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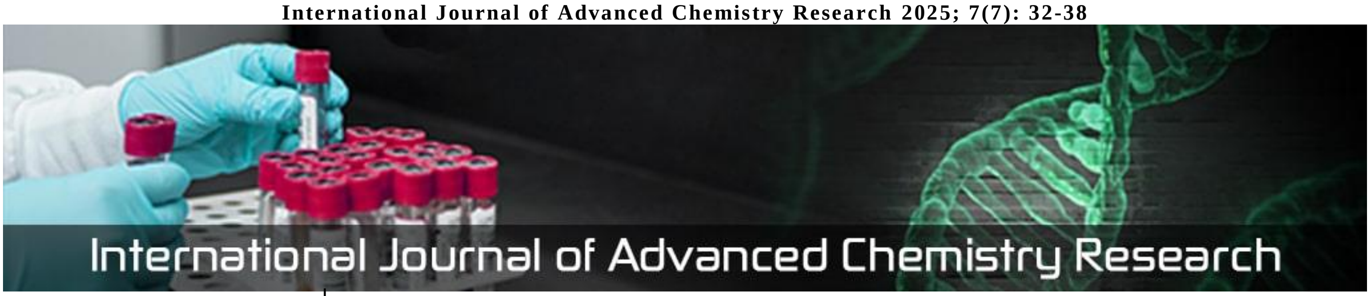

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Design and thermal evaluation of soluble polyazomethines based on 1,1-Bis[4-(4-benzaldehyde oxy)phenyl]cyclohexane

Rajesh Bhorkade, Shivaji Ghodke and Noormahmad Maldar

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Rajesh Bhorkade
Punyashlok Ahilyadevi Holkar
Solapur University, Solapur,
Maharashtra India, India

Shivaji D Ghodke
Assistant Professor,
Department of Chemistry, Arts
Science and Commerce College,
Naldrug, Tuljapur, Dharshiv,
Maharashtra, India

Noormahmad Maldar
Punyashlok Ahilyadevi Holkar
Solapur University, Solapur,
Maharashtra India, India

Corresponding Author:
Shivaji D Ghodke
Assistant Professor,
Department of Chemistry, Arts
Science and Commerce College,
Naldrug, Tuljapur, Dharshiv,
Maharashtra, India

Abstract

Polyazomethines (Schiff's base polymers) are thermally stable and environmentally resistant materials with potential in optoelectronic and photonic applications. In this study, novel poly(ether-azomethine)s were synthesized via solution polycondensation of 1,1-bis[4-(4-benzaldehyde oxy)phenyl]cyclohexane (BBPC) with various commercial diamines. The structures were confirmed by FT-IR and NMR spectroscopy. The resulting polymers exhibited good solubility in aprotic solvents and inherent viscosities ranging from 0.22 to 0.45 dL/g, indicating moderate molecular weights.

DSC and TGA analyses revealed glass transition temperatures (Tg) between 154 and 187 °C and excellent thermal stability, with decomposition temperatures up to 661 °C. XRD analysis showed that the polymers possessed partially crystalline to amorphous morphology. These findings suggest that the synthesized polymers are promising for high-performance thermal applications.

Keywords: Polyazomethines, Schiff's base polymers, thermal stability, photonic applications, FT-IR spectroscopy

1. Introduction

Polyazomethines are a class of polymers containing – CH = N – functional repeat units in the main polymer backbone. The aromatic azomethine linkage in polymer backbone is of special interest due to syn / anti – isomerism which has an effect on the thermal and photochromic properties. Aromatic polyazomethines exhibit good thermal stability and environmental resistance [1-12]. The – CH = N – linkage in polyazomethines is isoelectronics with – C = C – group and therefore finds applications in optoelectronics [13-22]. The first polymer of this class was synthesized by Adams *et al.* by polycondensation reaction between terephthalaldehyde and benzidine. In 1950 Marvel and Hill synthesized polyazomethines by solution polycondensation of aromatic dialdehydes with o-phenylene diamine, polyazomethines have high strength and high modulus [23-28].

2. Experimental

2.1 Materials

4-(P)fluorobenzaldehyde (spectrochem) was used as received, potassium carbonate was dried in oven at 150°C for 6 hours. Isopropyl alcohol (2-Proponol) was purified by distillation. DMAc was purified before use as described in chapter – 2 various commercial diamines (make-aldrich) were used as received LiCl was dried under oven at 150 °C for 6 hours.

