymers were obtained in the good yields (96 to 100 %) as pale yellow to white fibrous materials. The inherent viscosities of these polymers were in the range of 0.20 to 0.40 dL/g; this is indicated the formation of moderate to high molecular weight of polymers. Polymerization was carried out with 1 mmol of diamine and 1 mmol of diacid (BCMPP) (IV).

Table 2D.1 Yield and Viscosity of Poly(ether-amide)s

Polymer	**Monomers**		**Yield %**	**Inherent Viscosity dL/g** [a]
	Novel Diacid	Diamine		
SPA-1	BCMPP	ODA	100	0.20
SPA-2	BCMPP	MDA	99	0.28
SPA-3	BCMPP	p-PDA	100	0.40
SPA-4	BCMPP	SDA	97	0.35
SPA-5	BCMPP	BAPC	96	0.24
SPA-6	BCMPP	BAPB	96	0.21

[a] Inherent viscosities were measured at a concentration of 0.5 % (W/V) in **DMF** at 30°C.

The polyamides were characterized by infrared spectroscopy. Polyamide SPA-1 **(Fig 2D.8)** showed an absorption band at 3269 cm^{-1}(-NH stretching), a sharp band at 1495 cm^{-1} (characteristic for –NH bending) and absorption band at 1658 cm^{-1} (due to >C=O in amide group). The absorption band at 3035 cm,$^{-1}$ characteristic for aromatic –CH stretching; and absorption band at 2954 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed. Disappearance of absorption bands at 3500 and 3340 cm^{-1} indicated that all the acid and amine groups reacted completely to yield polyamide.

Similarly the Polyamide SPA-4 **(Fig 2D.9)** showed an absorption band at 3290 cm^{-1} (-NH stretching), a sharp band at 1500 cm^{-1} (characteristic for –NH bending) and absorption band at 1674 cm^{-1} (due to C=O in amide group). The absorption band at 3035 cm,$^{-1}$ characteristic for aromatic –CH stretching; and absorption band at 2953 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed. Disappearance of absorption bands at 3500 and 3340 cm^{-1} indicated that all the acid and amine groups reacted completely to yield polyamide.

The Polyamide SPA-5 **(Fig 2D.10)** showed an absorption band at 3309 cm^{-1} (-NH stretching), a sharp band at 1496 cm^{-1} (characteristic for –NH bending) and absorption band at 1669 cm^{-1} (due to C=O in amide group). The absorption band at 2980 cm,$^{-1}$ characteristic for aromatic –CH stretching; and absorption band at 2919 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed. Disappearance of absorption bands at 3500 and 3340 cm^{-1} indicated that all the acid and amine groups reacted completely to yield polyamide.

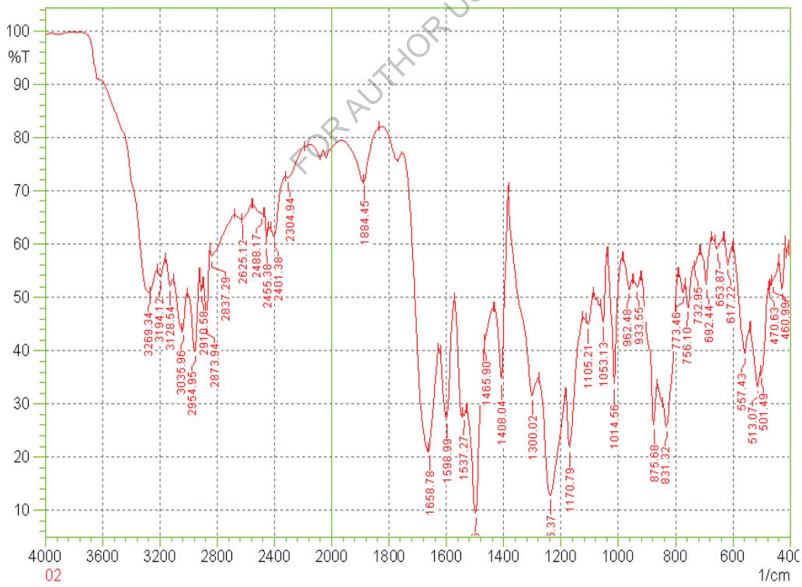


Fig 2D.8 FT-IR spectrum of SPA-1

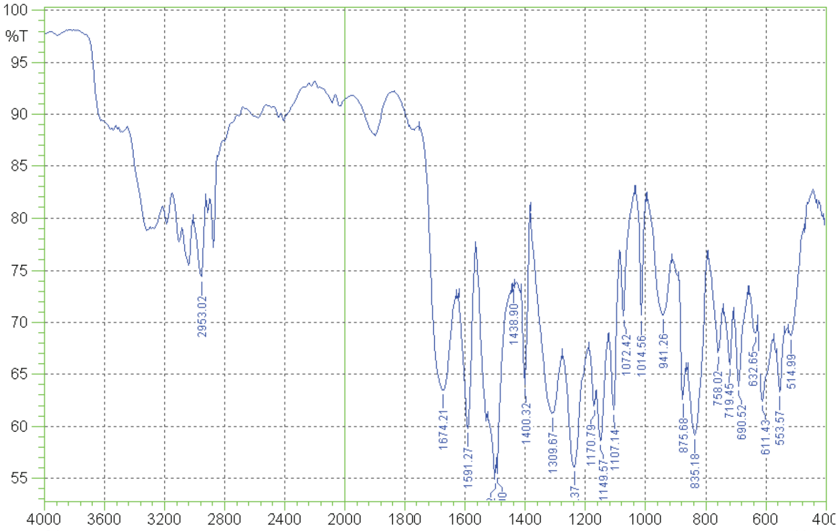


Fig 2D.9 FT-IR spectrum of SPA-4

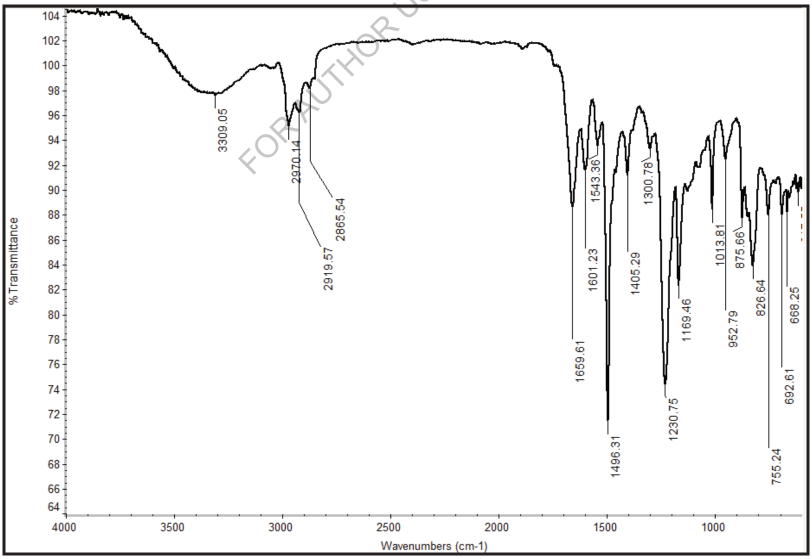


Fig 2D.10 FT-IR spectrum of SPA-5

2D.2.3 Properties of poly (ether-amide)

Solubility

Solubility characteristics of polyamides are tabulated in **Table 2D.2.** The solubility of polymers was determined in different common organic solvents. It was observed that polyamides synthesized from 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) exhibited better solubility in various polar aprotic solvents such as N-methylpyrrolidone (NMP), N, N-dimethyl sulphoxide (DMSO), N, N-dimethylacetamide (DMAc), N, N-dimethyl formamide (DMF). All these poly (ether -amide)s also dissolved in pyridine, and Conc. H_2SO_4. All these polyamides (SPA-1 to SPA-6) are insoluble in common solvents like THF, DCM and chloroform but polymers SPA-3 derived from p-PDA are insoluble in DMSO. On the other hand phenylated polyamides (SPA-6) partially soluble in DMSO. This may be assigned to the effect of cardo cyclopentylidene moiety with methylene and ether spacer unit in monomer structure.

