4.1 Introduction

The polymers that have (-CH=N-) linkages in polymer backbone called as Poly-imines or poly(Schiff base)s. Poly(Schiff base)s are classes of materials identified as polyazomethines. These conjugated polymers are mostly gorgeous because they show good mechanical strength [1], good thermal stability [2], photoconductivity [3] and optical properties [4]. Since this wide range of charming properties, polyazomethines have potential applications in many fields e.g. semiconductors, battery anodes or cathodes, advanced technology materials, integrated electro optics for switching, energy storage and conversion devices, displays [5-7], electroluminescence (EL) devices [8], etc. The first polyazomethine was described in 1923 as a result of polycondensation of terephthaldehyde and benzidine [9]. Since then, conjugated aromatic polyazomethines with different moieties on both sides of CH=N group have been described [10-12]. Polyazomethines can be synthesized by solution polycondensation [13], chemical vapour deposition [14-16] and oxidative polymerizations [17].

Yet, polyazomethines are usually infusible polymers and have poor solubility problems, which would minimize their practical applications. Several modified polyazomethines, such as poly(azomethine-ester)s [18], poly(azomethine-ether)s [19], poly(azomethine-carbonate)s [20], poly(amide-azomethine-ester)s [21], poly(acrylate-azomethine)s [22], thermosetting polyazomethines [23] poly(azomethine-sulfone)s [24-27] were produced with the aim to enhance the solubility, to reduce the melting temperature and to promote specific properties such as mesomorphism [28]. Numerous approaches have been reported to enhance the solubility of polyazomethines. The insertion of flexible alkyl and alkoxy groups as the substituents has been evidenced to be effective, though at the expense of their thermal stability [29-31]. The insertion of bulky substituents such as tetraphenylethylene, triphenylamine and diphenyl fluorene has been investigated [32-34]. The co-polymerization of electron rich, solubility-enhancing aromatic or heterocyclic units such as carbazole, thiophene and fluorene [35-38] has also been discovered.

4.2 Synthetic methods for preparation of polyazomethines

Aromatic polyazomethines are usually synthesized by solution polymerization and melt polymerization technique.
4.2.1 Solution polymerization

Schiff [39] in 1884 first described the condensation of amines with carbonyl compounds. These condensation products are denoted as Schiff bases. The Schiff base formation is a reversible reaction; hence, it is desirable to remove by-product formed during polymerization reaction by distillation or by using an azeotrope-forming solvents [40-41]. This is essential with diacyl or aryl alkyl ketones. Aromatic aldehydes react efficiently under mild conditions and at relatively low temperatures in a proper solvent or without it. The mechanism of this reaction has been studied by Pratt [42]. According to him it is a two step mechanism, consisting of an initial addition of the amine to the carbonyl to produce a carbinolamine, followed by dehydration to give the C=N bond.

![Schiff Base Formation Diagram](image)

The intermediates of aldehydes and aniline reaction have been isolated in the absence of solvent or in aqueous emulsions [43, 44]. These substances were isolated either as free bases or as their salts and were characterized as carbinolamine on the basis of elemental analysis. They decomposed readily in moist air and form aldehyde and amine. The reaction mechanism of azomethine formation is studied in the literature [45].

Adams and coworkers [46] in 1923 established for the first time polyazomethine preparation from terephthaldehyde and benzidine. The product was insoluble and infusible. In the period from 1950-1959 Marvel and coworkers [47-50] synthesized number of polyazines and polyazomethines from aromatic aldehydes with hydrazine and o-phenylene diamine and examined their chelate formation properties and thermal stability. Polyazomethines reported in the earlier literature prior to the work of Suematsu et al [51] were usually low molecular weight polymers. Hence researchers have tried repeatedly to synthesize polymers with high molecular weight but generally have failed
Chapter-4 Polyazomethines

due to the insolubility or infusibility of the products. In some cases low to intermediate solution viscosities have been stated [52].

The reaction between aromatic diamine and dialdehyde is fast at room temperature. Polymerization can be initiated in solution or in water free solvents such as N-methyl 2-pyrrolidinone, N, N-dimethyl acetamide.

During the production of polyazomethines the choice of solvent is very vital criterion to attain high molecular weight polymers. The most commonly used solvents for preparation of polyazomethines are dimethyl acetamide, acetic acid, m-cresol, n-amyl alcohol, benzene, etc. Suematsu et al [51] have proven that m-cresol is the best solvent for the synthesis of polyazomethines. The reaction in m-cresol is as fast as the reaction between acid chloride and amine in benzene. In amide solvent addition of anhydrous lithium chloride or water absorbing agents increases the molecular weight.

4.2.2 Melt polymerization

From dialdehyde and diamine

In melt polymerization technique polyazomethines are synthesized by heating a dialdehyde and a diamine at elevated temperature (150-260°C) under inert atmosphere. The synthesis of polyazomethines is a reversible reaction; hence the removal of byproduct water formed during the melt polymerization is very necessary to get the high molecular weight polymer. At elevated temperature the reaction proceeds fast in molten state with progressively increase in melt viscosity.

4.2.3 By exchange reaction

The synthesis of polyazomethines can also be attained in melt process by exchange reactions. This is termed as “Schiff’s-base-exchange reaction”. There are four types of exchange reactions.

4.2.3.1 Carbonyl exchange polymerization.

\[
\begin{align*}
\text{RCO} + \text{RC}=\text{N}\text{=CR}=\text{RC} + \text{RC}=\text{N}=\text{CRC}_6\text{H}_5 \\
\end{align*}
\]

Here R’ represents Ar”, or in the case of the azines a single bond between the two nitrogen atoms
4.2.3.2 Amine exchange

\[ n \text{H}_2\text{N-} \text{R}'\text{-NH}_2 + n \text{C}_6\text{H}_5\text{N=HCAr'CH=N} \text{C}_6\text{H}_5 \rightarrow (2n-1) \text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{N=HCAr'}\text{CH=NAr'}\text{N=} \] \[ n=\text{H}_2 \]

4.2.2.3 Bis exchange

The bis-exchange polymerization includes the mutual replacement of aldehyde and amine functions in two distinct Schiff bases to produce two new Schiff bases.

\[ n \text{C}_6\text{H}_5\text{N=HCAr'CH=N} \text{C}_6\text{H}_5 + n\text{C}_6\text{H}_5\text{CH=}\text{NR'}\text{N=} \text{HCC}_6\text{H}_5 \rightarrow (2n-1) \text{C}_6\text{H}_5\text{CH=NC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{N=HAr'}\text{CH=NR'}\text{N=} \] \[ n=\text{C}_6\text{H}_5 \]

4.2.2.4 Acetal exchange

The acetal exchange polymerization is expressed as follows.

\[ n(\text{RO})_2\text{HCAr'CH(OR)}_2 + n\text{ArCH=}\text{NR'}=\text{HCAr} \rightarrow (2n-1) \text{ArCH(OR)}_2 + (\text{RO})_2[=\text{HCAr'}=\text{NR''N=} ]_n=\text{HCAr} \]

Out of these four exchange reactions, the bis-exchange polymerization reaction is found to be the most reasonable when performed in melt polymerization. Numerous polyazomethines have been synthesized by melt polymerization technique [52-56].

4.3 Structure-property relationship in polyazomethines

A main drawback of the linear azomethine polymers is their incomplete solubility in most organic solvents due to their rigid chain structure, this also being the key reason for their low molecular weight [57-60]. Because the growing macromolecular chain comes out of solution during the polycondensation at low polymerization degrees; hence, high molecular weight polymers cannot be obtained.