2.2. Synthesis of Monomer

a) Synthesis of 1.1 – bis (4 – hydroxy phenyl) cyclohexane – BHPC (II)

In 500ml round bottom flask equipped with thermowell, condenser and magnetic stirrer were placed 47 gm (0.5 mol) of phenol and 24.5 g (0.25 mol) of cyclohexanone. To this solution 100 mL of conc. 36% HCl and 50 mL of glacial acetic acid were added. Resulting reaction mixture was stirred for 5 hours at 45°C and overnight at room temperature. The pink colour product was isolated by filtration and washed with hot water till it is free from phenol and acid and then with benzene. A crude bisphenol (BHPC) was purified by dissolving in minimum quantity of 2M 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 product. The product was filtered washed with water till acid free and dried. Finally the bisphenol was recrystallized from methanol get white shining crystals.

- **Yield:** 21.83 gm (91%)
- **M.P.:**188-190 °C

2.3. Polymer Synthesis:-

By using the aromatic dialdehyde monomer 1,1 – bis [4 – (4’ – benzaldehyde oxy) phenyl] cyclohexane BBPC (III) with various commercial diamines. Series of poly (ether – azomethine)s were prepared by solution polycondensation method is given below.

Synthesis of polyazomethine (PAM-1) from 1,1[4- (4 – benzaldehyde oxy) phenyl] cyclohexane, (BBPC) and 4, 4’ – sulphonyldianiline (SDA) diamine

In 100 mL three necked round bottom flask equipped with magnetic stirrer, calcium chloride guard tube, nitogen gas inlet were placed the 4, 4’ – sulphonyldianiline (SDA) diamine 0.248 g 1 mmol and dry distilled N, N dimethyl acetamide DMAc 3 mL containing 5% (0.150 g) dry LiCl mixture was stirred at room temperature to get the solution and then dialdehyde 1, 1 – bis [4 – (4 – benzaldehyde oxy) phenyl] cyclohexane – BBPC (III) (0.476 g 1 mmol) was added. The reaction mixture was stirred overnight at room temperature. Finally, the mixture was stirred for four hours at 140°C temperature. Then the solution was cooled to room temperature and poured in 200 mL water with rapid stirring the precipitated polymer (PAM-1) was filtered, washed with water, ethanol and dried in vacuum oven at 80 °C temperature for 6 hours.

- **Yield** = 93%

Other polyazomethines PAM-2 to PAM-5 were synthesized with similar procedure by using different diamines.

3. Results and Discussion

Polyazomethines, also known as polyimines or Schiff’s base polymers exhibit good thermal stability and environmental resistance and they are promising materials in optoelectronic and photonic applications. A remarkable characteristic of polyazomethines is their tendancy to increase in molecular weight and crystallinity upon thermal annealing a process that usually brings about as improvement in the mechanical properties of derived fibers. Melt polymerization techniques resulted in infusible materials which cannot be further fabricated into thin film or remoulded. To increase the molecular weight of the products various attempts were made by changing solvent catalyst, temperature, dehydrating agent etc. (the degree of polymerization ranged from 3 to 8 as calculated by nitrogen analysis for these polyazomethines)