Thus better solubility of these polyamides; as expected; can also be attributed to the combined effect of introduction of aliphatic methylene group, ether linkage in the polymer backbone and cyclopentylidene moiety.

Table 2D.2 Solubility behavior of Poly(ether-amide)s

Polymer	**Solvents**								
	DMF	DMAc	DMSO	NMP	Pyridine	THF	$CHCl_3$	DCM	C.H_2SO_4
SPA-1	+	+	+	+	+	-	-	-	+
SPA-2	+	+	+	+	+	-	-	-	+
SPA-3	+	+	-	+	+	-	-	-	+
SPA-4	+	+	+	+	+	-	-	-	+
SPA-5	+	+	+	+	+	-	-	-	+
SPA-6	+	+	±	+	+	-	-	-	+

+ : Soluble; - : Insoluble on heating; ± : Sparingly soluble

Thermal properties

Thermal behaviour of polymers were evaluated by means of thermogravimetric analysis and differential scanning calorimetry. **Table 2D.3** incorporate the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), 10 % Wt. loss temperature (T_d) and residual weight at 900°C.

The thermal stability of the polyamides was studied by thermogravimetric analysis **(Fig 2D.11)** at a heating rate of 10°C/ min in nitrogen atmosphere. The decomposition temperature at which 10 % weight loss (T_d), and char yields at 900°C were determined from the original thermograms. The T_d values range between 425 to 495°C respectively. Residual wt. % loss at 900°C was in the range of 38 to 53 %.

Table 2D.3 Physical properties of Poly(ether-amide)s

Polymer	**Thermal Behaviour** [b]			
	T_i °C	**T_d** °C	**T_g** °C	**Residual Wt % at 900**°C
SPA-1	305	475	208	48
SPA-2	295	455	200	47
SPA-3	325	495	220	53
SPA-4	295	475	186	44
SPA-5	285	425	181	38
SPA-6	295	475	177	46

[b] Temperature at which onset of decomposition was recorded by TG at a heating rate of 10°C /min.

Tg- Glass transition temperature determined at second heating by DSC at a heating rate of 10°C/min

T_d - Temperature of 10% decomposition

T_i- Initial decomposition temperature.

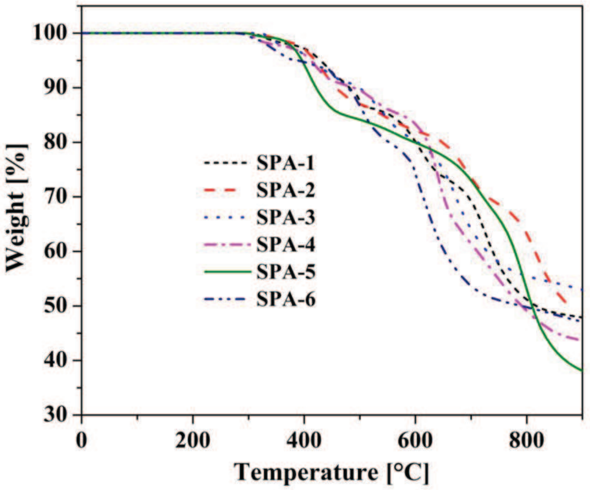


Fig 2D.11 TGA curve of Poly (ether-amide)s SPA-1 to SPA-6

The DSC curves shown in **Fig 2D.12** represents the T_g of polyamides synthesized from novel diacid (IV). The glass transition temperature (T_g) of various polyamides were in the range between 177°C to 220°C which is shown in **Table 2D.3**.The glass transition temperatures of the polymers SPA-1, SPA-2 and SPA-3 higher T_g value but SPA-4, SPA-5 and SPA-6 polymer indicated slightly lower T_g values. This can be explained on the basis of novel diacid and commercial diamine in corresponding polymers. Higher T_g for SPA-3 was due to structure of p-phenylene diamine.

The wide angle X-ray diffraction pattern of all polyamides is shown in **Fig 2D.13**. It is observed that all the polymers exhibit amorphous nature except SPA-3 shows semicrystalline nature due to para substituted phenylene diamine which can be attributed to the close packing of the chains. Introduction of cyclopentylidene moiety and aliphatic methylene linkage may have disrupted the chain regularity and packing leading to amorphous polyamides. Similarly introduction of diether-diamine containing cyclopentylidene moiety in SPA-5 and phenylated moiety in SPA-6; disturbs symmetry to large extent and polymers become more amorphous. Polymers from diamine like ODA, SDA, p-

PDA; are less amorphous which can be attributed to the close packing of the chains. Thus amorphous nature of the polymers was depending on the structures of diacid and diamines chosen for synthesis of polymers.

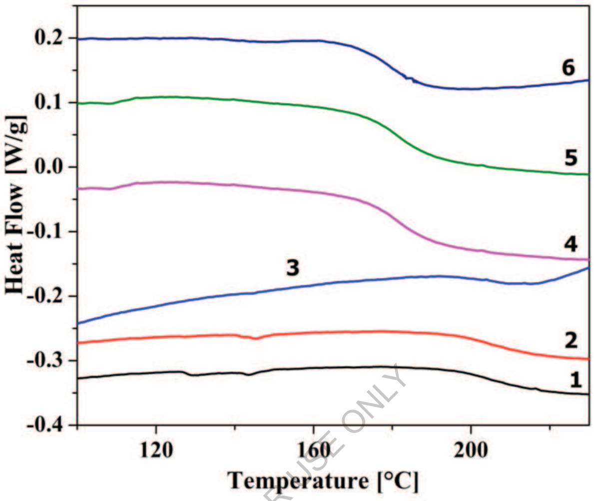


Fig 2D.12 DSC curve of Poly (ether-amide)s SPA-1 to SPA-6

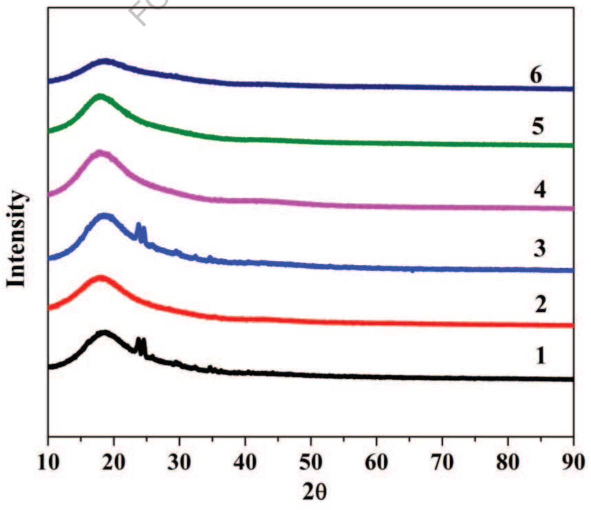


Fig 2D.13 XRD curve of Poly (ether-amide)s SPA-1 to SPA-6

2D.3 Summary and Conclusions

- A series of new polyamides containing methylene linkage and cardo cyclopentylidene moiety was synthesized by Yamazaki's phosphorylative polycondensation reaction of 1,1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP); (IV) and commercial diamines.
- Inherent viscosities of polyamides were in the range 0.20-0.40 dL/g indicating formation of medium to reasonably high molecular weight polymers.
- Polyamides were found soluble in DMF, DMAc, DMSO, NMP, and pyridine at room temperature or upon heating. This indicates that the incorporation of flexible methylene group and cardo cyclopentylidene moiety leads to a significant improvement in solubility of polyamides.
- Wide angle X-ray diffraction patterns indicated that polyamides containing methylene linkage and cardo cyclopentylidene were amorphous in nature.
- T_d values for polyamides were in the range 425°C -495°C indicating good thermal stability of polyamides.
- T_g values of polyamides were in the range 177°C -220°C. The depression in T_g values of polyamides could be attributed to the presence of pendent cyclopentylidene chains.
- A large difference in T_g and decomposition temperature of polyamides offers a broad processing window.
- Several novel aromatic poly(ether-amide)s containing cyclopentylidene cardo units in the polymer backbone were synthesized with the aim of improving the solubility and processability of polymers . The inherent viscosities of these polymers range from 0.20 to 0.40 dL/g. Most of these polymers are amorphous and soluble in a number of organic solvents, such as DMF, NMP, DMAc, and DMSO. The T_g's and T_d's for 10% weight loss were in range 177 to 220°C and 425 to 495 °C respectively, depending on the exact polymer structure