This difficulty is common for all organic conjugated polymers. There are some general techniques used to increase solubility of PAMs, such as:

a. Incorporation of flexible bonds between main chain aromatic rings [57, 61, 62].
b. Incorporation of pendant groups, i.e., aromatic or alkyl substituents, onto the polymer chain \([57-59, 63, 64]\).

Among the above mentioned approaches to increase solubility of PAMs, incorporation of alkyl groups or flexible spacers in the polymer backbone helps in significant decrease in \(T_g\) of the polymer, while on the other hand enhance solubility and processability via internal plasticization.

The representative examples of monomers to obtain organo-soluble PAMs are presented in Table 4.1.

**Table 4.1** List of the selected dialdehydes and diamines containing flexible chains used for synthesis of polyazomethines

<table>
<thead>
<tr>
<th>Dialdehyde/Diamine</th>
<th>Reference</th>
<th>Dialdehyde/Diamine</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="OC6H13CHO.png" alt="Image" /></td>
<td>28</td>
<td><img src="OCH2(CH2)8CH3.png" alt="Image" /></td>
<td>29</td>
</tr>
<tr>
<td><img src="OHCOC6H13.png" alt="Image" /></td>
<td>30</td>
<td><img src="OHCOC6H13.png" alt="Image" /></td>
<td>31</td>
</tr>
<tr>
<td><img src="OHCNO2.png" alt="Image" /></td>
<td>32</td>
<td><img src="OHC.png" alt="Image" /></td>
<td>33</td>
</tr>
<tr>
<td><img src="CH2(CH2)8CH3.png" alt="Image" /></td>
<td>111</td>
<td><img src="C8H17C8H17.png" alt="Image" /></td>
<td>111</td>
</tr>
<tr>
<td><img src="F3C.png" alt="Image" /></td>
<td>111</td>
<td><img src="NH2.png" alt="Image" /></td>
<td>111</td>
</tr>
</tbody>
</table>
Chapter 4 Polyazomethines

Chapter 4A: Synthesis and Characterization of Poly(ether-azomethines)s based on Dialdehyde Monomers

4A.1 Introduction

Poly(azomethine)s known as Schiff base polymers are isoelectronic to their carbon analogues as poly$(\rho$-phenylene vinylene)s, making them appropriate alternatives to conventional conjugated materials and are auspicious materials in photonic and optoelectronic applications [65-67]. Poly(azomethine)s have thermal stability, good mechanical strength, semiconducting properties, nonlinear optical properties and ability to form metal chelates [68-73]. The fascinating properties of poly(azomethine)s are due to the presence of conjugated backbone and imine sites [74]. The imine group (\(-\text{HC}=\text{N}-\)) with a lone pair of electrons in the backbone can produce intra or inter-molecular interactions such as hydrogen bonding with other groups and has the capability for protonation and complexation with metal ions, which has a great effect on their chemical and physical properties [75-80]. Numerous of these polymers form mesophases on heating but their high melting points and limited solubility due to their stiff rod-like chain structure make both their characterization and processing difficult. Numerous modifications of the chemical structure have been used in order to lower the transition temperature and to enhance the solubility of aromatic poly(azomethine)s. These approaches include: incorporation of structural irregularities such as kinks, bents or crank-shaft units [81-84], bulky pendent groups [84-96], flexibilising moieties [97-103], asymmetric substitution [104, 105], etc. An introduction of pendent alkyl chains along the polymer backbone is another approach to obtain soluble poly(azomethine)s [106-109]. The flexible side chains are supposed to act as a bound solvent for the rigid polymeric backbone [110].

In order to get processable poly(azomethine)s, a new dialdehyde \(\text{viz.}\), 1, 1-bis [4-(4-benzaldehyde oxy) phenyl] cyclopentane containing a pendent cyclopentylidene moiety was considered as a useful monomer.

The objective of the present work was to produce a series of poly(azomethine)s containing cardo cyclopentylidene moiety and ether linkages and to investigate the effect of the presence of cyclopentylidene moiety on the polymer properties such as solubility and thermal behavior. Thus, a series of poly(azomethine)s was prepared by high temperature solution polycondensation of 1, 1-bis[4-(4-benzaldehyde oxy) phenyl]
cyclopentane with several aromatic diamines, *viz.*, MDA, ODA, SDA, etc. The synthesized poly(azomethine)s were characterized by inherent viscosity measurements, solubility tests, FT-IR spectroscopy, X-ray diffraction studies, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC).

4A.2 Experimental

4A.2.1 Materials

All the solvents / chemicals were purified before use by following the standard procedures. 4,4’-oxydianiline; 4,4’-methylenedianiline and 4,4’-sulfonyl dianiline were purchased from Sigma Aldrich and used as received. The p-phenylene diamine was purified by recrystallisation in ethanol. The monomers 1, 3-bis(4-aminophenoxy) benzene and 1,1’-bis(4(4-aminophenoxy) phenyl) cyclopentane were purified by crystallization in ethanol. DMF, DMAc were purified as described in chapter 2A.2.1, cyclopentanone, 4-fluoronitrobenzene was purchased from Spectrochem and phenol purchased from S.D. fine chemicals and used as received.

4A.2.2 Synthesis of new diether-dialdehyde

4A.2.2.1 Synthesis of 1, 1-bis(4-hydroxy phenyl) cyclopentane

Bisphenol was synthesized as per the procedure reported in Chapter 2C.2.2.2

4A.2.2.2 Synthesis of 1, 1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane (BBPC)

In a 500 mL three neck round bottom flask equipped with a reflux condenser, a calcium chloride guard tube, a thermowell, a nitrogen gas inlet and a magnetic stirrer, were placed 12.7 g (0.05 mol) 1, 1-bis (4-hydroxy phenyl) cyclopentane and 12.412 g (0.1 mol) (10.54 mL) 4- fluoro benzaldehyde in 125 mL N, N-dimethyl formamide. To this solution added 13.821 g (0.1 mol) anhydrous K$_2$CO$_3$ under vigorous stirring. The resulting reaction mixture was kept at reflux temperature for 12 h; then cooled to room temperature and diluted with water to precipitate the product. The dialdehyde product was isolated by filtration, washed with water and dried. The crude product was purified by recrystallization from ethanol. The structure of novel dialdehyde was confirmed by FT-IR and $^1$H NMR.

Yield: 21.90 g (95 %)

M.P.:106°C.

IR (KBr): 2961(C-H stretch), 2834, 1686 (C=O), 1577, 1496, 1423, 1237, 1210, 1153, 1102, 1014, 878,867, 833, 820, 761 cm$^{-1}$. 

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4A.2.3 Synthesis of poly(ether-azomethine)s from 1, 1-bis[4-(4-benzaldehyde oxy) phenyl]cyclopentane

In a 100 mL three necked round bottom flask equipped with a reflux condenser, a magnetic stirrer, a calcium chloride guard tube and a nitrogen gas inlet were placed [0.001 mol; 0.200 g of 4,4'-oxydianiline (ODA)] in 3 mL N,N-dimethyl acetamide (DMAc) containing 5% lithium chloride (0.150 g). After the mixture became clear, 0.462 g (0.001 mol) 1, 1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane was added in flask and the resulting mixture was stirred overnight. Finally, the polymerization mixture was heated at 140°C for 4 h. The resulting viscous mass was added to a large excess of water. The fibrous polymer was isolated by filtration. The polymer was washed several times with hot water to remove any inorganic impurities and was dried under vacuum at 60°C overnight.

4A.3 Results and discussion

Aromatic polyazomethines (Schiff’s base polymers) or polyimines have been classified as highly conjugated materials which are usually insoluble and intractable. Insolubility of these polymers makes solution synthesis difficult.

