

Synthesis And Characterization of Novel Processable Poly (Ether-Azomethine)S Containing Cardo Cyclopentylidene Moiety

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Abstract: The novel dialdehyde 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane (III) (BBPC) was synthesized starting from cyclopentanone and phenol to give 1, 1-Bis (4-hydroxy phenyl) cyclopentane (II); followed by reaction with *p*- fluorobenzaldehyde in *N, N*-dimethyl formamide (DMAc), containing anhydrous potassium carbonate. New series of poly (ether – azomethine)s were synthesized from (BBPC) with different diamines such as 4, 4'- diamino diphenyl ether (ODA), 4,4'-diaminodiphenyl methane (MDA), 4-aminophenyl sulfone (SDA), *p*-phenylene diamines, etc. in DMAc with 5 wt% LiCl by solution polycondensation technique. Inherent viscosities of these polymers were in the range 0.19 to 0.42 dL/g indicating formation of moderate molecular weights. These polymers exhibited good solubility in various polar aprotic solvents such as *N*-methylpyrrolidone (NMP), *N, N*-dimethylacetamide (DMAc) and *N,N*-dimethyl formamide (DMF), etc. X-Ray diffraction pattern of polymers showed that introduction of cardo cyclopentylidene moiety containing ether linkage would disrupt the chain regularity and packing, leading to amorphous nature. Thermal analysis by TGA showed excellent thermal stability of polymers. The structure- property correlation among these polyazomethines were studied; in view of their potential applications as high performance polymers.

Keywords: 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane; cardo poly(ether-azomethine)s, thermal properties, XRD.

I. Introduction

Aromatic polyazomethines are known as a class of thermally stable polymers, and are usually prepared by polycondensation of aromatic diamines with aromatic dialdehydes^{1,2}. Aromatic polyazomethines have been classified as conjugated high molecular weight polymers which exhibit good mechanical, optical and electrical properties; due to presence of azomethine linkages in the polymer backbone³⁻⁴. However, they have serious limitations for industrial application due to their poor solubility, high melting temperature and relatively low molecular weight than other hetero-atom containing polymers.

During recent years many efforts have been made with aim to modify the monomer units to achieve processable polyazomethines such as incorporation of cardo groups like cyclohexylidene, diphenyl thiophene⁸, difluorene units⁹, etc.

To enhance the processability of aromatic polyazomethines, the present study describes a successful preparation of new soluble and processable aromatic polyazomethines without much sacrifice of thermal stability by incorporation of cyclopentylidene cardo moiety into the polymer backbone. For this, a new aromatic dialdehyde monomer having cardo cyclopentylidene moiety with ether linkage was designed and synthesized, which was subjected to polycondensation with various aromatic diamines.

II. Experimental

General Considerations:

Viscosity measurements were carried out with a 0.5% (w/v) polymer solution in *N*-methyl pyrrolidone (NMP) and some were in Conc. H₂SO₄ at 30 °C with an Ubbelohde Suspended Level Viscometer. ¹H NMR (400-MHz) spectra were recorded on a Bruker ARX 300 instrument the reference was 0 ppm with tetramethylsilane (¹H)]. An IR spectrum was recorded on a PerkinElmer 1720X Fourier transform infrared (FTIR) spectrophotometer with KBr pellets. Differential scanning calorimetry (DSC) measurements were made on a TA Instruments DSC 2920 at a heating-cooling rate of 10 °C/min under nitrogen. The *T*_g was taken at the middle of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments TGA-2950. A heating rate of 10 °C/min was used for the determination of the decomposition temperature (*T*_d) at a 10% weight loss under nitrogen.