Chapter-2E:Synthesis and characterization of Poly(ether-amide)s based on Methyl Substituted Diacid Monomers

Even though polyamides have become of great commercial importance, the fabrication of unsubstituted aromatic polyamides has usually proved to be difficult because, they show affinity to decompose during, or even before melting and are insoluble in most common organic solvents. However, processing of these materials is challenging due to their limited solubility and infusibility. To overcome these limitations, many efforts have been made to enhance the processing characteristics of these polyamides while retaining other advantageous properties. Some of the approaches that have been successful are the introduction of bulky pendent groups [240-244], flexible alkyl side chains [245, 246], unsymmetrical substituents [247, 248], heterocyclic rings [249, 250], and cardo groups [251, 252]. Recently Guo, D.D., et.al. reported diacid monomer and polymer therefrom bearing ether linkages and methyl substitution in the backbone [253]. It has been established that combining aryl ether, methylene linkages, bulky methyl substituent and cardo groups along the polymer backbone could increase the solubility of polyamides without sacrificing their high thermal properties. Therefore, there has been an increased interest in the synthesis of polyamides with methyl substituents bearing ether and methylene linkages in the polymer backbone in order to enhance their processability.

In the present study, synthesis and characterization of seven new polyamides SPA-7 to SPA-13 containing cyclopentylidene moieties in the main chain is reported from the Yamazaki's phosphorylative polycondensation reaction of 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP) and 4, 4'-diamino diphenyl ether, 4,4'-diamino diphenyl methane, 1,4- phenylene diamine, 4,4'-diamino diphenyl sulfone, 1, 1 bis (4-(4'-aminophenoxy)phenyl) cyclopentane and 1, 3-bis(4-amino phenoxy)benzene by using N-methyl-2-pyrrolidone (NMP), triphenylphosphite and pyridine as condensing agents. These polymers have a cyclopentylidene ring as cardo moiety and ether ; methylene flexible linkage as well as methyl substituent in the main chain for improving solubility in organic solvents without much sacrificing thermal stability. Therefore preparation of soluble and processable polyamides has been a major research interest. It is highly desirable that these polymers be soluble in some specific organic solvents to facilitate processing, however they should retain resistance to common solvents during their use.

2E.1 Experimental

2E.1.1 Materials

- The p-Phenylene diamine was purified by recrystallization in ethanol.
- The monomers 1, 3-bis(4-aminophenoxy) benzene (BAPB) and 1, 1’-bis(4(4-aminophenoxy)phenyl)cyclopentane (BAPC) were recrystallized from ethanol.

2E.1.2 Synthesis of methyl substituted Diether-Diacid monomer

2E.1.2.1 Synthesis of 1, 1-bis(4-hydroxy 3-methyl phenyl) cyclopentane (BHMPC)(I)

Bisphenol (I) was synthesized as per procedure reported in Chapter 2A.1.2.1

2E.1.2.2 Synthesis of 1, 1-bis[4-(4-acetyl phenoxy)-3-methyl phenyl] cyclopentane (II)

In a 500 mL three neck round bottom flask equipped with calcium chloride guard tube, thermowell, N_2 gas inlet and magnetic stirrer, were placed 14.1 g 1, 1-bis(4-hydroxy 3-methyl phenyl)cyclopentane (I) (0.05 mol) and 13.814 g 4-fluoroacetophenone (0.1 mol) in 125 mL N,N-dimethyl acetamide (DMAc), then 13.82 g of anhydrous K_2CO_3 was added. The resulting reaction mixture was refluxed for 12 h, allowed to cool at room temperature and precipitated the product from solution by addition of water. The product was isolated by filtration, washed with water then methanol and finally dried under vacuum.

Yield: 23.30 g (89.96 %)

M.P.: 130°C.

IR: 2955, 2866,1666,1597,1491,1273,1252,1180,1130,1019,881,769,688 cm^{-1}

2E.1.2.3 Synthesis of 1, 1-bis[4-(4-thioacetomorpholide phenoxy)-3-methyl phenyl] cyclopentane (III)

In a 100 mL round bottom flask equipped with reflux condenser and magnetic stirrer were placed 10.36 g (0.02 mol) of 1, 1-bis[4-(4-acetyl phenoxy)-3-methyl phenyl] cyclopentane (II); 1.84 g (0.06 mol) of sulphur and 5.227 g (0.06 mol) of morpholine (5.2 mL). The resulting reaction mixture was stirred initially under gentle reflux until the evolution of hydrogen sulphide subsides and more vigorously for 14 h at 140°C. The reaction mixture was allowed to cool and 90 mL ethanol was added to obtain buff colored product which was filtered, washed with excess of ethanol and dried.

Yield: 11.80 g (81.94 %)

M.P.:110°C.

IR: 2969, 2861, 1657, 1594, 1490, 1230, 1181, 1062,898,747 cm^{-1}.

2E.1.2.4 Synthesis of 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP) (IV)

In a 500 mL round bottom flask equipped with reflux condenser, magnetic stirrer were placed 10.80 g (0.015 mol) of 1, 1-bis [4- (4- thioacetomorpholide phenoxy)-3-methyl phenyl] cyclopentane (III) and 200 mL ethanolic 10% NaOH solution, the reaction mixture was refluxed with stirring for 15 h. Then the most of ethanol was distilled out under reduced pressure. To the residual product 200 mL hot water was added and filtered. The filtrate was acidified by 1:1 HCl. The precipitated product was filtered, washed thoroughly with hot water and dried. Then product was dissolved in Sodium bicarbonate solution and reprecipitated from 1:1 HCl. Filtered product washed thoroughly with water, dried under vaccum.

Yield: 7.45 g (90 %)

M.P.: 90-94°C.

IR: 3324 (-OH stretch), 2989, 2869, 1702(C=O stretch), 1601, 1492, 1230, 1162, 1014, 810, 668 cm^{-1}.

^{1}H NMR (DMSO, δ): 7.28(d, 2H); 7.16(s, 2H); 7.09(d, 4H); 6.92(d, 4H); 6.80(d, 2H); 3.62(s, 4H); 2.30(m, 4H); 2.20(s, 6H); 1.70 (m, 4H).

^{13}C NMR (DMSO, δ): 177.86(C=O);157.38; 152.02; 46.68; 132.46; 130.56; 129.96; 125.67; 119.27; 117.35; 54.95 (quaternary C); 40.26 (methylene CH_2); 38.93; 23.02;16.47($-CH_3$).

Mass: 549.05 (m-1 Peak)

2E.1.3 Synthesis of poly(ether-amide)s from 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane

In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0.552g 1, 1-bis [4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP), 0.200 g (1 mmol) 4,4'-diaminodiphenyl ether (ODA), 0.115 g lithium chloride [5 wt % based on solvent N-methyl pyrrolidone (NMP) and pyridine mixture] and 0.744g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 mL pyridine and 2mL NMP. The mixture was stirred vigorously and temperature was slowly raised to 100°C over a period of 30 min. The mixture was heated at 100°C for 3h under nitrogen. After cooling the resulting viscous solution was poured into 200 mL of methanol under vigorous stirring. The precipitated polymer (SPA-7) was filtered, washed with methanol and dried. The polymer was purified by dissolving in N, N-dimethylacetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol and dried under vacuum at 100°C for 6 h. The yield was 96% and the inherent viscosity of polymer in DMAc was 0.30 dL/g.

