SYNOPSIS

High Performance Polymers (HPP) is one of the specialty areas within polymer science. It has been recognized as a separate area within polymer chemistry for more than 60 years. Like many scientific disciplines, it has received most of its momentum from the space program owing to the need for ablative systems, high temperature adhesives and coating and heat- and flame-resistant fibers.

As a loose definition, high performance polymers include all polymeric materials which exhibit thermal stability above 200°C and in addition have outstanding mechanical, electrical, optical, surface and rheological properties. High performance polymers such as polyimides, poly(ester-amide)s, poly(ester-imide)s, poly(ether-amide)s, poly(ether-azomethine)s and polyesters with high thermal stability and good mechanical properties have been identified for a variety of applications, e.g., as engineering plastics for aerospace industries, in optical and electronic devices and also as films or membranes. But the high regularity and high rigidity of the backbone of high performance polymers results in strong interchain interactions, high melting points and low solubility. Therefore, in spite of having excellent combination of properties, most of the high-performance polymers have some serious drawbacks, e.g. insolubility in common organic solvents, intractability and infusibility that make their processing difficult and frequently limit their utility in several advanced technological applications.

The objective of the present research was to use cyclopentanone as a starting material to design and produce several difunctional monomers such as aromatic diamines, diacids and dialdehydes. Important considerations in designing monomers were: i) meta-linkage introduces “kinks” to the main chain which decrease the rigidity of the polymer backbone and inhibit packing, thus reducing the interchain interactions leading to enhanced solubility, ii) the presence of cardo cyclopentane ring alongwith the polymer backbone reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect and sequentially help in enhanced processability, iii) the presence of flexible methyl group on aromatic ring offers asymmetry to the polymer backbone leading to constitutional isomerism, which could impart interesting properties to the derived polymers. The second objective of this work was to investigate the effect of incorporation of pendent or cardo cyclopentane ring on the polymer properties, such as solubility, inherent viscosity, crystallinity and thermal stability.
For this study, cardo cyclopentylidene moiety containing novel monomers such as bis(ether-carboxylic acid), bis(ester-amine), bis(ether-amine),bis(ether-aldehyde) and polymers such as poly(ether-imide)s, poly(ester-amide)s, co-poly(ether-amide)s, poly(ester-imide)s, poly(ester-amide)s, co-poly(ester-amide)s, poly(ether-azomethine)s and co-poly(ether-azomethine)s were synthesized and characterized, thus, permitting the establishment of a reliable structure-property relationship.

Based on these objectives, the work has been presented in four chapters as below.

1) CHAPTER-1

The general introduction to polymers and high performance polymers, historical developments, types of polymers and review of affecting factors to the thermal stability and processability has been discussed. The approaches to improve thermal stability, solubility, structure property relationship, application and literature work on earlier investigations etc. are summarized. The scope and objectives of research work is also summarized.

2) CHAPTER-2

General introduction of polyamides, review of polyamides synthesis methods and their properties with applications are presented in this chapter. Chapter – 2 is divided into five sections as 2A, 2B, 2C, 2D and 2E.

SECTION-2A

This section deals with the synthesis of novel methyl substituted aromatic-aliphatic diether-diamine; 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) and homopolyamides therefrom(Scheme-1). A well-developed Yamazaki’s phosphorylation polycondensation method was used to prepare polyamides by polycondensation with number of diacids to yield high molecular weight copolyamides. Resulting copolymers were characterized by measurement of inherent viscosity, solubility, IR-spectroscopy and thermal analysis. The effect of methyl substitution and cardo cyclopentylidene moiety in polymer backbone on properties of polymers is also reported.

SECTION-2B

Copolymerization is also one of the approach to improve the solubility without losing appreciable thermal stability. Therefore it was interesting to synthesize number of high performance polymers/co-polymers with enhanced solubility in some organic solvents without much sacrificing thermal stability. Thus section-2B deals with the use...
of same monomer as chapter 2A i.e. 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC).

The BAMPC was used to synthesize co-poly(ether-amide)s with TPC and/or IPC using low temperature solution polycondensation method (Scheme-1). These poly(ether-amide)s and co-poly(ether-amide)s were characterized by the inherent viscosity, solubility, infrared spectroscopy, thermal studies and X-ray diffraction study. Structure property relation was investigated.