Hence in the present work, soluble poly(ether-azomethine)s were produced from novel dialdehyde viz, 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane with various diamines in DMAc. The resulting polymers were characterized by FT-IR spectroscopy, inherent viscosity, solubility tests, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction studies.

4A.3.1 Synthesis of 1, 1-bis [4- (4-benzaldehyde oxy) phenyl] cyclopentane

The novel dialdehyde 1,1-bis [4-(4-benzaldehyde oxy) phenyl] cyclopentane (II) (BBPC) was synthesized by reacting cyclopentanone with phenol to yield 1, 1-bis (4-hydroxy phenyl) cyclopentane (I); followed by reaction with p- fluorobenzaldehyde in N, N-dimethyl formamide, containing anhydrous potassium carbonate (Scheme 4A.1). The structure of novel dialdehyde was confirmed by FT-IR and $^1$H NMR, $^{13}$C NMR and Mass spectroscopy.
The infrared spectrum of (BBPC) (Fig 4A.1) exhibited characteristic absorptions at 2961 cm\(^{-1}\) is due to (C-H stretching) vibrations of aliphatic cyclopentane C-H. Band at 1237 cm\(^{-1}\) is due to (C-O-C stretching). The absorption band at 1686 cm\(^{-1}\) is due to (C=O stretch) stretching vibration of aldehyde group.
Proton $^1$H NMR spectrum \(\text{(Fig 4A.2)}\) of (BBPC) showed singlet at 9.91 $\delta$ due to two formyl protons and multiplet in the range of 7.85 to 6.99 $\delta$ due to aromatic protons as expected with desired integration and splitting pattern. Peaks at 2.34 and 1.78 $\delta$ are due to methylene protons of cyclopentane moiety.

$^{13}$C NMR spectrum \(\text{(Fig 4A.4)}\) of (BBPC) showed twelve NMR signals corresponding twelve types of different carbons of which aldehyde carbon (-CHO) appeared at 190 $\delta$; whereas quaternary carbons showed signals at 163, 153, 145 and 55 $\delta$. The $>\text{CH}$ carbons appeared at 132, 131,128, 120, and 118 $\delta$, whereas CH$_2$ carbons gave NMR signals at 39, 22 $\delta$ confirming the formation of dialdehyde monomer (BBPC). The formyl carbon is obviously most down field as evidenced by DEPT-135 also. The DEPT-135 spectrum \(\text{(Fig 4A.4)}\) of (BBPC) also confirms the formation of dialdehyde monomer (BBPC), where in all the quaternary carbons are absent in the spectrum and the peaks of CH carbons are upper side and CH$_2$ appeared at down side.
Fig 4A.2 $^1$H NMR spectrum of 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane

Fig 4A.3 $^{13}$C NMR spectrum of 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane
The mass spectrum of novel dialdehyde (BBPC) (Fig 4A.5) showed molecular ion peak at m/e 463 (m+1) corresponding to molecular weight of (BBPC).
4A.3.2 Synthesis of poly(ether-azomethine)s from 1, 1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane

A series of poly(ether-azomethine)s were synthesized as outlined in Scheme 4A.2 by elevated temperature solution polymerization of BBPC with various diamines viz; MDA, ODA, SDA, etc. in DMAC containing LiCl. Lithium chloride was used to absorb water formed during the polycondensation. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in water. The inherent viscosities of all these polymers were determined in NMP and ranged from 0.19 to 0.42 dL/g. The data of these poly(ether-azomethine)s are presented in Table 4A.1.

Scheme 4A.2 Synthesis of poly(ether-azomethine)s HPAM -1 to HPAM- 6
Table 4A.1 Yield and viscosity of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomers</th>
<th>Yield</th>
<th>Inherent Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>New Dialdehyde</td>
<td>Diamine</td>
<td>%</td>
</tr>
<tr>
<td>HPAM-1</td>
<td>BBPC</td>
<td>ODA</td>
<td>98</td>
</tr>
<tr>
<td>HPAM-2</td>
<td>BBPC</td>
<td>MDA</td>
<td>99</td>
</tr>
<tr>
<td>HPAM-3</td>
<td>BBPC</td>
<td>p-PDA</td>
<td>99</td>
</tr>
<tr>
<td>HPAM-4</td>
<td>BBPC</td>
<td>SDA</td>
<td>92</td>
</tr>
<tr>
<td>HPAM-5</td>
<td>BBPC</td>
<td>BAPC</td>
<td>98</td>
</tr>
<tr>
<td>HPAM-6</td>
<td>BBPC</td>
<td>BAPB</td>
<td>99</td>
</tr>
</tbody>
</table>

\(^{a}\)Inherent viscosities were measured at a concentration of 0.5 % (W/V) in NMP and conc.\(\text{H}_{2}\text{SO}_{4}\) at 30°C.

Structural Characterization

The polymers were characterized by the infrared spectroscopy. The IR spectrum of poly (ether-azomethine) HPAM-1, **Fig 4A.6** showed the characteristic absorption at 1619 cm\(^{-1}\) (\(-\text{CH}=\text{N}-\) stretching). The sharp bands occurring at 1223 and 1157 cm\(^{-1}\) in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the (C-O-C) ether linkage. The presence of bands at 3060 and 2950 cm\(^{-1}\) can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at 829 cm\(^{-1}\) indicates para catenation of aromatic rings.

The IR spectrum of poly (ether-azomethine) HPAM-3, **Fig 4A.7** showed the characteristic absorption at 1621 cm\(^{-1}\) (CH = N stretching). The sharp bands occurring at 1239 and 1159 cm\(^{-1}\) in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The presence of bands at 3040 and 2950 cm\(^{-1}\) can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at 830 cm\(^{-1}\) indicates para catenation of aromatic rings.

The IR spectrum of poly (ether-azomethine) HPAM-4, **Fig 4A.8** showed the characteristic absorption at 1625 cm\(^{-1}\) (CH = N stretching). The sharp bands occurring at 1236 and 1145 cm\(^{-1}\) in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the (C-O-C) ether linkage. The presence of bands at 3027 and
2961 cm\(^{-1}\) can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at 828 cm\(^{-1}\) indicates para catenation of aromatic rings.

**Fig 4A.6** FT-IR spectrum of HPAM-1

**Fig 4A.7** FT-IR spectrum of HPAM-3
4.3.3 Properties of poly (ether-azomethine)s

Solubility properties

Solubility characteristics of poly (ether-azomethine)s are summarized in Table - 4A.2. It is observed that poly (ether-azomethine) (HPAM-4) synthesized from sulphone diamine (SDA) exhibited excellent solubility in common organic solvents and also in various polar aprotic solvents such as N-methylpyrrolidone (NMP), dimethyl sulphoxide (DMSO), N, N’-dimethylacetamide (DMAc), N, N’-dimethyl formamide (DMF). Polymer HPAM-1, HPAM-2, HPAM-4 and HPAM-6 are also showing excellent solubility in polar aprotic solvent NMP as well as organic solvents like THF, DCM and chloroform. Polymer HPAM-3 synthesized from p-phenylene diamine exhibit insolubility behavior due to its stiff structure attributed more close packing of polymer chains. Thus moderate solubility of these polymers, as expected; can be attributed to the introduction of carbo cyclopentylidene moiety and ether linkages in the polymer backbone.
Table 4A.2 Solubility Behavior of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer codes</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF</td>
</tr>
<tr>
<td>HPAM-1</td>
<td>+</td>
</tr>
<tr>
<td>HPAM-2</td>
<td>-</td>
</tr>
<tr>
<td>HPAM-3</td>
<td>-</td>
</tr>
<tr>
<td>HPAM-4</td>
<td>+</td>
</tr>
<tr>
<td>HPAM-5</td>
<td>±</td>
</tr>
<tr>
<td>HPAM-6</td>
<td>+</td>
</tr>
</tbody>
</table>

+: Soluble; -, Insoluble; ±: partly soluble

Thermal properties

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. Table 4A.1 incorporate the thermal data such as glass transition temperature ($T_g$), initial decomposition temperature ($T_i$), 10% mass decomposition temperature ($T_d$), and residual weight at 900°C.