The poly(ether-amide)s SPA-8 to SPA-13 was synthesized with varying diamines by similar procedure.

IR Spectrum

SPA-7: 3307; 2969; 1660; 1603; 1494; 1405; 1227; 1165; 1013; 757; 826; 690 cm^{-1}.

SPA-10: 3344; 2970; 2915; 2853; 1663; 1589; 1400; 1181; 1073; 826; 668 cm^{-1}.
SPA-11: 3306;2970;2911;1663;1601;1492;1168;1014;826;703 cm^{-1}.

2E.2 Results and Discussion

In the present work, methyl substituted diacid containing cyclopentylidene moiety, viz. 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl]cyclopentane (BCMMP); (IV) have been synthesized and used as building blocks for preparation of methyl substituted poly(ether-amide)s. These methyl substituted poly(ether-amide)s were characterized by IR, inherent viscosity, solubility, thermal study and XRD pattern.

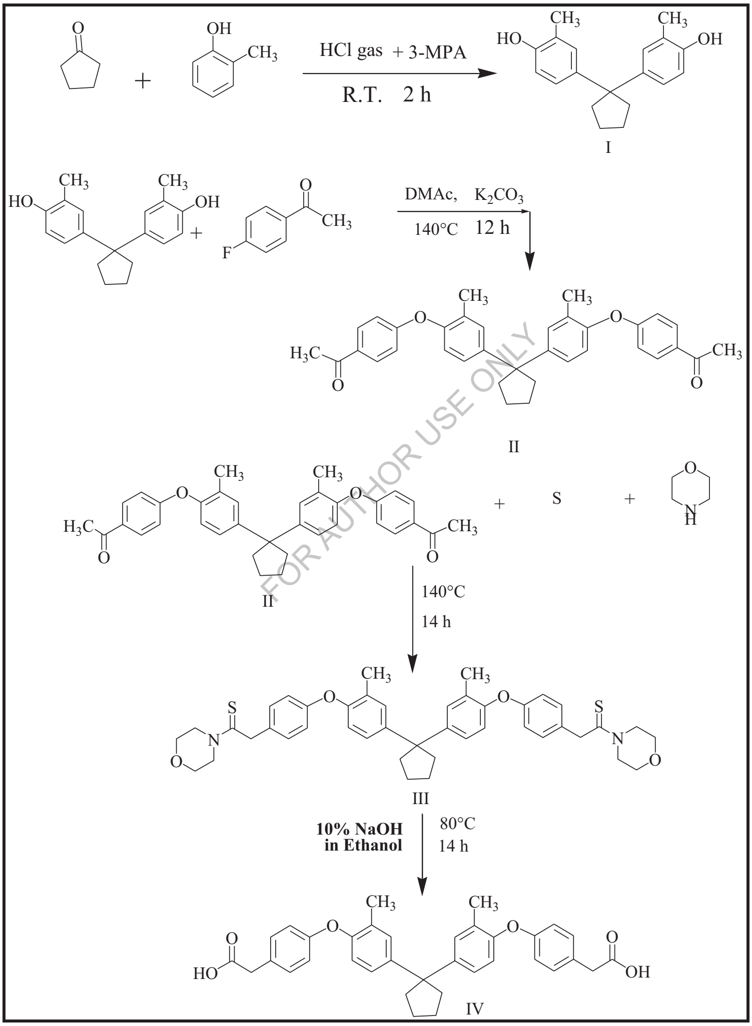
2E.2.1 Synthesis of 1, 1-bis [4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane

The novel dicarboxylic acid, 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl]cyclopentane (BCMMP); (IV) was synthesized from phenol and cyclopentanone in several steps **(Scheme. 2E.1).**

The 1, 1-bis(4-hydroxy-3-methyl phenyl) cyclopentane (I) was synthesized by reacting o-cresol with cyclopentanone in presence of 3-MPA as catalyst. The 1, 1-bis[4-(4-acetyl phenoxy)-3-methyl phenyl] cyclopentane (II) was obtained by reaction of BHMPC with 4-fluoroacetophenone and potassium carbonate in DMAc. Structure of (II) was confirmed by infrared spectroscopy.

The infrared spectrum of II (**Fig 2E.1**) showed medium strong absorption bands at 2955 and 2866 cm^{-1} showing the presence of aliphatic C-H stretching corresponding to the in phase and out phase vibration of cyclopentane ring and methylene groups. Spectrum also shows absorption near 1491 due to C-H bending vibration. Absorption at 1666 cm^{-1} of carbonyl (>C=O) stretching adsorption indicated acetyl carbonyl moiety. The peak at 1252 and 1019 shows C-O-C stretch.

The formation of intermediate thiomorpholide derivative (III) was confirmed by infrared spectroscopy. The infrared spectrum of III (**Fig 2E.2**) showed medium strong absorption bands at 2969 and 2861 cm^{-1}, due to the presence of aliphatic C-H stretching corresponding to the in phase and out phase vibration of cyclopentane unit and methylene group. Spectrum also shows absorption near 1490 cm^{-1} due to C-H bending vibration. The appearance of absorption at 1230 cm^{-1} (>C=S) confirm formation of thiomorpholide.



Scheme 2E.1 Synthesis of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP)

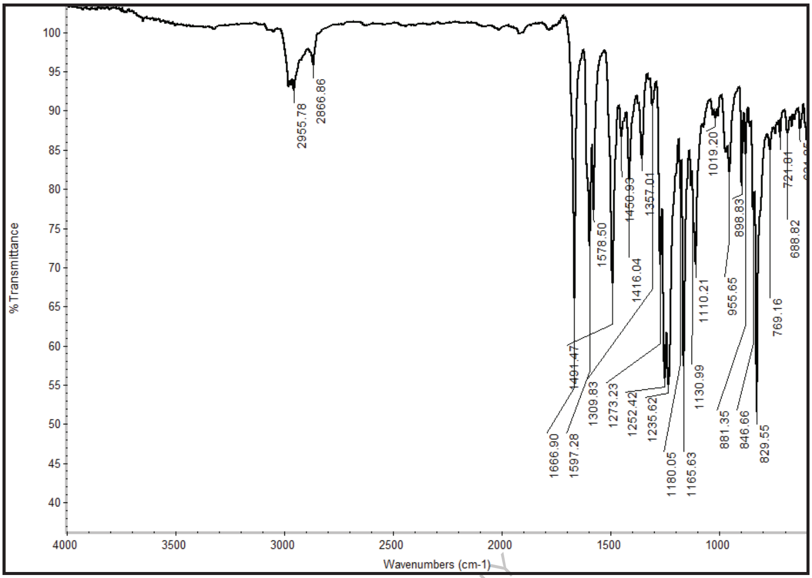


Fig 2E.1 FT-IR spectrum of 1, 1-bis [4- (4-acetyl phenoxy)-3-methyl phenyl] cyclopentane

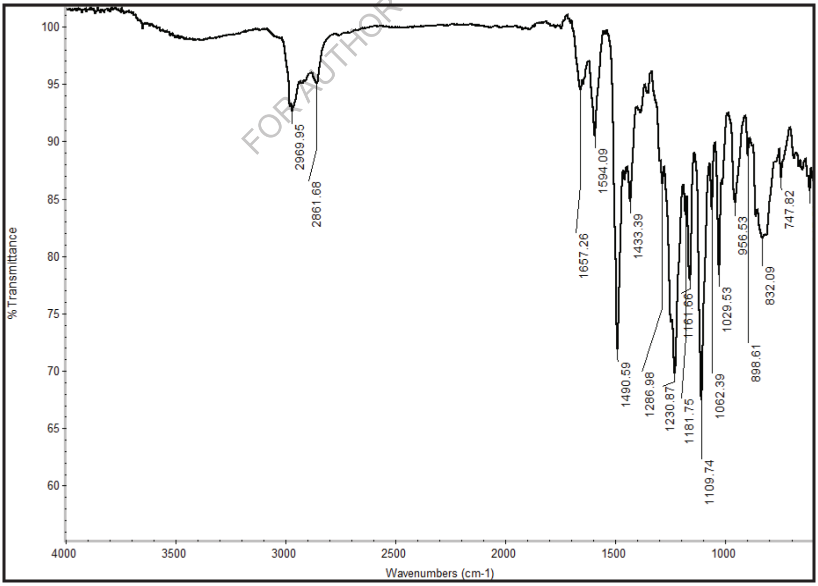


Fig 2E.2 FT-IR spectrum of 1, 1-bis [4- (4- thioacetomorpholide phenoxy)-3-methyl phenyl] cyclopentane

The 1, 1-bis[4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (IV) was obtained by the Conrad Willgerodt reaction with Kindler variation.