III. Materials

All the solvents / chemicals were purified before use by following the standard procedures. 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 prepared in the laboratory by reaction of resorcinol and 1, 1-Bis (4-hydroxy phenyl) cyclopentane with p-fluoronitrobenzene in DMF in the presence of anhydrous K₂CO₃; the dinitro compounds formed was reduced to the respective diamine by hydrazine hydrate in the presence of catalytic amount of 10% Pd/C with ethanol as solvent⁹. N, N-dimethylformamide was vacuum distillation, N, N-dimethylacetamide was purified by vacuum distilled from P₂O₅. Cyclopentanone, Phenol, 4-fluoronitrobenzene were purchased from Spectrochem and used as received. 4,4'-Oxydianiline; 4,4'-methylenedianiline and 4,4'-sulfonyl dianiline were purchased from Aldrich and used as received.

Monomer Synthesis

a) Synthesis of 1, 1-bis (4-hydroxy phenyl) cyclopentane (I):

In a 500 mL round bottom flask equipped with a thermowell, a condenser and a magnetic stirrer were placed 141 g (1.5 mol) 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

b) Synthesis of 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane (II)

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 K₂CO₃ with 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 ¹H NMR.

Yield: 21.90 g (95 %) ; M.P.:106 °C.

IR (KBr): 2961, 2834, 1686, 1577, 1496, 1423, 1237, 1210, 1153, 1102, 1014, 878,867, 833, 820, 761 cm⁻¹.

¹H NMR (CDCl₃, d, ppm): 9.91 (s, 2H, CHO), 7.85 (d, *J* = 9.4 Hz, 4H), 7.33(d, *J* = 9.4 Hz, 4H), 7.08 (d, *J* =9.4 Hz, 4H, H2), 6.99 (d, *J* = 9.4 Hz, 4H, H3),2.34 (d,4H,),1.78(d,4H).

¹³C NMR(CDCl₃, d, ppm): 185,163,153,145,132,128,120,118,78, 54, 39, 22.

Polymerization:

Polymerization of novel dialdehyde with various aromatic diamines was performed by direct solution polycondensation method to yield high molecular weight polyazomethines. A typical procedure for synthesis of polyazomethines is given below.

Synthesis of polyazomethines:

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.

IV. Results And Discussion

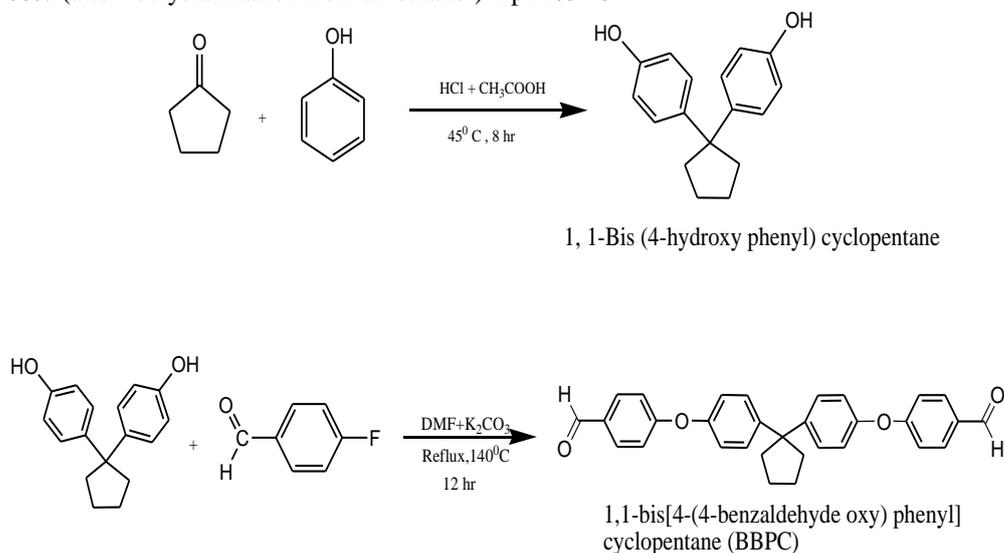
Aromatic polyazomethines (Schiff's base polymers) or polyimines have been classified as highly conjugated materials which are generally insoluble and intractable. Insolubility of these polymers makes solution synthesis difficult.