SECTION -2C

This section describes the synthesis of novel 1,3-bis(ester-amine)s i.e. 1, 1-bis(3-aminobenzoyloxy phenyl) cyclopentane (m-BABPC) which were useful to synthesize modified aromatic polymers having enhanced processability and solubility (Scheme-2). Some success in enhancing the solubility of aromatic polymers was achieved by incorporation of cardo group. In addition to cardo moiety; it was thought that incorporation of ester linkage, meta catenation and copolymerization approach would have improved physical properties as well as processability. Therefore new aromatic dister-diamines containing preformed diester linkages were prepared and used as building blocks to obtain thermally stable polymers and copolymers by low temperature solution polycondensation. These poly(ester-amide)s and co-poly(ester-amide)s were characterized by the inherent viscosity, solubility, infrared spectroscopy, thermal studies and X-ray diffraction study. Structure property relation was investigated.

SECTION -2D

This deal with synthesis of novel diether-dicarboxylic acid contains methylene carboxy group i.e. 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP). The novel dicarboxylic acid, 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) was synthesized starting from phenol and cyclopentanone in several steps. The 1, 1-bis(4-hydroxy phenyl) cyclopentane (I) was synthesized 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. 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. Thiomorpholide derivative on alkaline hydrolysis yielded the 1, 1-bis[4-(4-carboxy methylene phenoxy)
phenyl] cyclopentane (BCMPP) (Scheme-3). The purification and spectral characterization of diether-diacid compound has been described. Further the chapter includes synthesis of new poly(ether-amide)s by Yamazaki’s phosphorylation polycondensation method with various commercial diamines. Polymers were obtained in quantitative yields with moderate to high molecular weight as evidenced by viscosities. These novel polymers were characterized by inherent viscosity measurement, solubility, FT-IR spectroscopy, thermal analysis and x-ray diffraction study. These polymers were found highly soluble in organic solvents and exhibited high thermal stability.

SECTION -2E

Incorporation of cyclopentylidene cardo group, ether linkages, methylene spacers and pendant methyl substitution into polymer backbone is one of the approaches to improve the solubility without losing appreciable thermal stability. Some high performance materials based on cyclopentylidene moiety have been reported, however there are no reports on the aromatic aliphatic dicarboxylic acid containing cardo cyclopentylidene moiety, ether linkages, pendant methyl substitution and methylene carboxy group. Therefore it was interesting to synthesize the novel diacid and number of high performance polymers with improved thermal stability, and enhanced solubility in some organic solvents to understand the effect of methylene linkages, ether linkages, pendant methyl substitution and cyclopentylidene moiety on resulting high performance polymeric materials. Thus section-2E deals with the synthesis of novel dicarboxylic acid i.e. 1, 1-bis [4-(4-carboxy methylene phenoxy)-3-methyl phenyl]cyclopentane (BCMMP), starting from cyclopentanone and o-cresol followed by various steps and its characterization by physical constant, IR, NMR (\(^1\)H and \(^{13}\)C), mass spectroscopy. The dicarboxylic acid (BCMMP) was used to synthesize poly (ether–amide)s from seven different aromatic diamines using Yamazaki’s phosphorylation method (Scheme-4). These poly (ether–amide)s were characterized by the inherent viscosity, solubility, infrared spectroscopy, thermal studies and X-ray diffraction study. Structure property relation was investigated.

3) CHAPTER-3

This chapter deals with literature survey on polyimides, many synthetic methods; properties and applications of polyimides.

Aromatic polyimides (PIs) have received a status as high-performance materials in the aerospace and microelectronics industries in the form of moldings, films and
reinforced composites, owing to their excellent thermal stability, good chemical and radiation resistance, mechanical and electrical properties. However, aromatic PIs show poor processing performance such as high melting temperature and limited solubility in most organic solvents as a result of the rigid backbones which, together with highly conjugated aromatic structures and intermolecular charge transfer complex (CTC), further lead to intense coloration, reduced optical transparency and high dielectric constant, hence limiting their applications in optoelectronic and microelectronic fields such as flexible display and printed circuit. Polymer structure modification becomes necessary for such difficulties to be overcome. It has been reported that the improvement of the practical properties like the tractability, optical and dielectric properties of PIs could be effectively achieved by introduction of flexible linkage, bulky substituents, and structurally unsymmetrical segments into the polymer backbone. From the viewpoint of synthetic methodology, the cardo-type structure could be incorporated into polymer backbone in terms of diamine monomers that are readily achieved by reacting cardo-type diol with the amine precursor such as m-nitrobenzoyl chloride or p-chloronitrobenzene for ester or ether linkages respectively. Chapter-3 is divided into two sections as 3A and 3B.

SECTION -3A

This section deals with the synthesis of polymers from BAMPC with various aromatic dianhydrides to form poly(ether-imide)s (Scheme-1). These polyimides were obtained in good yield by two step polycondensation method i.e. synthesis of polyamic acid followed by thermal imidization. These polyimides were soluble in many organic solvents. Thus better solubility of these polymers; as expected due to two ether linkages, pendant methyl substitution and cardo type cyclopentylidene moiety in the polymer backbone. The polymers were characterized by inherent viscosity, solubility, FT-IR, thermal properties and XRD studies.