Thiomorpholide derivative on alkaline hydrolysis yielded the 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (IV). The structure of IV was confirmed by IR, NMR (^{1}H and ^{13}C) and mass spectroscopy.

The infrared spectrum of (BCMMP); IV (**Fig 2E.3**) showed absorption bands at 3324 (-COOH stretching) and 1702 cm^{-1} (C=O) indicating the presence of carboxyl group. IR spectrum also showed the absorption bands at 2989 and 2869 cm^{-1} corresponding to the in plane and out of plane stretching vibrations of the ($-CH_2-$) of the methylene group, methyl group and cyclopentane unit. Spectrum also shows absorption near 1492 cm^{-1} due to C-H bending vibration.

The proton NMR spectrum (**Fig 2E.4**) of IV showed the NMR singlet at 3.62δ corresponding to methylene (2H) group of $-CH_2COOH$. The signals in the range of 7.28 to 6.80 δ of (14H) are attributed to the aromatic protons of phenylene rings whereas signal at 2.30 and 1.70 δ are assigned to cyclopentane proton. The signal appears at 2.20 singlet attributed to methyl group attached to aromatic ring.

^{13}C NMR spectrum (**Fig 2E.5**) of (BCMMP); (IV) showed sixteen NMR signals corresponding sixteen types of different carbons of which carbonyl carbon appeared at 177.86 δ for (C=O); whereas quaternary carbons showed signals at 157.38; 152.02; 146.68; 132.46 and 54.95 δ. The CH carbons appeared at 130.56; 129.96; 125.67; 119.27; 117.35 δ, whereas CH_2 carbon gave NMR signals at 40.26, 38.93, 23.02 δ and methyl carbons shows at 16.47 δ confirms the formation of methyl substituted diacid (BCMMP);(IV) monomer.

The DEPT spectrum (**Fig 2E.6**) of (BCMMP);(IV) also confirms the diacid monomer wherein all the quaternary carbons are absent in the spectrum and the peaks of CH carbons are upper sides at 130.57, 130.00, 125.68, 119.28,117.40, 117.35 δ and CH_2 appeared at down side at 40.27, 38.92, 23.00 δ. The primary methyl carbon also shows signal upper side at 16.49δ confirms that presence of methyl substituent to aromatic ring.

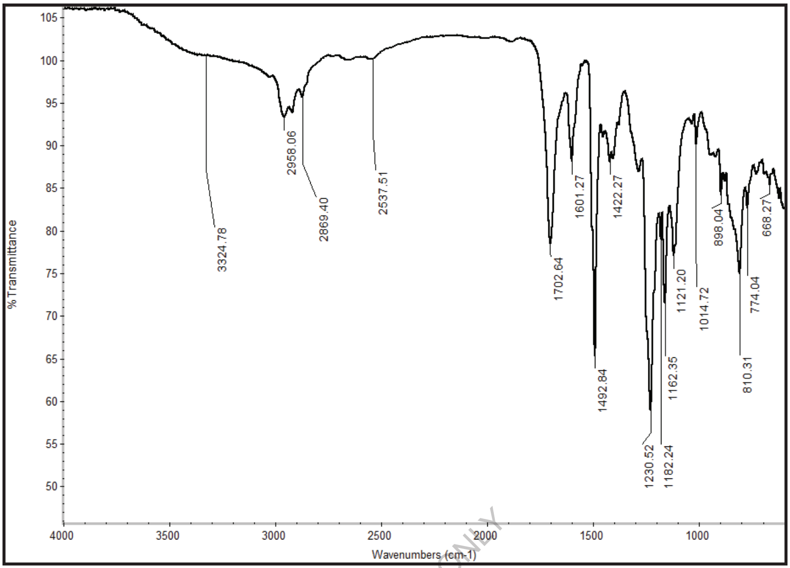


Fig 2E.3 FT-IR spectrum of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP)

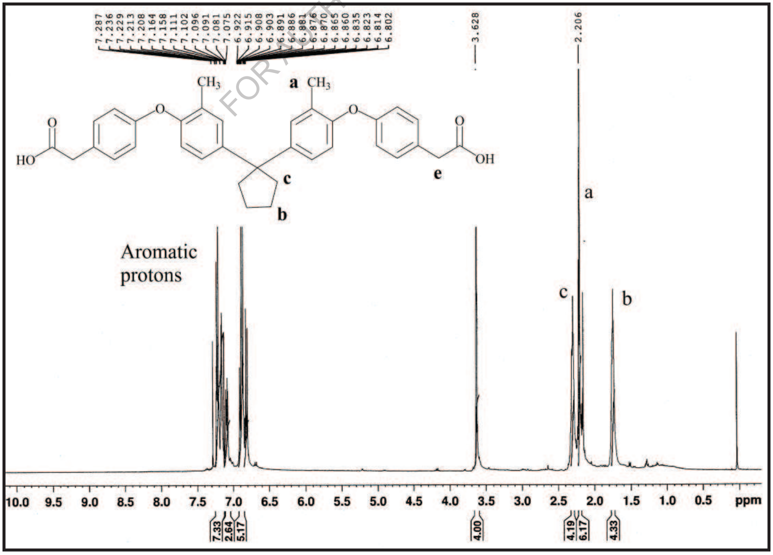


Fig 2E.4 ^{1}H NMR spectrum of 1, 1-bis [4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP)

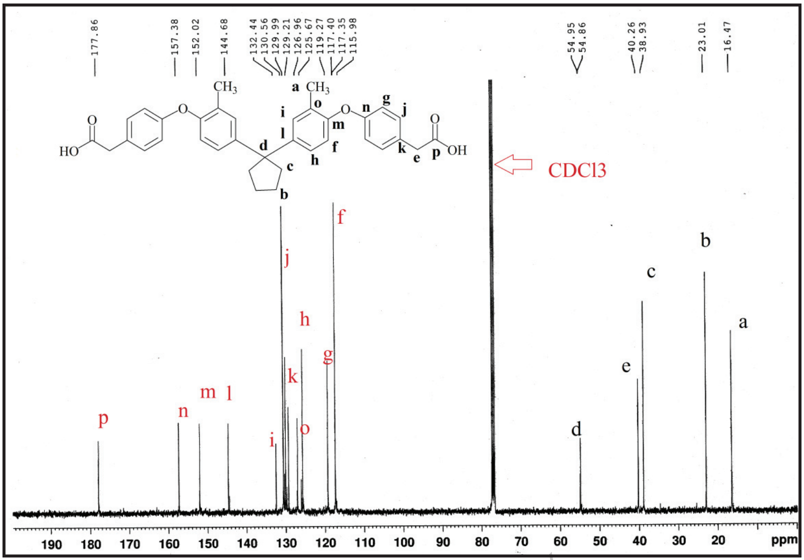


Fig 2E.5 ^{13}C NMR spectrum of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP)