In the present work, poly (ether – azomethine)s were synthesized 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.

Synthesis of monomer 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane (III) (BBPC)

The novel dialdehyde 1,1-bis [4-(4-benzaldehyde oxy) phenyl] cyclopentane (III) (BBPC) was synthesized by reacting cyclopentanone with phenol to yield 1, 1-Bis (4-hydroxy phenyl) cyclopentane (II); followed by reaction with p- fluorobenzaldehyde in N, N-dimethyl formamide, containing anhydrous potassium carbonate¹⁰ (Scheme-1). The structure of novel dialdehyde was confirmed by FT-IR and ¹H NMR.

Yield: 60% (after recrystallization from an ethanol) mp: 105 °C.



Scheme -1: Synthesis of 1,1-bis[4-(4-benzaldehyde oxy) phenyl] cyclopentane (BBPC)

The infrared spectrum (KBr) of (BBPC) 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).

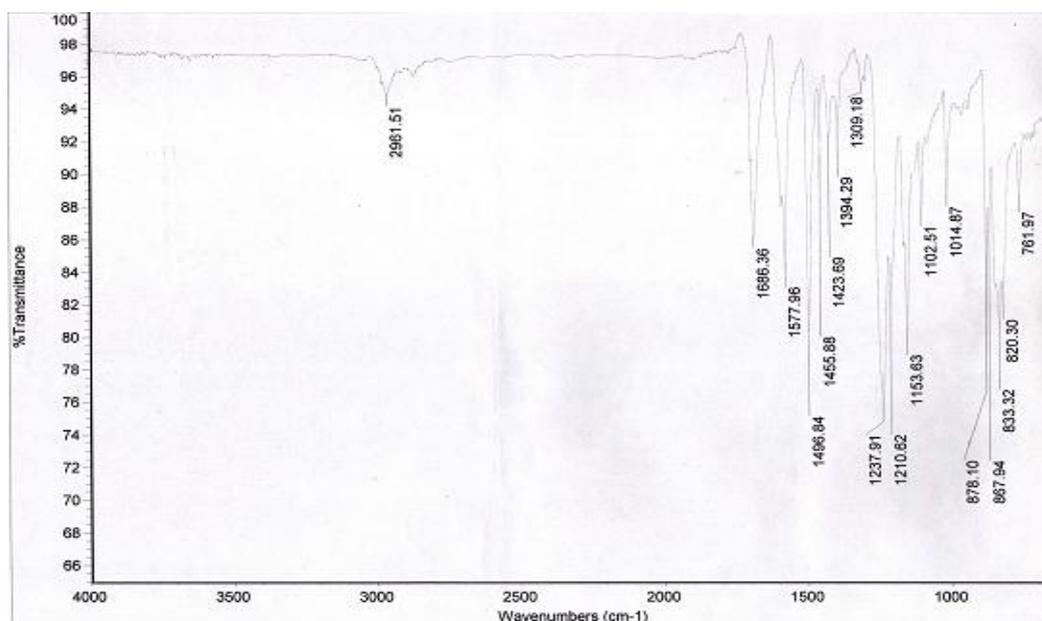


Figure 1: FT-IR of dialdehyde (BBPC)

Proton ¹H NMR spectrum (Fig. 2) of (III) showed singlet at 9.91 δ due to two formyl protons and multiplete in the range of 7.85 to 6.99 δ due to aromatic protons as expected with desired integration and splitting pattern. Peaks at 2.34 and 1.78 δ are due to methylene protons of cyclopentane moiety.