Table 4A.1 Physical properties of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thermal Behaviour b</th>
<th>Residual Wt % at 900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$ °C in N₂</td>
<td>$T_d$ °C in N₂</td>
</tr>
<tr>
<td>HPAM-1</td>
<td>405</td>
<td>493</td>
</tr>
<tr>
<td>HPAM-2</td>
<td>405</td>
<td>441</td>
</tr>
<tr>
<td>HPAM-3</td>
<td>415</td>
<td>467</td>
</tr>
<tr>
<td>HPAM-4</td>
<td>405</td>
<td>445</td>
</tr>
<tr>
<td>HPAM-5</td>
<td>410</td>
<td>464</td>
</tr>
<tr>
<td>HPAM-6</td>
<td>405</td>
<td>469</td>
</tr>
</tbody>
</table>

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

$T_i$ – Initial decomposition temperature.

$T_g$: Glass transition temperature determined at second heating by DSC at a heating rate of 10 °C/min

$T_d$ – Temperature of 10% decomposition
The thermal stability of the poly (ether–azomethine)s outlined in Fig 4A.9 was studied at a heating rate of 10°C/min in nitrogen atmosphere by thermogravimetric analysis.

The \( T_d \) temperature at which 10% weight loss occurred, and char yields at 900°C were determined from thermograms. \( T_d \) values were in the range of 441°C to 493°C. The initial decomposition temperature \( (T_i) \) is in the range 405°C to 415°C. In general, these polymers, like other poly-Schiff bases, exhibited good thermal stability in nitrogen; 10% weight loss only takes place when they are heated beyond 441°C in nitrogen. The char yields remained at 900°C are in the range 28% to 40%.

**Fig 4A.9** TGA curve of poly(ether-azomethine)s HPAM-1 to HPAM-6

All these polymers showed a \( T_g \) indicative of an amorphous or glassy morphology. The glassy morphology of these polymers is due to the presence of cardo groups in the polymer backbone, which inhibited the crystalline packing. All the polymers show \( T_g \) in between 164-192°C. The \( T_g \) of polymer HPAM-3 was not detected by DSC; it is attributed to presence of rigid structure of p-phenylene diamine.
The DSC curves (Fig 4A.10) represent the $T_g$ values of poly(ether-azomethine)s.

Fig 4A.10  DSC curves of Poly(ether-azomethine)s HPAM-1 to HPAM-6

Fig 4A.11  XRD curves of Poly(ether-azomethine)s HPAM-1 to HPAM-6
Poly(ether-azomethine)s were also characterized by the wide angle X-ray diffractometer. The x-ray diffraction pattern of all poly (ether-azomethine)s is shown in Fig 4A.11. It is observed that, the polymer (HPAM-4) is highly amorphous in nature. This may be attributed to the introduction of cardo cyclopentylidene moiety and diamine SDA which may have disrupted the chain regularity and packing leading to amorphous nature. On the contrary, HPAM-3 and HPAM-5 polymers exhibited more semicrystalline nature, this may be due to the close packing of the chains leading to crystalline nature.
Chapter-4 Polyazomethines

4A.4 Summary and Conclusions

1. A series of new poly(ether-azomethine)s containing ether linkage and cardo cyclopentylidene moiety was synthesized by elevated temperature solution polycondensation of 1, 1-bis [4- (4-benzaldehyde oxy) phenyl] cyclopentane and commercial aromatic diamines.

2. Inherent viscosities of polyazomethines were in the range 0.19-0.42 dL/g indicating formation of medium to reasonably moderate molecular weight polymers.

3. Some of Polyazomethines were found to be soluble in DMF, NMP, DMAc, THF and CHCl₃ at room temperature or upon heating. This indicates that the incorporation of cardo cyclopentylidene moiety leads to a significant improvement in solubility of polyazomethines.

4. Wide angle X-ray diffraction patterns indicated that polyazomethines containing ether linkage and cardo cyclopentylidene were amorphous in nature. Some of polyazomethines found crystalline also.

5. \(T_d\) values for polyazomethines were in the range 441°C-493°C indicating good thermal stability of polyazomethines.

6. \(T_g\) values of polyazomethines were in the range 164-192°C. The depression in \(T_g\) values of polyazomethines could be attributed to the presence of ether linkages and cardo cyclopentylidene moiety.

7. A large difference in \(T_g\) and decomposition temperature of polyamides offers a broad processing window.
Chapter 4B: Synthesis and characterization of Poly(ether-azomethine)s based on Methyl Substituted Dialdehyde Monomers

4B.1 Introduction

Aromatic polyazomethines, containing C=N linkage show good mechanical properties, excellent thermal stability and in some cases, liquid crystalline morphology [114]. In addition, acts as high performance fiber and have metal-chelating ability [115,116], they have been also studied for the opto-electrical applications such as hole transport layer for OLED, non-linear optics (NLO), semiconductor, photovoltaic cell [117-120]. But major drawback of polyazomethines is their incomplete solubility in most common organic solvents [121-125]. High molecular weight polymers are problematic to gain because; the growing macromolecular chains precipitate out of the solution during polycondensation. Furthermore, their high melting temperature and insolubility makes them intractable for processing by conventional techniques. Exertions devoted towards obtaining soluble and fusible polyazomethines include: incorporation of flexible spacer between main chain aromatic rings; insertion of pendant groups i.e. aromatic or alkyl substituents, introduction of methyl group into the polymer chain, insertion of structural irregularities such as kinks, bents, crankshaft-shaped units, etc.[126-142]. It is usually recognized that presence of an alkyl group and ether linkage in polymer backbone imparts segmental mobility to the polymer, improves the solubility and lowers the glass transition temperature.

Here in reported the synthesis of new series of methyl substituted poly(ether-azomethine)s from newly synthesized methyl substituted dialdehyde and from different commercial diamines

4B.2 Experimental

4B.2.1 Materials

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

1. 3-mercapto propanoic acid, 4, 4’-oxydianiline; 4, 4’-methylenedianiline and 4, 4’-sulfonyl dianiline were purchased from Sigma Aldrich and used as received.
2. The p-phenylene diamine was purified by recrystallisation in ethanol.
3. The monomers 1, 3-bis(4-aminophenoxy) benzene and 1, 1’- bis(4-aminophenoxy) phenyl) cyclopentane were prepared in the laboratory by reported procedure.

4. DMF was purified as described in chapter 2A.2.1.

5. Cyclopentanone, 4-fluoronitrobenzene was purchased from Spectrochem and O-cresol purchased from s. d. fine chemicals and used as received.