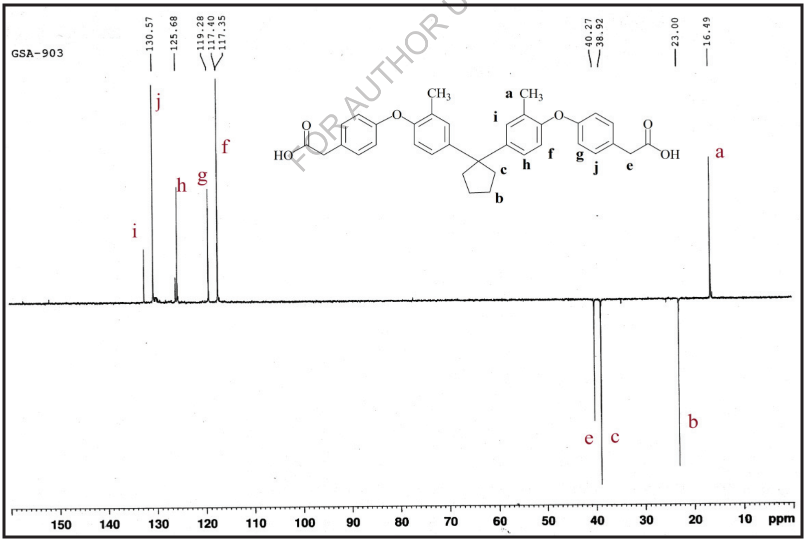


Fig 2E.6 DEPT spectrum of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP)

The mass spectrum of (Fig 2E.7) BCMMP (IV) showed molecular ion peak at m/e (m-1) 549.05 corresponding to molecular weight of BCMMP.

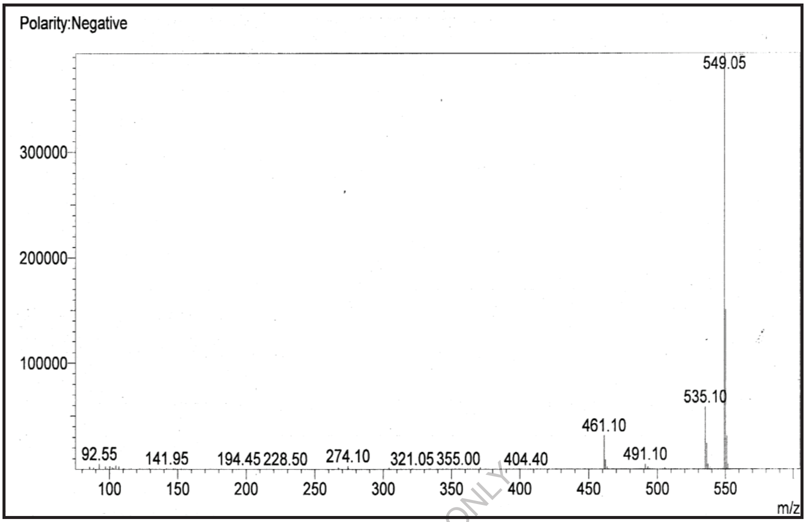
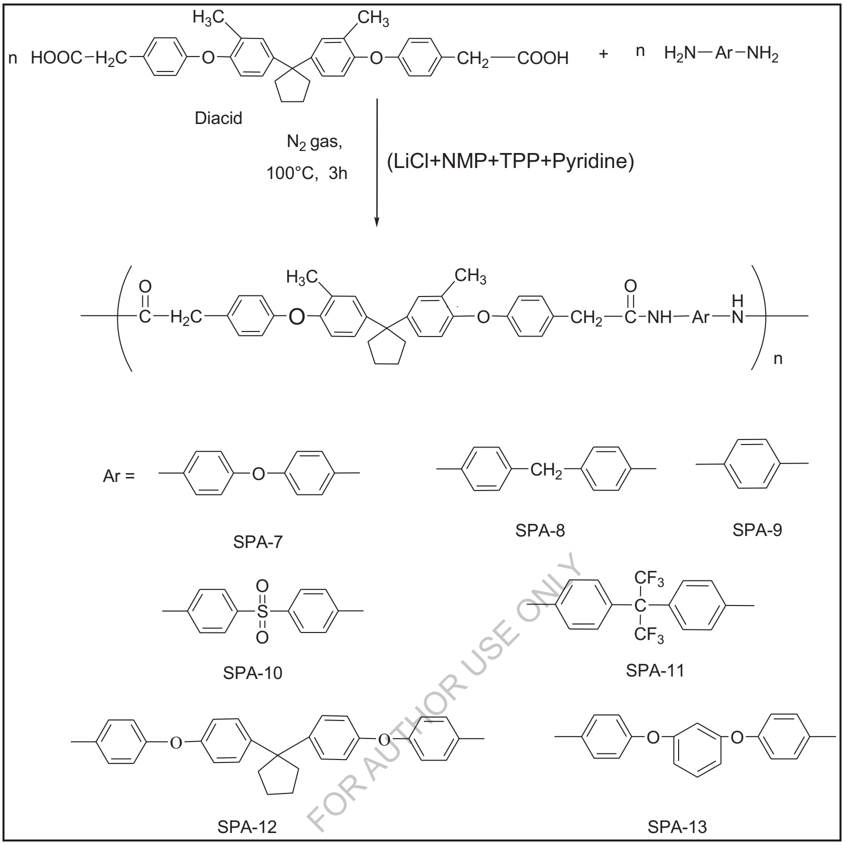


Fig 2E.7 Mass spectrum of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (BCMMP)

2E.2.2 Synthesis of poly(ether-amide)s from 1, 1-bis[4-(4-carboxy methylene phenoxy) 3-methyl phenyl]cyclopentane

The methyl substituted poly(ether-amide)s were synthesized by Yamazaki's phosphorylation method [228]. Series of methyl substituted poly (ether-amide)s were synthesized from the stoichiometric quantities of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane(BCMMP);(IV) and various aromatic diamines by direct polycondensation method (Scheme 2E.2), Triphenyl phosphite was used as the condensing agent, where in the mixture of NMP and pyridine (4.1 by volume) containing 8 wt. % anhydrous lithium chloride was employed as solvent. The polymerization was carried out at 100°C for 3 h. The different aromatic diamines were used for polymerization. The polymerization preceded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in methanol.



Scheme 2E.2 Synthesis of polyether-amides from 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane

The yield and viscosity of polyamides produced from 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl] cyclopentane (IV) are presented in **Table 2E.1**. All the polymers were obtained in the good yields (96 to 100 %) as pale yellow to white fibrous materials. The inherent viscosities of these polymers were in the range of 0.30 to 0.42 dL/g; this is indicated the formation of moderate to high molecular weight of polymers. Polymerization was carried out with 1 mmol of methyl substituted diacid (BCMMP) (IV) and 1 mmol of diamine.

Table 2E.1 Yield and Viscosity of Poly(ether-amide)s

Polymer	**Monomers**		**Yield %**	**Inherent Viscosity dL/g** [a]
	Novel Diacid	Diamine		
SPA-7	BCMMP	ODA	96	0.30
SPA-8	BCMMP	MDA	97	0.35
SPA-9	BCMMP	p-PDA	100	0.42
SPA-10	BCMMP	SDA	96	0.25
SPA-11	BCMMP	6-FDA	98	0.33
SPA-12	BCMMP	BAPC	98	0.32
SPA-13	BCMMP	BAPB	99	0.30

[a] Inherent viscosities were measured at a concentration of 0.5 % (W/V) in **DMF** at 30°C.