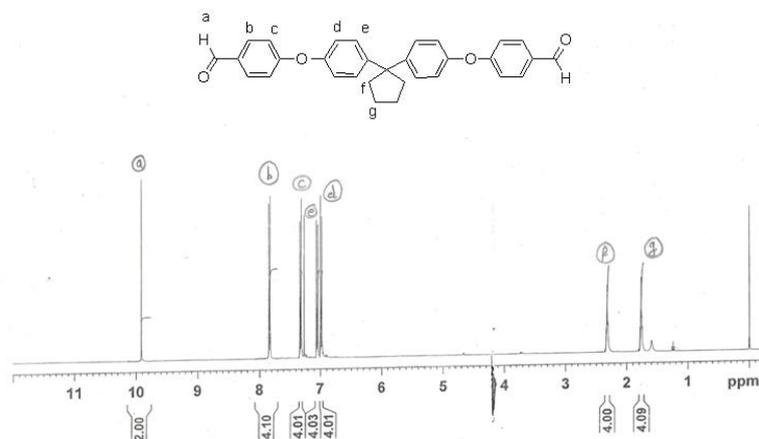


Figure 2: ¹H NMR of dialdehyde

¹³C NMR spectrum (Fig. 3) of (III) showed thirteen NMR signals corresponding twelve types of different carbons of which aldehyde carbon (-CHO) appeared at 190 δ for; whereas tertiary carbons showed signals at 163, 153, 145 and 75 δ. The CH carbons appeared at 132, 128, 120, and 118 δ, whereas CH₂ carbons gave NMR signals at 39, 22 δ confirming the formation of dialdehyde monomer (III). The formyl carbon is obviously most down field as evidenced by DEPT also. The DEPT spectrum (Fig. 4) of (III) also confirms the formation dialdehyde monomer (III), where in all the quaternary carbons are absent in the spectrum and the peaks of CH carbons are upper side and CH₂ appeared at down side.

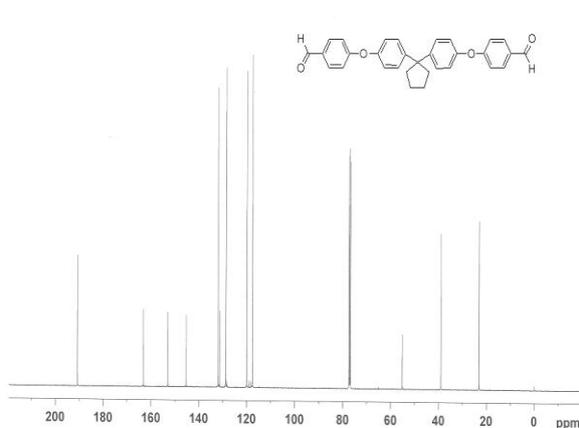


Figure 3: ¹³C NMR of dialdehyde

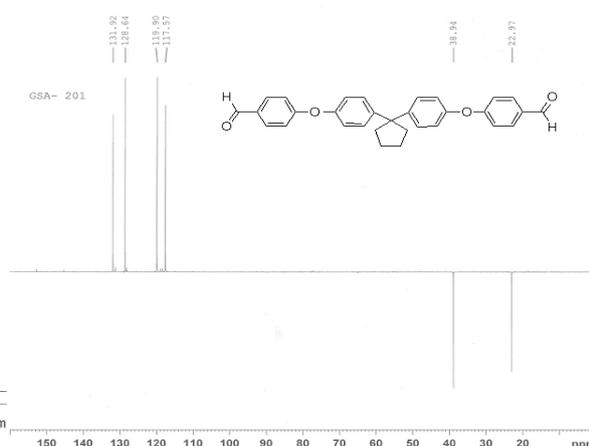


Figure 4: DEPT of dialdehyde

Polymerization:

a) Synthesis of poly (ether – azomethine)s:

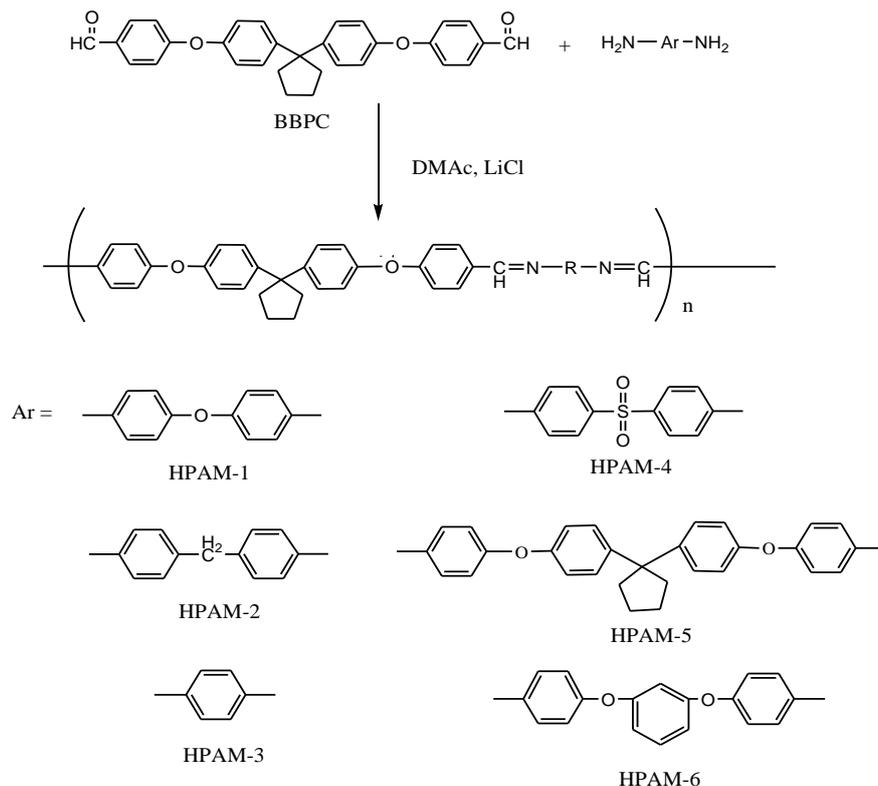
A series of poly(ether-azomethine)s were synthesized (Scheme-2) by condensation of BBPC with various diamines by solution polymerization in DMAc. The polymerization proceeded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in water. The 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 -1.

Table -1: Physical properties of Poly(ether-azomethine)s

Polymer	Thermal Behaviour ^a		Yield %	Inherent Viscosity dL/g ^b
	T _g °C in N ₂	T ₁₀ °C in N ₂		
HPAM-1	164	493	98	0.30
HPAM-2	191	441	99	0.42
HPAM-3	190	467	99	0.25
HPAM-4	192	445	92	0.19
HPAM-5	192	464	98	0.28
HPAM-6	192	469	99	0.27

^aTemperature at which onset of decomposition was recorded at a heating rate of 10 °C/min.

^bInherent viscosity was measured at a concentration of 50mg/10 ml in NMP and conc.H₂SO₄ at 30°C.



Scheme-2: Synthesis of poly(ether-azomethine)s HPAM -1 to HPAM- 6

The polymers were characterized by the infrared spectroscopy. The IR spectrum of poly (ether – azomethine) HPAM-1, Fig. 5 showed the characteristic absorption at 1624 cm^{-1} (CH = N stretching). The sharp bands occurring at 1242 and 1157 cm^{-1} in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the ether linkage. The presence of bands at 2920 and 3036 cm^{-1} can be assigned to aromatic and aliphatic (C-H stretching) vibrations (of cyclopentane methylene).