4B.2.2 Synthesis of new methyl substituted diether-dialdehyde

4B.2.2.1 Synthesis of 1, 1-bis (4-hydroxy 3-methyl phenyl) cyclopentane

Bisphenol synthesized as per procedure reported in Chapter No. 2A.2.2.1

4B.2.2.2 Synthesis of 1, 1-bis[4-(4-benzaldehydeoxy)-3-methyl phenyl]cyclopentane (BBMPC)

In a 500 mL three neck round bottom flask equipped with reflux condenser, calcium chloride guard tube, thermowell, N₂ gas inlet and magnetic stirrer, were placed 14.10 g (0.05 mol) 1, 1-bis (4-hydroxy 3-methyl phenyl) cyclopentane and 12.412 g (0.1 mol) (10.54 mL) 4-fluoro benzaldehyde in 125 mL N, N-dimethyl formamide. To this solution added 13.821 g (0.1 mol) anhydrous K₂CO₃ with stirring. The resulting mixture was refluxed for 10 h; then cooled to room temperature and diluted with water to precipitate the product from solution. The product was isolated by filtration, washed with water, dried and purified by recrystallisation from ethanol. The structure of novel dialdehyde was confirmed by FT-IR, ¹H NMR, ¹³C NMR and Mass spectroscopy.

Yield: 23.76 g (97 %)

M.P.: 220°C.

IR: 2960 (C-H stretch), 1686 (C=O stretch), 1595, 1492, 1254, 1179, 827 cm⁻¹.

¹H NMR (CDCl₃, d, ppm): 9.92 (s, 2H, CHO), 7.85 (d, J = 9.4 Hz, 4H), 7.28(d, J = 9.4 Hz, 4H), 7.19-6.91 (6H), 2.40 (m, 4H), 2.20 (s, 6H, -CH₃), 1.80 (m).

¹³C NMR (CDCl₃, d, ppm): 190.68 (C=O), 163.44, 150.54, 145.92, 131.99, 130.88, 129.81, 120.51, 116.46, 55.65, 38.93, 22.99, 16.36.

4B.2.3 Synthesis of poly(ether-azomethine)s from 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane

In a 100 mL three necked round bottom flask equipped with a reflux condenser, a magnetic stirrer, a calcium chloride guard tube and a nitrogen gas inlet were placed [0.001 mol; 0.200 g of 4,4’-oxydianiline (ODA)] in 3 mL N,N-dimethyl acetamide
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(DMAc) containing 5% lithium chloride (0.150 g). After the mixture became clear, 0.490 g (0.001 mol) 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane was added in flask and the resulting mixture was stirred overnight. Finally, the polymerization mixture was heated at 140°C for 4 h. The resulting viscous mass was added to a large excess of water. The fibrous polymer was isolated by filtration. The polymer (HPAM-7) was washed several times with hot water to remove any inorganic impurities and was dried under vacuum at 60°C overnight. The yield was 99% and the inherent viscosity of polymer in NMP was 0.32 dL/g.

The polyazomethines HPAM-8 to HPAM-13 were synthesized with varying diamines by similar procedure.

**IR Spectrum**

**HPAM 7**: 3010, 2962, 1624, 1599, 1497, 1224, 1157, 830 cm⁻¹.

**HPAM 9**: 3015, 2911, 1623, 1586, 1492, 1230, 1156, 852 cm⁻¹.

**HPAM 11**: 3039, 2952, 1624, 1599, 1492, 1224, 1157, 828 cm⁻¹.

**4B.3 Results and discussion**

A new dialdehyde monomer with ether linkage, cyclopentylidene cardo moiety and pendant methyl group viz, 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane was utilized. To study the effect of ether linkage, cyclopentylidene cardo moiety and pendant methyl substitution on solubility behavior; a series of polyazomethines was synthesized by high temperature solution polycondensation of 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane with commercially available aromatic diamines. These poly(azomethine)s were characterized by IR spectroscopy, inherent viscosity, solubility, thermal analysis and XRD study.

**4B.3.1 Synthesis of 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane**

The novel methyl substituted dialdehyde 1, 1-bis [4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane (BBMPC) was synthesized as outlined in Scheme 4B.1 by reacting cyclopentanone with o-cresol to yield 1, 1-bis (4-hydroxy 3-methyl phenyl) cyclopentane (I); followed by reaction with p-fluorobenzaldehyde in N, N-dimethyl formamide, containing anhydrous potassium carbonate. The structure of novel dialdehyde was confirmed by FT-IR and \(^1\)H NMR, \(^{13}\)C NMR and Mass spectroscopy.
**Scheme 4B.1** Synthesis of 1, 1-bis [4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane

The infrared spectrum of (BBMPC) (Fig 4B.1) exhibited characteristic absorptions at 2960 cm\(^{-1}\) is due to (C-H stretching) vibrations of aliphatic cyclopentane C-H. Band at 1254 and 1179 cm\(^{-1}\) is due to (C-O-C stretching). The absorption band at 1688 cm\(^{-1}\) is due to (C=O stretch) stretching vibration of aldehyde group. The absorption band at 827 cm\(^{-1}\) is due to para catenation of aldehyde group.
Proton $^1$H NMR spectrum (Fig 4B.2) of (II) (BBMPC) showed singlet at 9.92 $\delta$ due to two formyl protons (-CHO) and multiplet in the range of 7.85 to 6.91 $\delta$ due to aromatic protons as expected with desired integration and splitting pattern. Peaks at 2.40 and 1.80 $\delta$ are due to methylene protons of cyclopentane moiety. The peak at 2.20 $\delta$ for six protons is due to methyl group present as pendant substitution on aromatic ring.

$^{13}$C NMR spectrum (Fig 4B.3) of (BBPC) showed fifteen NMR signals corresponding to fourteen types of different carbons of which aldehyde carbon (-CHO) appeared at 190.68 $\delta$; whereas quaternary carbons showed signals at 163.44, 150.54, 145.92 and 55.65 $\delta$. The CH carbons appeared at 131.99, 130.88, 129.81, 126.08, 120.51 and 116.46 $\delta$, whereas CH$_2$ carbons gave NMR signals at 38.93, 22.99 $\delta$ and 16.36 $\delta$ for methyl group confirming the formation of methyl substituted dialdehyde monomer (BBMPC). The formyl carbon is obviously most down field as evidenced by DEPT-135 also.
Fig 4B.2 $^1$H NMR spectrum of 1, 1-bis [4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane

Fig 4B.3 $^{13}$C NMR spectrum of 1, 1-bis [4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane
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The DEPT-135 spectrum (Fig 4B.4) of (BBMPC) also confirms the formation of dialdehyde monomer (BBPC), where in all the quaternary carbons are absent in the spectrum and the peaks of CH carbons and primary methyl carbons are upper side and CH$_2$ appeared at down side.

![DEPT-135 spectrum of 1, 1-bis [4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane](image1)

The mass spectrum of novel dialdehyde (BBMPC) (Fig 4B.5) showed molecular ion peak at m/e 491.20 (m+1) corresponding to molecular weight of (BBMPC).

![Mass spectrum of 1, 1-bis [4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane](image2)
4B.3.2 Synthesis of poly(ether-azomethine)s from 1, 1-bis [4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane

A series of methyl substituted poly(ether-azomethine)s were synthesized as outlined in Scheme 4B.2 by elevated temperature solution polymerization of BBMPC with various diamines viz; MDA, ODA, SDA, BAPC, etc. in DMAc containing LiCl. Lithium chloride was used to absorb water formed during the polycondensation. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in water. The inherent viscosities of all these polymers were determined in NMP and ranged from 0.20 to 0.38 dL/g. The data of these poly (ether – azomethine)s are presented in Table 4B.1.