The structures of polymers were characterized by infrared spectroscopy. The representative spectra of SPA-7, SPA-10 and SPA-11 are discussed below. polyamide SPA-7 **(Fig 2E.8)** showed an absorption band at 3307 cm^{-1}(-NH stretching), a sharp band at 1494 cm^{-1} (characteristic for –NH bending) and absorption band at 1660 cm^{-1} (due to C=O in amide group). The absorption band at 3036 cm,$^{-1}$ characteristic for aromatic –CH stretching; and absorption band at 2969 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed.

The Polyamide SPA-10 **(Fig 2E.9)** showed an absorption band at 3344 cm^{-1} (-NH stretching), a sharp band at 1492cm^{-1} (characteristic for –NH bending) and absorption band at 1663 cm^{-1} (due to C=O in amide group). The absorption band at 2970 and 2853 cm^{-1} corresponding for aliphatic (–CH stretch) methylene linkage were observed.

The Polyamide SPA-11 **(Fig 2E.10)** showed an absorption band at 3306 cm^{-1} (-NH stretching), a sharp band at 1500 cm^{-1} (characteristic for –NH bending) and absorption band at 1663 cm^{-1} (due to C=O in amide group). The absorption band at 2970 cm,$^{-1}$ characteristic for aliphatic (–CH stretch) methylene linkage were observed.

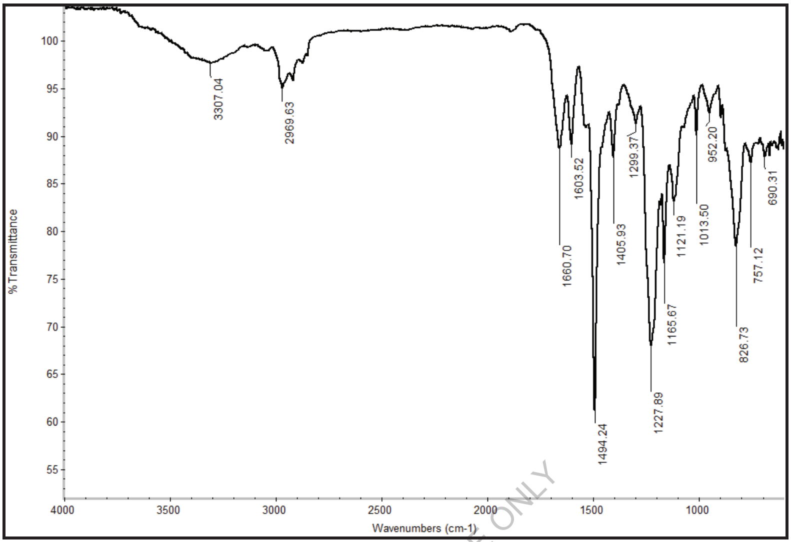


Fig 2E.8 FT-IR spectrum of SPA-7

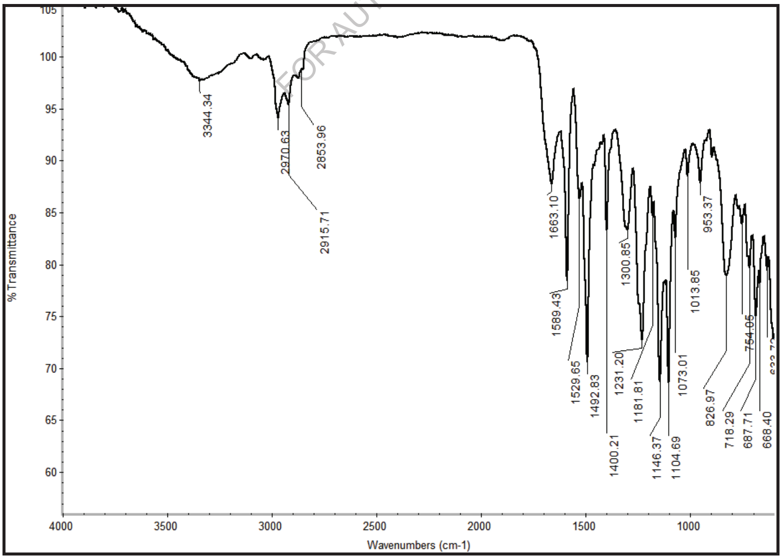


Fig 2E.9 FT-IR spectrum of SPA-10

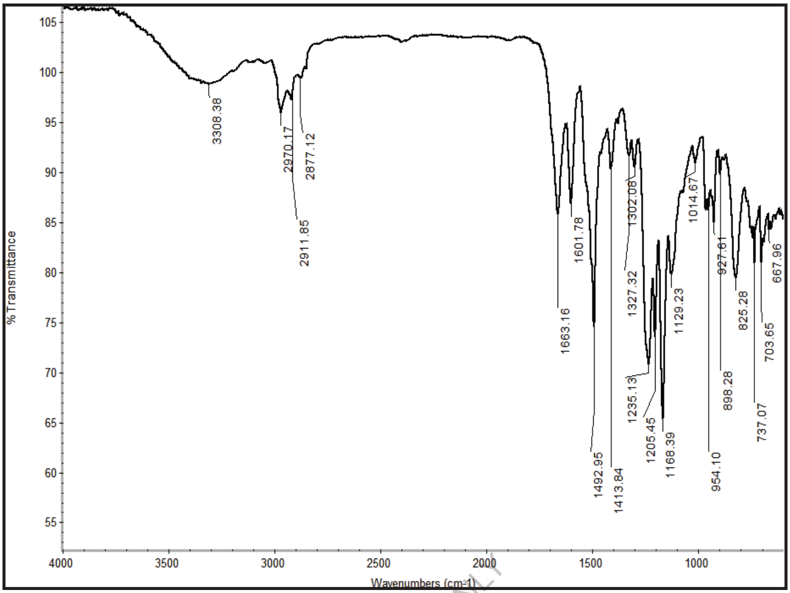


Fig 2E.10 FT-IR spectrum of SPA-11

2E.2.3 Properties of Methyl substituted poly(ether-amide)s

Solubility

Solubility characteristics of polyamides are tabulated in **Table 2E.2.**

Table 2E.2 Solubility Behavior of Poly (ether-amide)s

Polymer	**Solubility**								
	DMF	DMAc	DMSO	NMP	Pyridine	C.H_2SO_4	THF	DCM	$CHCl_3$
SPA-7	+	+	+	+	+	+	-	-	-
SPA-8	+	+	+	+	+	+	-	-	-
SPA-9	+	+	+	+	+	+	-	-	-
SPA-10	+	+	+	+	+	+	-	-	-
SPA-11	+	+	+	+	+	+	-	-	-
SPA-12	+	+	+	+	+	+	-	-	-
SPA-13	+	+	+	+	+	+	-	-	-

+ : Soluble; - : Insoluble on heating; ± : Sparingly soluble

The solubility of polymers was determined in different common organic solvents. It was observed that polyamides synthesized from 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl]cyclopentane (IV) exhibited better solubility in various polar aprotic solvents such as N-methylpyrrolidone (NMP), N, N-dimethyl sulphoxide (DMSO), N, N-dimethylacetamide (DMAc), N, N-dimethyl formamide (DMF), pyridine. All these methyl substituted poly (ether -amide)s also dissolved in Conc. H_2SO_4. All these polyamides (SPA-07 to SPA-13) are insoluble in common solvents like THF, DCM and chloroform. This may be assigned to the effect of cardo cyclopentylidene moiety with methylene and ether spacer unit as well as methyl substitution on aromatic chain in monomer structure. Thus better solubility of these polyamides; as expected can also be attributed to the combined effect of introduction of aliphatic methylene group, ether linkage in the polymer backbone, methyl substitution and cyclopentylidene moiety.

Thermal Properties

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. **Table 2E.3** incorporate the thermal data such as glass transition temperature (T_g), 10% Wt. loss temperature (T_d), initial decomposition temperature (T_i) and residual weight at 900°C.