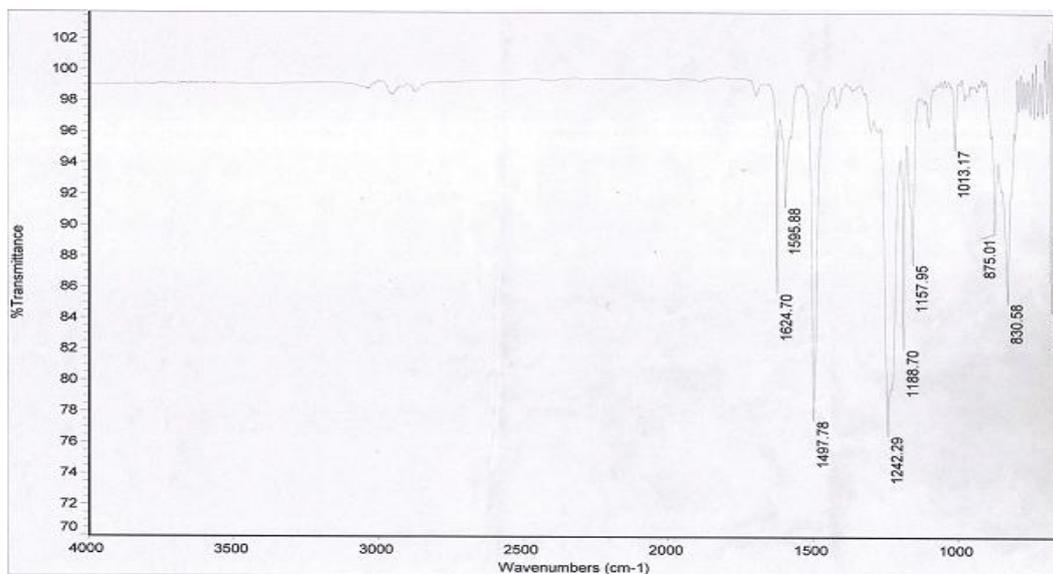


Figure 5: FT-IR of HPAM-1

^1H NMR spectrum of HPAM-1 is given in Fig. 6 which showed the formation of imine bonds was confirmed from the signals at 8.43 ppm and other expected corresponding characteristic peaks. FTIR and ^1H NMR spectra did not show any signals corresponding to the terminal $-\text{CHO}$ or $-\text{NH}_2$ groups, indicating high conversion. Solubility characteristics of poly (ether – azomethine)s are summarized in Table - 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), N,N-dimethyl sulphoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethyl formamide (DMF). Polymer HPAM-1, - 2, - 4 and -6 are also showing excellent solubility in polar aprotic solvents. Polymer HPAM-4 synthesized from p-phenylene diamine exhibit insolubility behavior due to its stiff structure. Thus better solubility of these polymers, as expected; can be attributed to the introduction of cardo cyclopentylidene moiety in the polymer backbone. The superior solubility of these polymers is due to the presence of cardo groups and ether linkage¹¹⁻¹⁴.