Scheme 4B.2 Synthesis of Poly(ether-azomethine)s from 1, 1-bis [4- (4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane (HPAM-7 to HPAM-12)
Table 4B.1 Yield and Viscosity of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Monomers</th>
<th>Yield %</th>
<th>Inherent Viscosity dL/g a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Novel Dialdehyde</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPAM-7</td>
<td>BBMPC</td>
<td>ODA</td>
<td>99</td>
</tr>
<tr>
<td>HPAM-8</td>
<td>BBMPC</td>
<td>MDA</td>
<td>99</td>
</tr>
<tr>
<td>HPAM-9</td>
<td>BBMPC</td>
<td>p-PDA</td>
<td>100</td>
</tr>
<tr>
<td>HPAM-10</td>
<td>BBMPC</td>
<td>SDA</td>
<td>99</td>
</tr>
<tr>
<td>HPAM-11</td>
<td>BBMPC</td>
<td>BAPC</td>
<td>99</td>
</tr>
<tr>
<td>HPAM-12</td>
<td>BBMPC</td>
<td>BAPB</td>
<td>99</td>
</tr>
</tbody>
</table>

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

Structural Characterization

The polymers were characterized by the infrared spectroscopy. The IR spectrum of poly (ether-azomethine) HPAM-7, Fig. 4B.6 showed the characteristic absorption at 1624 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1224 and 1157 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the (C-O-C) ether linkage. The presence of bands at 3010 and 2962 cm⁻¹ can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at 830 cm⁻¹ indicates para catenation of aromatic rings.

The IR spectrum of poly (ether-azomethine) HPAM-9, Fig.4B.7 showed the characteristic absorption at 1623 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1230 and 1156 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the (C-O-C) ether linkage. The presence of bands at 3015 and 2911 cm⁻¹ can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at 832 cm⁻¹ indicates para catenation of aromatic rings.

The IR spectrum of poly(ether-azomethine) HPAM-11, Fig 4B.8 showed the characteristic absorption at 1624 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1224 and 1157 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The presence of bands at 3039 and
2952 cm\(^{-1}\) can be assigned to aromatic and aliphatic (C-H stretching) vibrations. The vibration at 828 cm\(^{-1}\) indicates para catenation of aromatic rings.

**Fig 4B.6** FT-IR spectrum of HPAM-7

**Fig 4B.7** FT-IR spectrum of HPAM-9
4B.3.3 Properties of poly(ether-azomethine)s

Solubility properties

Solubility characteristics of methyl substituted poly(ether-azomethine)s are summarized in Table 4B.2. It is observed that poly(ether-azomethine) (HPAM-10) synthesized from sulphone diamine (SDA) exhibited excellent solubility in common organic solvents and also in various polar aprotic solvents such as N-methylpyrrolidone (NMP), N, N-dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethyl formamide (DMF). All these Polyazomethines (HPAM-7 to HPAM-12) are also showing excellent solubility in polar aprotic solvent NMP and DMF. Polymer HPAM-9 synthesized from p-phenylene diamine exhibit less solubility due to its rigid structure ascribed more close packing of polymer chains. Thus good improvement in solubility of these polymers, as expected; can be due to the introduction of cardo cyclopentylidene moiety, pendant methyl substitution and ether linkages in the polymer backbone.
Table 4B.2 Solubility Behavior of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF</td>
</tr>
<tr>
<td>HPAM-7</td>
<td>+</td>
</tr>
<tr>
<td>HPAM-8</td>
<td>+</td>
</tr>
<tr>
<td>HPAM-9</td>
<td>+</td>
</tr>
<tr>
<td>HPAM-10</td>
<td>+</td>
</tr>
<tr>
<td>HPAM-11</td>
<td>±</td>
</tr>
<tr>
<td>HPAM-12</td>
<td>+</td>
</tr>
</tbody>
</table>

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

Thermal properties

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. Table 4B.3 incorporate the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), 10 % decomposition temperature (T_d) and residual weight at 900°C.

Table 4B.3. Physical properties of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Thermal behaviour b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_i °C in N₂</td>
</tr>
<tr>
<td>HPAM-7</td>
<td>296</td>
</tr>
<tr>
<td>HPAM-8</td>
<td>323</td>
</tr>
<tr>
<td>HPAM-9</td>
<td>360</td>
</tr>
<tr>
<td>HPAM-10</td>
<td>316</td>
</tr>
<tr>
<td>HPAM-11</td>
<td>320</td>
</tr>
<tr>
<td>HPAM-12</td>
<td>303</td>
</tr>
</tbody>
</table>

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

T_g: Glass transition temperature determined at second heating by DSC at a heating rate of 10 °C/min
T_i – Temperature of 10% decomposition
T_d – Initial decomposition temperature.
n.d* - T_g not detected by DSC.
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The thermal stability of the methyl substituted poly(ether-azomethine)s outlined in Fig 4B.9 was studied at a heating rate of 10°C/min in nitrogen atmosphere by thermogravimetric analysis. The \( T_d \) temperature at which 10 % weight loss occurred, and char yields at 900°C were determined from thermograms. \( T_d \) values were in the range of 444°C to 501°C. In general, these polymers, like other poly-Schiff bases, exhibited good thermal stability in nitrogen; 10% weight loss only takes place when they are heated beyond 444°C in nitrogen. The initial decomposition temperatures \( (T_i) \) are in the range 296°C to 360°C. The char yields remained at 900°C are in the range 31% to 50%.

![TGA curve of Poly(ether-azomethine)s HPAM-7 to HPAM-12](image)

**Fig 4B.9** TGA curve of Poly(ether-azomethine)s HPAM-7 to HPAM-12

The DSC curves (Fig 4B.10) represent the \( T_g \) values of methyl substituted poly(ether-azomethine)s. All these polyazomethines exhibit a \( T_g \) indicative of an amorphous or glassy morphology. The glassy morphology of these polyazomethines is due to the presence of cardo groups and pendant methyl substitution in the polymer backbone, which inhibited the crystalline packing. All the polyazomethines show \( T_g \) in between 155-204°C. The \( T_g \)
of polymer HPAM-9 was not detected by DSC, it is attributed to presence of rigid structure of p-phenylene diamine.

The methyl substituted Poly(ether-azomethine)s were also characterized by the wide angle X-ray diffractometer. The X-ray diffraction pattern of all poly(ether-azomethine)s is shown in Fig 4B.11. It is observed that, the polymer (HPAM-12) is highly amorphous in nature. This may be attributed to the introduction of cardo cyclopentylidene moiety of novel dialdehyde monomer and meta catenation of amine BAPB which may have disrupted the chain regularity and packing, leading amorphous nature. On the contrary, HPAM-10 polymer exhibited semicrystalline nature; this may be due to presence of p-phenylene diamine leading to the close packing of the chains. X-Ray diffractograms of all polymers exhibited a broad halo in the wide angle region (at about 20 ≈ 20°) indicating that all the polymers were amorphous in nature, it can be attributed to presence of pendant methyl substitution, cardo cyclopentylidene moiety and ether linkage in the polymer backbone.
Fig 4B.11 XRD curves of Poly(ether-azomethine)s HPAM-7 to HPAM-12
4B.4 Summary and Conclusions

1. A series of new poly(ether-azomethine)s containing ether linkage, pendant methyl substitution and cardo cyclopentylidene moiety was synthesized by elevated temperature solution polycondensation of 1, 1-bis[4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane and commercial aromatic diamines.

2. Inherent viscosities of polyazomethines were in the range 0.20-0.38 dL/g indicating formation of medium to reasonably moderate molecular weight polymers.

3. Some of Polyazomethines were found to be soluble in DMF, NMP, DMAc, and DMSO at room temperature or upon heating. This indicates that the incorporation of cardo cyclopentylidene moiety, pendant methyl substitution and ether linkage leads to a significant improvement in solubility of polyazomethines.

4. Wide angle X-ray diffraction patterns indicated that polyazomethines containing ether linkages, methyl substitution and cardo cyclopentylidene moiety were amorphous in nature except HPAM-9 is semicrystalline in nature.