The thermal stability of the polyamides was studied by thermogravimetric analysis **(Fig 2E.11)** at a heating rate of 10°C/min in nitrogen atmosphere. The decomposition temperature at which 10% weight loss (T_d), initial decomposition temperature (T_i) and char yields at 900°C were determined from the original thermograms. The T_d values range between 413°C to 464°C respectively. Residual wt. % loss at 900°C was in the range of 23 to 51 %.

Table 2E.3 Physical properties of Poly(ether-amide)s

Polymer	Thermal Behavior [b]			
	T_i °C in N_2	T_d °C in N_2	T_g °C	Residual Wt % at 900°C
SPA-07	296	441	200	47
SPA-08	296	452	202	23
SPA-09	320	464	n.d.*	51
SPA-10	289	449	205	37
SPA-11	295	420	195	39
SPA-12	276	423	210	46
SPA-13	274	413	195	42

[b] Temperature at which onset of decomposition was recorded by TG at **a** heating rate of 10°C/min.

Tg- Glass transition temperature determined at second heating by DSC at a heating rate of 10°C/min

T_d – Temperature of 10% decomposition

T_i – Initial decomposition temperature.

n.d*- T_g not detected by DSC.

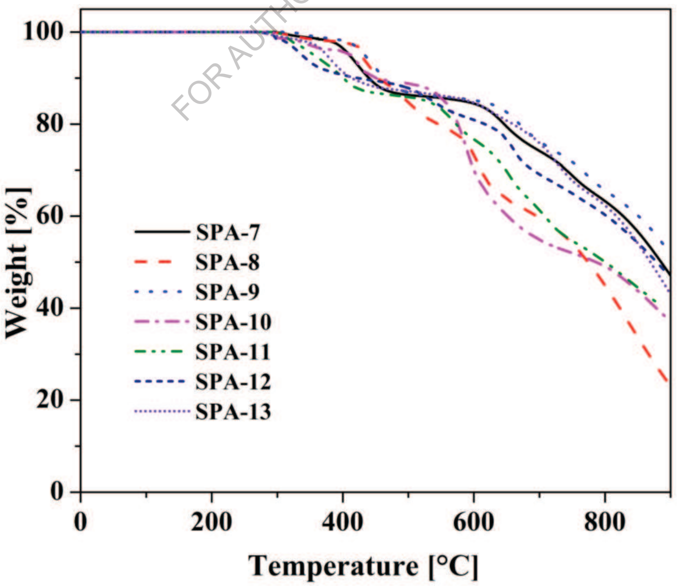


Fig 2E.11 TGA curve of poly(ether-amide)s SPA-17 to SPA-13

The DSC curve shown in **Fig. 2E.12** represents the T_g of polyamides synthesized from novel methyl substituted diacid (BCMMP); (IV). The glass transition temperatures of these polyamides are in the range of 195 to 210°C.

Among all the synthesized polyamides, T_g value of SPA-9 was not detected by DSC, because of the highest rigidity, which inhibited the molecular motion. The incorporation of rigid units along a polymer backbone restricts the free rotation of the macromolecular chains and leads to increase T_g values. Whereas in the SPA-7, SPA-8, SPA-10, SPA-11, SPA-12 and SPA-13, the presence of flexible bonds lowers the rigidity of its backbone and reduces the T_g values.

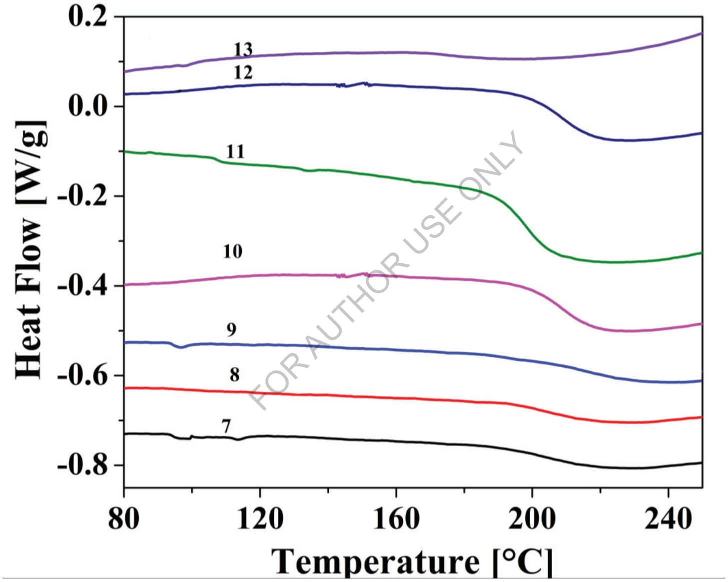


Fig 2E.12 DSC curve of poly(ether-amide)s SPA-7 to SPA-13

The wide angle X-ray diffraction pattern of all polyamides is shown in **Fig 2E.13**. It is observed that all the polymers exhibit amorphous nature. Introduction of cyclopentylidene moiety, methyl substituent and aliphatic methylene linkage may have disrupted the chain regularity and packing leading to amorphous polyamides. Similarly introduction of diether-diamine containing cyclopentylidene moiety in SPA-12 and phenylated moiety in SPA-13; disturbs symmetry to large extent and polymers become more amorphous. Thus amorphous nature of the polymers was depending on the structures of novel diacid and diamines chosen for synthesis of polymers.

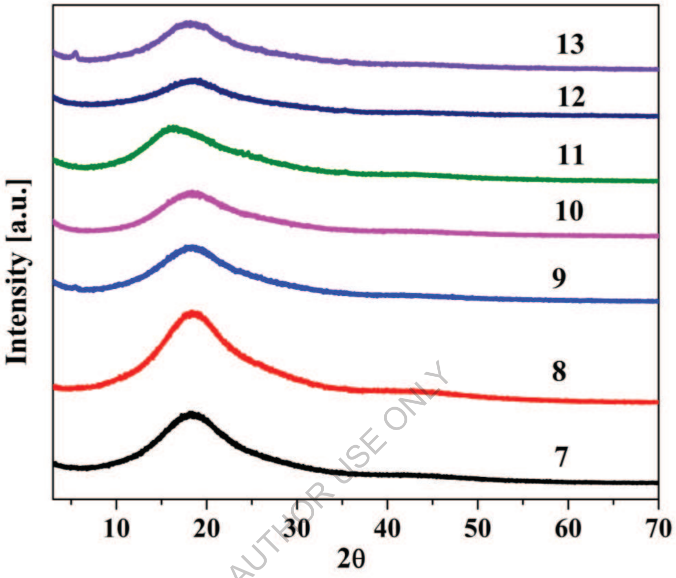


Fig 2E.13 XRD curve of Poly (ether-amide)s SPA-7 to SPA-13

2E.3 Summary and Conclusions

- A series of new poly(ether-amide)s containing pendent methyl group, methylene spacer, ether linkage and cardo cyclopentylidene moiety was synthesized by the direct polycondensation of 1, 1-bis[4-(4-carboxy methylene phenoxy)-3-methyl phenyl]cyclopentane and commercial aromatic diamines.
- Inherent viscosities of polyamides were in the range 0.25-0.42 dL/g indicating formation of medium to reasonably high molecular weight polymers.
- Polyamides were found to be soluble in DMF, DMAc, DMSO, NMP, and pyridine at room temperature or upon heating. This indicates that the

incorporation of pendent flexible methyl group, methylene spacer and cardo cyclopentylidene moiety leads to a significant enhancement in solubility of polyamides.

- Wide angle X-ray diffraction patterns indicated that polyamides containing pendent Methyl group, methylene spacer and cardo cyclopentylidene were amorphous in nature.
- T_d values for polyamides were in the range 413°C-464°C indicating good thermal stability of polyamides.
- T_g values of polyamides were in the range 195°C-210°C. The depression in Tg values of polyamides could be attributed to the presence of pendent methyl groups, methylene spacer and cardo cyclopentylidene moiety.
- A large difference in T_g and decomposition temperature of polyamides offers a broad processing window.

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