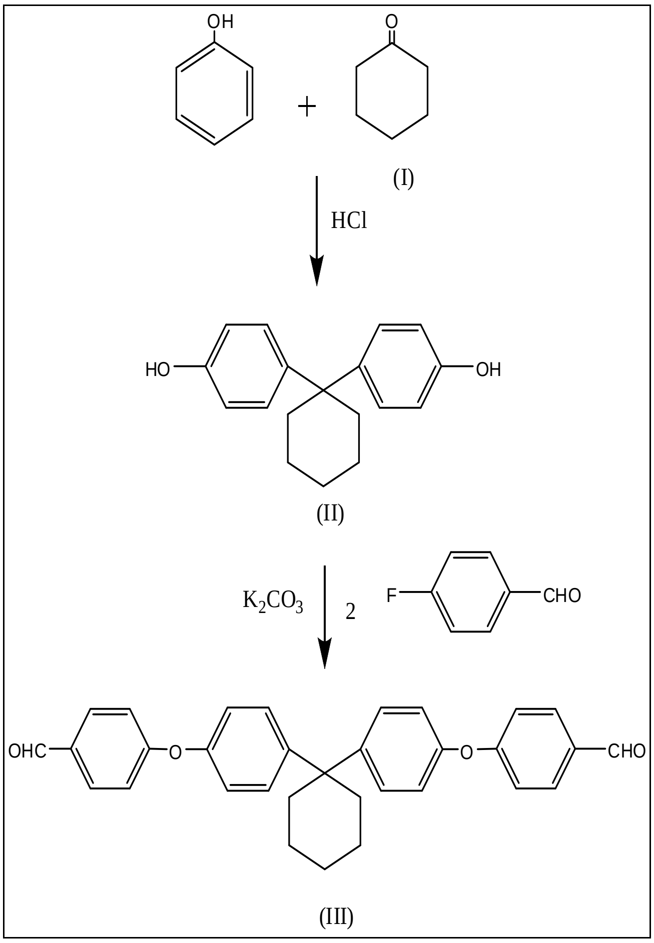
It is generally recognized that an aryl ether linkage imparts properties such as better solubility and melt processing characteristics and improved toughness in comparison with those of the polymers without an aryl – ether linkage. To synthesize high molecular weight polyazomethines, D.’Alelio et al. used melt polymerization technique and by exchange reaction. The purpose of the present study is to investigate the effect of incorporation of flexible ether linkage methylene linkages and performed amide group in polyazomethine polymer backbone. Thus in the present work poly (ether – azomethine)s were synthesized from novel dialdehyde. 1,1bis [4- (4 – benzaldehyde oxy) phenyl] cyclohexane BBPC (III) with different commercial diamines by solution poly condensation technique. The resulting polyazomethine were characterized by FT – IR spectroscopy, inherent viscosity, solubility tests, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction studies.

3.1 Synthesis of Monomer

The novel aromatic dialdehyde 1, 1 – bis [4 – (4 – benzaldehyde oxy) phenyl] cyclohexane BBPC (III) was synthesized by starting from cyclohexanone in two steps (scheme 2) 1,1 – bis (4 – hydroxyl phenyl) cyclohexane BHPC (II) was obtained as described in chapter 2A whereas 1,1 – bis [4 – (4- benzaldehyde oxy) phenyl] cyclohexane BBPC (III) was synthesized by condensation of (II) with 4(p) – fluorobenzaldehyde in N, N – dimethylacetamide containing anhydrous potassium carbonate.

The structures of BHPC and BBPC were confirmed by FT-IR,. FT-IR spectrum of BHPC (Fig.1) showed characteristic absorption bands at 3365(-OH), 2930 (–CH), 1691 (-C=C-), 1491 (-CH_2-), 1208 (-C-C-), 1103 (-C-O-), 819 cm^{-1} (Ar-H).

The infrared spectrum of BBPC (Fig. 2) showed characteristic absorption bands at 2931 (–CH), 2851 (-CHO), 1689 (-C=C-), 1496 (-CH_2-), 1208 (-C-C-), 1169 (-O-), 1103 (-C-O-), 831 cm^{-1} (Ar- H)