5. $T_d$ values for polyazomethines were in the range 444°C-501°C indicating good thermal stability of polyazomethines.

6. $T_g$ values of polyazomethines were in the range 155-204°C. The depression in $T_g$ values of polyazomethines could be attributed to the presence of ether linkages, pendant methyl substitution and cardo cyclopentylidene moiety.

7. A large difference in $T_g$ and decomposition temperature of polyamides offers a broad processing window.
Chapter 4C: Synthesis and characterization of Co-poly(etherazomethine)s based on Methyl Substituted Diamine Monomers

4C.1 Introduction

Polyazomethines with a wide range of applications have had frequent increasing interest due to having a lot of valuable properties such as excellent mechanical strength and high thermal stability as well as their optoelectronic properties and semiconductivity [143-145]. Yet, these applications have been limited by their poor solubility in common organic solvents and low molecular weights. Moreover, the relatively rare availability of new dialdehyde monomers also hindered the chemical structure modifications of polyazomethines. Several approaches have been reported to enhance the solubility of polyazomethines. The insertion of flexible alkyl and alkoxy groups as the substituents has been proved to be operative, although at the expense of their thermal stability [146-148]. The integrations of bulky substituents such as tetraphenylethylene, triphenylamine and diphenylfluorene have been investigated [149-151]. The co-polymerization as well as electron rich, solubility-enhancing aromatic or heterocyclic unit such as carbazole, thiophene and fluorene [152-155] has also been discovered.

The chemical alterations of polyazomethines are mainly attained by synthesizing new diamine and then polymerizing them with commercially available dialdehydes TPA and/or IPA. These efforts targeting at either solubility improvement or investigating their thermal stability. Hence here in reported the synthesis of new series of poly(etherazomethine)s from newly synthesized methyl substituted diamines and from commercial IPA/TPA

4C.2 Experimental Methods

4C.2.1 Materials

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

1. 3-mercapto propanoic acid, 10% Pd/C, terephthaldehyde & isophthaldehyde were purchased from Sigma Aldrich and used as received.
2. The p-phenylene diamine was purified by recrystallisation in ethanol.
3. Potassium carbonate (K₂CO₃) was dried under vacuum at 150°C for 6 h.
4. DMF, DMAc were purified as described in chapter 2A.2.1.
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5. Cyclopentanone, 4-fluoronitrobenzene were purchased from Spectrochem and O-cresol, hydrazine hydrate purchased from S.D. fine chemicals and used as received.

4C.2.2 Synthesis of new methyl substituted diether-diamine

4C.2.2.1 Synthesis of 1, 1-bis(4-hydroxy 3-methyl phenyl) cyclopentane

Bisphenol synthesized as per procedure reported in Chapter No. 2A.2.2.1

4C.2.2.2 Synthesis of 1, 1-bis[4-(4-nitro phenoxy)-3-methyl phenyl] cyclopentane

Diether-dinitro synthesized as per procedure reported in Chapter No. 2A.2.2.2

4C.2.2.3 Synthesis of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

Diether-diamine synthesized as per procedure reported in Chapter No. 2A.2.2.3

4C.2.3 Synthesis of poly (ether-azomethine)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 reflux condenser, a magnetic stirrer, a calcium chloride guard tube and a nitrogen gas inlet were placed [0.001 mol; 0.464 g of 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC)] in 3 mL N, N-dimethyl acetamide (DMAc) containing 5% lithium chloride (0.150 g). After the mixture became clear, 0.134 g (0.001 mol) terephthalaldehyde (TPA) was added in flask and the resulting mixture was stirred overnight. Finally, the polymerization mixture was heated at 140°C for 4 h. The resulting viscous mass was added to a large excess of water. The fibrous polymer was isolated by filtration. The polymer (SPAM-1) was washed several times with hot water to remove any inorganic impurities and was dried under vacuum at 60°C overnight. The yield was 99% and the inherent viscosity of polymer in NMP was 0.39 dL/g.

The polyazomethines and co-polyazomethines SPAM-2 to SPAM-5 were synthesized with varying mol proportion of TPA and IPA by similar procedure.

4C.3 Results and discussion

In order to obtain processable polyazomethines, a new diamine monomer with ether linkage, cardo moiety and pendant methyl group viz, 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane was utilized. To study the effect of ether linkage, cyclopentylidene cardo moiety and methyl substitution on solubility behavior, a series of copolyazomethines was synthesized by high temperature solution polycondensation of 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane with commercially available aromatic dialdehydes such as terephthaldehyde, isophthaldehyde and a mixture of...
Homo and Co-polyazomethines were characterized by inherent viscosity measurements, solubility tests, FTIR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

4C.3.1 Synthesis of 1, 1-bis[4-(4-aminophenoxy)-3-methyl phenyl] cyclopentane

Scheme 4C.1 as reported in Chapter-2A outlines the route for the synthesis of diamines containing preformed ether linkages. The novel bis(ether-amine) viz, 1, 1-bis[4-(4-aminophenoxy)-3-methyl phenyl]cyclopentane (BAMPC) was synthesized starting from cyclopentanone in several steps.
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1, 1-bis (4-hydroxy-3-methyl phenyl) cyclopentane (I) was obtained as described in chapter 2A. The 1, 1-bis [4- (4-nitro phenoxy)-3-methyl phenyl] cyclopentane (II) was prepared by condensation of 1, 1-bis (4-hydroxy-3-methyl phenyl) cyclopentane (I) with 4- Chloronitrobenzene. The structure of (II) was confirmed by IR and NMR spectra and discussed in chapter 2A.

1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC) (III) was prepared by catalytic hydrogenation of the bis(ether-nitro) compound (II) by using hydrogen Pd/C catalyzed reduction. The structure of new bis(ether-amine) (III) was confirmed by IR, NMR and mass spectra discussed in chapter 2A.

4C.3.2 Synthesis of poly(ether-azomethine)s from 1, 1-bis[4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

A series of methyl substituted homo and co-poly(ether-azomethine)s were synthesized as outlined in Scheme 4C.2 by elevated temperature solution polymerization of BAMPC with dialdehydes TPA and/or IPA in DMAc containing LiCl. Lithium chloride was used to absorb water formed during the polycondensation. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in water. The inherent viscosities of all these polymers were determined in NMP and ranged from 0.20 to 0.38 dL/g. The data of these poly (ether-azomethine)s are presented in Table 4B.1.
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![Diagram of poly(ether-azomethine) structure]

**Scheme 4C.2** Synthesis of poly(ether-azomethine)s (SPAM-1 to SPAM-5)

**Table 4C.1** Yield and Viscosity of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Monomers</th>
<th>Yield %</th>
<th>Inherent Viscosity dL/g a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diamine</td>
<td>TPA</td>
<td>IPA</td>
</tr>
<tr>
<td></td>
<td>BAMPC Mol%</td>
<td>Mol%</td>
<td>Mol%</td>
</tr>
<tr>
<td>SPAM-1</td>
<td>100</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>SPAM-2</td>
<td>100</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>SPAM-3</td>
<td>100</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>SPAM-4</td>
<td>100</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>SPAM-5</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

aInherent viscosity was measured at a concentration of 0.5 % (W/V) in NMP at 30°C
Structural Characterization

The polymers were characterized by the infrared spectroscopy. The IR spectrum of poly (ether-azomethine) SPAM-1, Fig 4C.1 showed the characteristic absorption at 1624 cm\(^{-1}\) (CH = N stretching). The sharp bands occurring at 1229 and 1121 cm\(^{-1}\) in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The presence of bands at 2970 and 2865 cm\(^{-1}\) can be assigned to asymmetric and symmetric aliphatic (C-H stretching) vibrations. The vibration at 827 cm\(^{-1}\) indicates para catenation of aromatic rings.