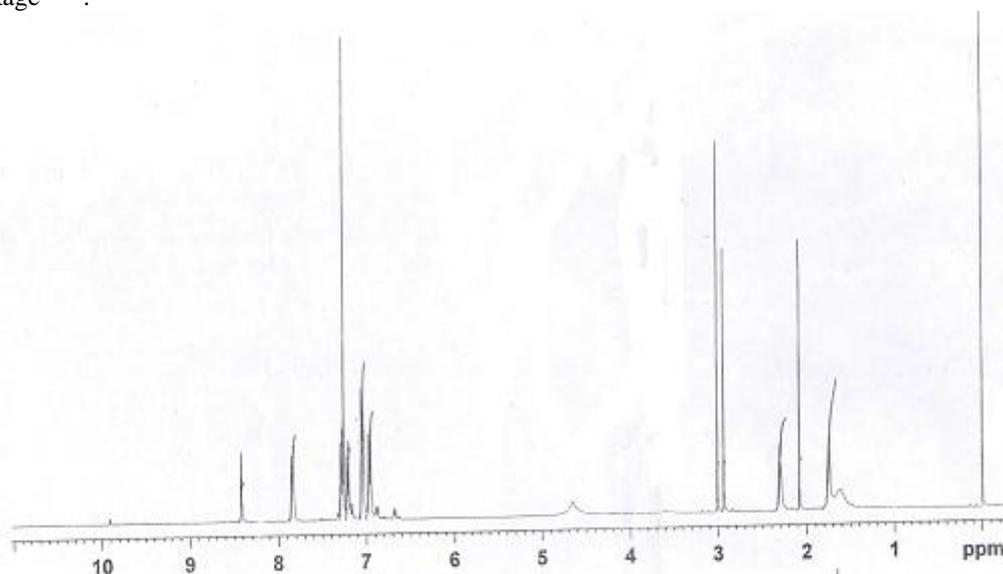


Figure 6: ¹H NMR of HPAM-1

Table-2: Solubility Behavior of Poly(ether-azomethine)s

Polymer codes	Solvents								
	DMF	DMAc	DMSO	NMP	Pyridine	THF	CHCl ₃	DCM	C.H ₂ SO ₄
HPAM-1	+	+	-	+	+	+	+	+	+
HPAM-2	-	±	-	+	+	+	±	+	+
HPAM-3	-	-	-	-	-	-	-	-	+
HPAM-4	+	+	+	+	+	+	+	+	+
HPAM-5	±	±	±	±	±	±	±	±	+
HPAM-6	+	+	-	+	+	+	+	+	+

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

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. Table 1 incorporate the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), maximum decomposition temperature (T_{max}) and residual weight at 800 °C.

The thermal stability of the poly (ether – azomethine)s was studied at a heating rate of 10 °C/min in nitrogen atmosphere by thermogravimetric analysis. The initial decomposition temperature (T_i), (T_{10}) temperature at which 10 % weight loss occurred, and char yields at 900 °C were determined from thermograms. T_i and T_{10} values were in the range of 350 to 385 °C and 441 to 492 °C respectively. In general, these polymers, like other poly-Schiff bases,¹⁵⁻¹⁷ exhibited good thermal stability in nitrogen; 10% weight loss only takes place when they are heated beyond 441 °C in nitrogen.

The DSC curves represent the T_g values of poly (ether – azomethine)s. All these polymers manifest 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 packing¹³. All the polymers shows T_g in between 164-192 °C. The higher T_g of HPAM- 5 compared to the T_g of other polymers is due to the presence of bulky unit.

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. 7. It is observed that, the polymer (HPAM-4) is highly amorphous in nature. This may be attributing 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 - 5 polymers exhibited more crystalline nature, this may be due to the close packing of the chains leading to crystalline nature.

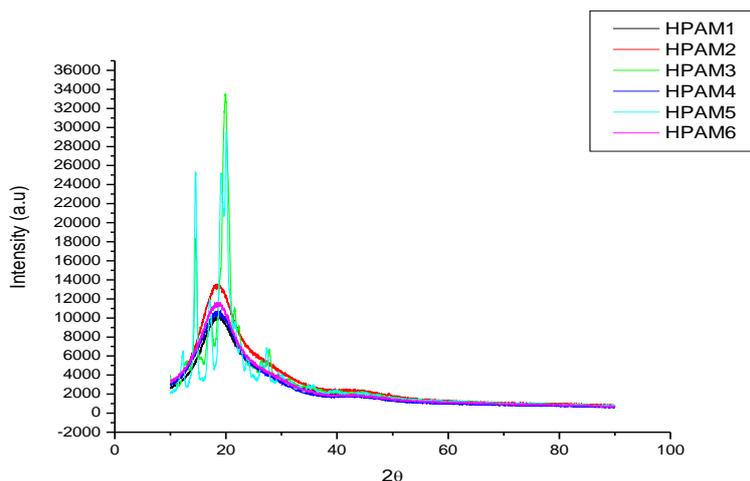


Figure 7: XRD curves of HPAM-1 to HPAM-6

V. Conclusions

Series of new aromatic poly(ether-azomethine)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 0.19 to 0.42 dL/g. The most of these polymers are amorphous and soluble in a number of organic solvents, such as DMF, NMP, DMAc, THF and CHCl_3 . The T_g 's in nitrogen and T_d 's for 10% weight loss in nitrogen range from 164 to 192 °C and 441 to 492 °C, respectively, depending on the exact polymer structure.

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