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

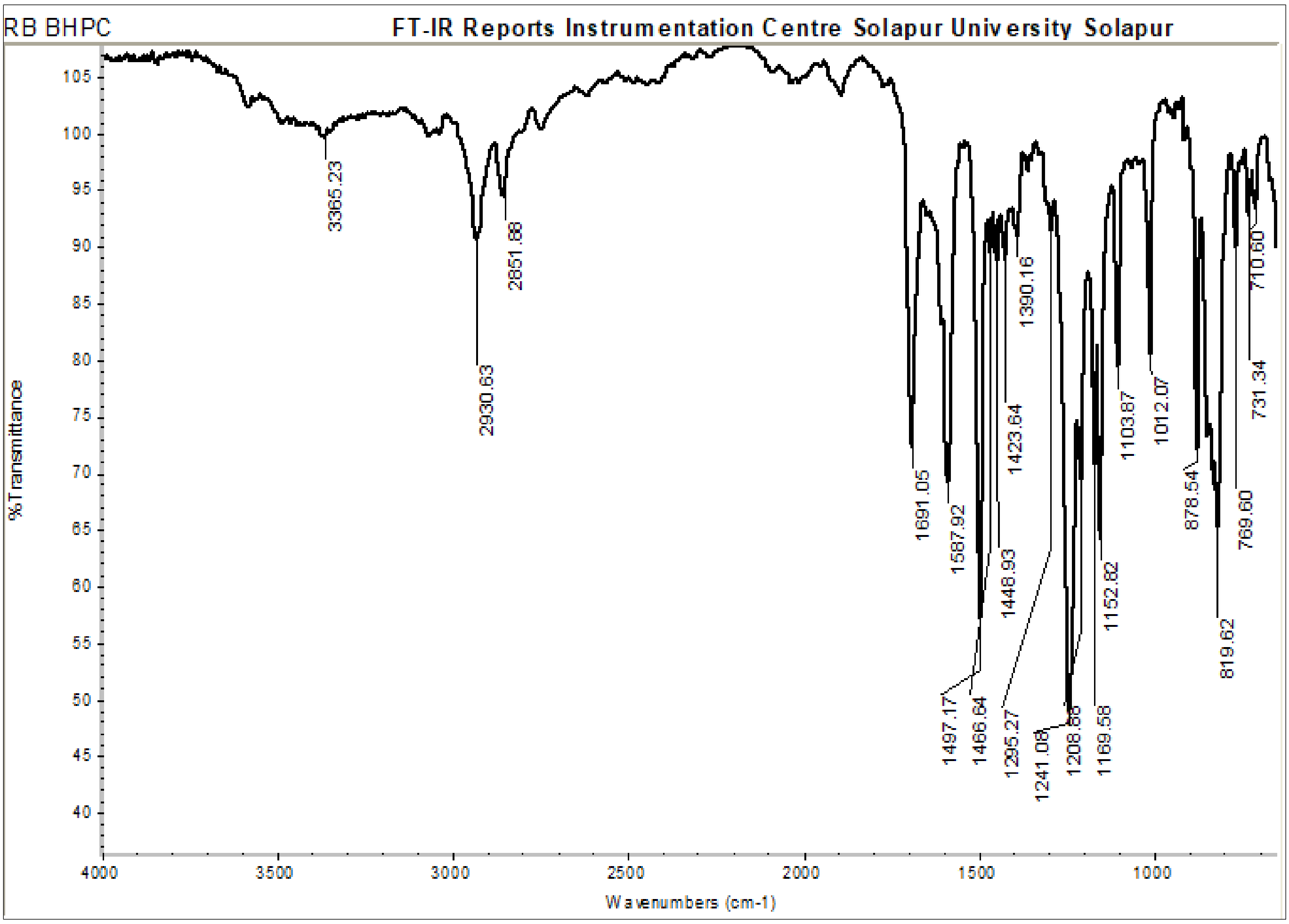