SECTION -3B

This section describes the synthesis of poly(ester-imide)s from m-BABPC with different aromatic dianhydrides (Scheme-2). These polymers were obtained in good yields and had good inherent viscosities. The polymers were characterized by inherent viscosity, solubility, FT-IR, DSC, TGA and XRD.
4) CHAPTER - 4

This chapter deals with introduction, literature survey, synthesis methods, properties and application of polyazomethines.

The polymers that contain \(-\text{CH=N-}\) linkages in polymer backbone called as Poly(Schiff base)s. Poly(Schiff base)s are classes of materials known as polyazomethines. These conjugated polymers are mostly attractive because they show good mechanical strength, attractive thermal stability, photoconductivity and optical properties. Because of this wide range of attractive properties, polyazomethines have potential applications in many fields, e.g. battery anodes or cathodes, advanced technology materials, semiconductors, energy storage and conversion devices, electroluminescence (EL) devices, integrated electro-optics for switching, displays, etc.

However, polyazomethines are usually infusible polymers and have poor solubility, drawbacks which would minimize their practical applications. Numerous modified polyazomethines such as poly(azomethine-ester)s, poly(azomethine-ether)s, poly(azomethine-carbonate)s, poly(amide-azomethineester)s, poly(acrylate-azomethine)s, thermosetting polyazomethines, poly(azomethine-sulfone)s were synthesized with the aim to reduce the melting temperature, to increase the solubility and to endorse specific properties such as mesomorphism. Several strategies have been reported to enhance the solubility of polyazomethines. The incorporation of flexible alkyl and alkoxy groups as the substituents has been proved to be effective, although at the expense of their thermal stability. The integrations of bulky substituents such as tetraphenylethylene, triphenylamine and diphenylfluorene have been investigated. The copolymerization of electron rich, solubility-enhancing aromatic or heterocyclic units such as carbazole, thiophene and fluorene has also been explored. In this topic we have reported poly(ether-azomethine)s synthesized from various novel dialdehyde and commercial diamines. This chapter is divided into three sections as 4A, 4B and 4C.

SECTION-4A

This section agreements with the synthesis of novel dialdehyde i.e. 1, 1-bis [4-(4-benzaldehyde oxy) phenyl] cyclopentane (BBPC) and its characterization by physical constant, IR, NMR \((^1\text{H and } ^{13}\text{C})\), mass spectroscopy (Scheme-5). This chapter also describes synthesis of poly (ether-azomethine)s by elevated temperature solution polycondensation method in DMAc containing LiCl. The polyazomethines were
characterized by viscosity, solubility, FT-IR spectroscopy, X-Ray diffraction studies and thermal analysis.

**SECTION -4B**

This section deals with the synthesis of methyl substituted novel dialdehyde i.e. 1, 1-bis[4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane (BBMPC) and its characterization by physical constant, IR, NMR (\(^1\)H and \(^{13}\)C), mass spectroscopy (Scheme-6). This chapter also describes synthesis of methyl substituted poly(ether–azomethine)s by elevated temperature solution polycondensation method in DMAc containing LiCl. The polyazomethines were characterized by inherent viscosity, solubility, FT-IR spectroscopy, X-Ray diffraction studies and thermal analysis.

**SECTION -4C**

The chemical modifications of polyazomethines are also achieved by synthesizing new diamine and then co-polymerizing them with commercially available dialdehydes TPA and/or IPA (Scheme-1). These attempts targeting at either solubility improvement or investigating their thermal stability

This section deals with the synthesis of methyl substituted novel diamine i.e. 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) and its characterization by physical constant, IR, NMR (\(^1\)H and \(^{13}\)C), mass spectroscopy. This chapter also describes preparation of methyl substituted co-poly(ether–azomethine)s by elevated temperature solution polycondensation method in DMAc containing LiCl. The polyazomethines were characterized by inherent viscosity, solubility, FT-IR spectroscopy, X-Ray diffraction studies and thermal analysis.
Scheme 1. Synthesis of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl]Cyclopentane and polymers therefrom.
Scheme 2. Synthesis of 1, 1-bis (3-aminobenzoyloxy phenyl) cyclopentane and polymers therefrom.
Scheme 3. Synthesis of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane and polymers therefrom.
Scheme 4. Synthesis of 1, 1-bis [4- (4-carboxy methylene phenoxy)-3-methyl phenyl] poly(ether-amide)s.
Scheme 5. Synthesis of 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane and polymers therefrom
Scheme 6. Synthesis of 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane and polymers therefrom