The IR spectrum of poly (ether-azomethine) SPAM-3, Fig 4C.2 showed the characteristic absorption at 1623 cm\(^{-1}\) (CH = N stretching). The sharp bands occurring at 1229 and 1156 cm\(^{-1}\) in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The presence of bands at 2969 and 2846 cm\(^{-1}\) can be assigned to asymmetric and symmetric aliphatic (C-H stretching) vibrations. The vibration at 832 cm\(^{-1}\) indicates para catenation of aromatic rings.

The IR spectrum of poly (ether-azomethine) SPAM-5, Fig 4C.3 showed the characteristic absorption at 1621 cm\(^{-1}\) (CH = N stretching). The sharp bands occurring at 1234 and 1122 cm\(^{-1}\) in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The presence of bands at 2970 and 2872 cm\(^{-1}\) can be assigned to asymmetric and symmetric aliphatic (C-H stretching) vibrations. The vibration at 835 cm\(^{-1}\) indicates para catenation of aromatic rings.

![Fig 4C.1 FT-IR spectrum of SPAM-1](image-url)
Fig 4C.2 FT-IR spectrum of SPAM-3

Fig 4C.3 FT-IR spectrum of SPAM-5
4C.3.3. Properties of Co-poly(ether-azomethine)s

Solubility properties

Solubility characteristics of methyl substituted poly(ether-azomethine)s are summarized in Table 4C.2. It is observed that the entire poly (ether-azomethine) SPAM-1 to SPAM-5 exhibited solubility in organic solvent N-methylpyrrolidone (NMP) and also shows partial solubility in solvents such as THF and DCM. All these Polyazomethines (SPAM-1 to SPAM-5) are insoluble in solvents such as DMF, DMAc and DMSO. Polymer SPAM-1 synthesized from terephthaldehyde (TPA) exhibit less solubility due to its stiff structure attributed more close packing of polymer chains. But polyazomethine SPAM-4 shows better solubility in solvents DMF, DMAc, NMP and DMSO, thus good improvement in solubility of these polymer, as expected; can be attributed to the copolymerization of novel diamine with TPA and IPA, introduction of cardio cyclopentylidene moiety, pendant methyl substitution and ether linkages in the polymer backbone.

Table 4C.2. Solubility behavior of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF</td>
</tr>
<tr>
<td>SPAM-1</td>
<td>-</td>
</tr>
<tr>
<td>SPAM-2</td>
<td>±</td>
</tr>
<tr>
<td>SPAM-3</td>
<td>±</td>
</tr>
<tr>
<td>SPAM-4</td>
<td>+</td>
</tr>
<tr>
<td>SPAM-5</td>
<td>±</td>
</tr>
</tbody>
</table>

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

Thermal properties

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. Table 4C.3 incorporate the thermal data such as glass transition temperature \(T_g\), initial decomposition temperature \(T_i\), 10% decomposition temperature \(T_d\) and residual weight at 900°C.
Table 4C.3. Physical properties of Poly(ether-azomethine)s

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Thermal behaviour</th>
<th>Residual Wt % at 900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$ °C</td>
<td>$T_d$ °C</td>
</tr>
<tr>
<td>SPAM-1</td>
<td>416</td>
<td>486</td>
</tr>
<tr>
<td>SPAM-2</td>
<td>414</td>
<td>474</td>
</tr>
<tr>
<td>SPAM-3</td>
<td>410</td>
<td>456</td>
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<tr>
<td>SPAM-4</td>
<td>414</td>
<td>484</td>
</tr>
<tr>
<td>SPAM-5</td>
<td>409</td>
<td>470</td>
</tr>
</tbody>
</table>

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

$T_g$ - 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 methyl substituted poly(ether-azomethine)s outlined in Fig 4C.4 was studied at a heating rate of 10°C/min in nitrogen atmosphere by thermogravimetric analysis. $T_d$ values were in the range of 456°C to 486°C. In general, these polymers, like other poly-Schiff bases, exhibited good thermal stability in nitrogen; 10% weight loss only takes place when they are heated beyond 456°C in nitrogen. The initial decomposition temperature ($T_i$) were in the range of 409°C to 416°C. The residual weight at 900°C were in the range of 16%-19%.

The DSC curves (Fig. 4C.5) represent the $T_g$ values of methyl substituted poly(ether-azomethine)s.

All these polyazomethines exhibits a $T_g$ indicative of an amorphous or glassy morphology. The glassy morphology of these polyazomethines is due to the presence of cardo groups and pendant methyl substitution in the polymer backbone as well as copolymerization, which inhibited the crystalline packing. All the polymers show $T_g$ in between 165-178°C. The higher $T_g$ of SPAM-5 compared to the $T_g$ of other polymers is due to the usage of terephthaldehyde (TPA) which exhibits rigid structure attributed more close packing of polymer chians.
Fig 4C.4 TGA curve of Poly(ether-azomethine)s SPAM-1 to SPAM-5

Fig 4C.5 DSC curve of Poly(ether-azomethine)s SPAM-1 to SPAM-5
X-Ray diffractograms of polymers exhibited a broad halo in the wide angle region (at about $2\theta \approx 20^\circ$) indicating that, the polymers were amorphous in nature. The methyl substituted Poly (ether-azomethine)s were also characterized by the wide angle X-ray diffractometer. The X-ray diffraction pattern of all poly (ether-azomethine)s is shown in Fig 4C.6. It is observed that, the polymer (SPAM-4) is highly amorphous in nature. This may be attributed to the copolymerization of novel diamine with IPA and TPA, introduction of cardo cyclopentylidene moiety of novel diamine monomer, methyl substitution and ether linkages which may have disrupted the chain regularity and packing leading amorphous nature. On the contrary, SPAM-1 polymer exhibited semicrystalline nature; this may be due to presence of para catenation of TPA leading to the close packing of the chains.

![Fig 4C.6 XRD curve of Poly (ether-azomethine)s SPAM-1 to SPAM-5](image-url)
4C.4 Summary and Conclusions

1. A series of new poly (ether-azomethine)s containing copolymerization, ether linkage, pendant methyl substitution and cardo cyclopentylidene moiety was synthesized by elevated temperature solution polycondensation of 1,1-bis[4-(4-amino 3-methyl phenoxy) phenyl] cyclopentane and commercial aromatic TPA/IPA.

2. Inherent viscosities of polyazomethines were in the range 0.20-0.39 dL/g indicating formation of medium to reasonably moderate molecular weight polymers.

3. Polyazomethine SPAM-4 was found to be soluble in DMF, NMP, DMAc, and DMSO at room temperature or upon heating. This indicates that the incorporation of cardo cyclopentylidene moiety, pendant methyl substitution, ether linkage and copolymerization of diamine with TPA/IPA leads to a significant improvement in solubility of polyazomethines.

4. Wide angle X-ray diffraction patterns indicated that polyazomethines containing ether linkages, pendant methyl substitution, cardo cyclopentylidene moiety and copolymerization were more amorphous in nature except SPAM-1 is semicrystalline in nature.

5. T_d values for polyazomethines were in the range 456°C-486 °C indicating good thermal stability of polyazomethines.

6. T_g values of polyazomethines were in the range 165°C-178°C. The depression in T_g values of polyazomethines could be attributed to the presence of ether linkages, pendant methyl substitution, cardo cyclopentylidene moiety and copolymerization approach.

7. A large difference in T_g and decomposition temperature of polyamides offers a broad processing window.
Chapter 4 Polyazomethines

References

44. Sprung, M. M.; Chem. Rev., 26, 297, 1940.
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