Fig 1: FT- IR Spectrum of BHPC

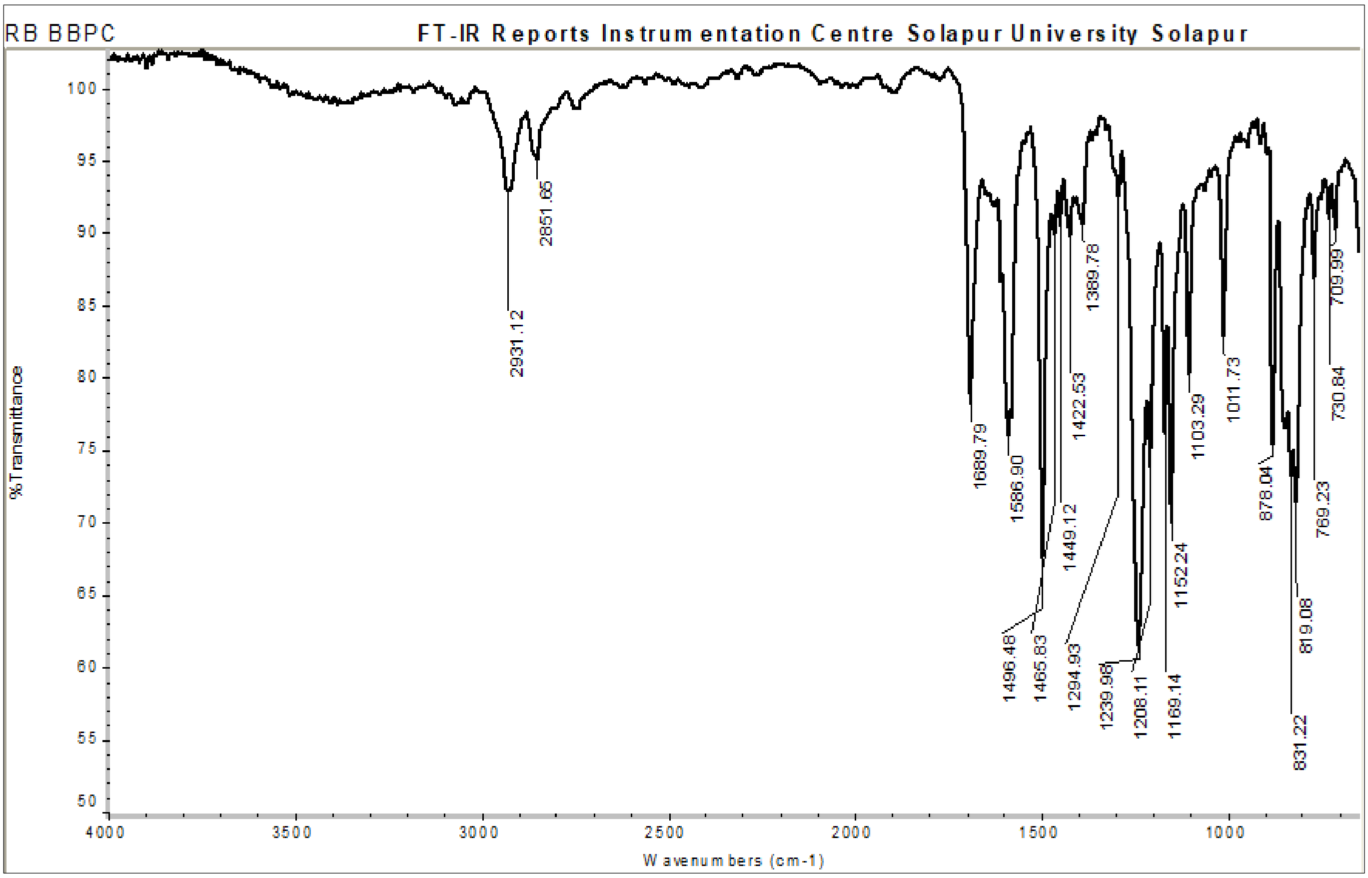
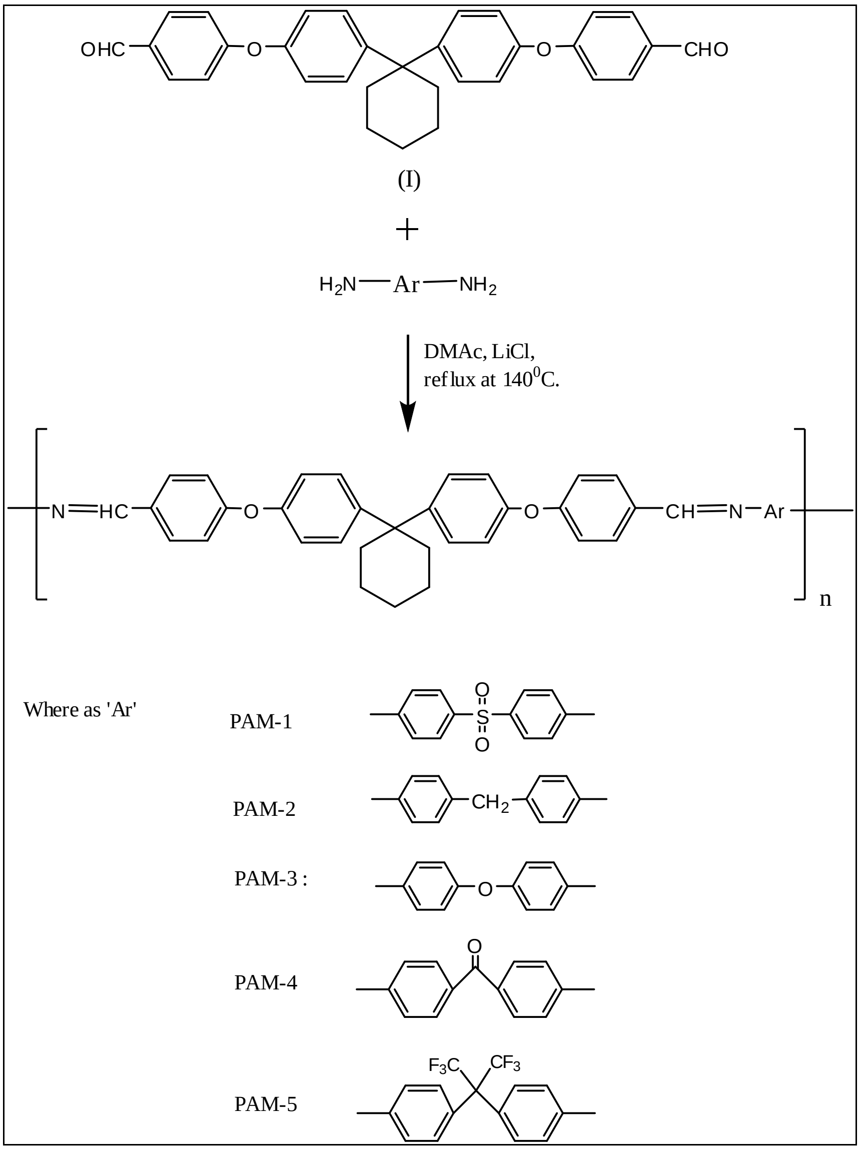


Fig 2: FT- IR Spectrum of BBPC

3.2. Polymerization

Synthesis of poly(ether azomethine)s

A series of polymers was synthesized by condensation of aromatic dialdehyde BBPC (III) with different commercial diamines by elevated temperature solution polymerization in DMAc. The resulting polymers was precipitated by pouring into water.



Scheme 2: Synthesis of poly (ether azomethine)s from BBPC (III) and different diamines.

The results of the synthesis of poly(ether – azomethine)s are presented in (Table No. 1). All the polymers were obtained in the quantitative yields (92 to 94%). The inherent viscosities of these (polyazomethine)s were in the range 0.22 to 0.45dL/gm indicating the formation of moderate to high molecular weight polymers.

Table: 1 Yield and Inherent Viscosity of poly (ether – azomethine)s synthesized from BBPC (III) and different diamines.

Table 1: Yield and Inherent viscosity of polyazomethynes (PAM-1 to PAM-5) from dialdehyde (BBPC) and diamines by solution polycondensation method.

Sr. No.	Polymer code	Diamine	Dialdehyde	Yield (%)	Inherent Viscosity $^c\eta$ inh (dL/g)
1.	PAM-1	3,3- Sulphonyldianililne - SDA	BBPC	94	0.28
2.	PAM-2	Methylene dianiline- MDA	BBPC	93	0.23
3.	PAM-3	Oxydianiline -ODA	BBPC	92	0.31
4.	PAM-4	4,4-Diamino benzophenone	BBPC	93	0.42
	PAM-5	Hexafluoroisopropylidine diamine – 6-FDA	BBPC	94	0.45

a. Polymerization was carried out with 1 mmol each of BBPC (III) and diamine (s).
b. BBPC (III); 1,1 – bis [4- (4 – benzaldehyde oxy) phenyl] cyclohexane.
c. Inherent viscosity measured with a 0.5% (w/v) polymer solution in NMP.

The formation of poly(ether-azomethine)s was confirmed by FT-IR spectra. A representative IR-spectrum of polyazomethine PAM-4 based on 4,4-Diamino benzophenone is shown in (Fig. 3) and showed characteristic absorption band of azomethine linkage (CH=N) at 1683cm^{-1}. The disappearance of carbonyl band at round 1700 cm^{-1} due to monomoric dialdehyde and N-H of amino group at 3446, 3372cm^{-1} confirmed the formation of polyazomethine. Other characteristic absorption band at 2923 (aliphatic-CH), 3040 (aromatic–CH) 1234 and 1167 (asymmetrical and symmetrical vibrations of ether linkage) were also observed.

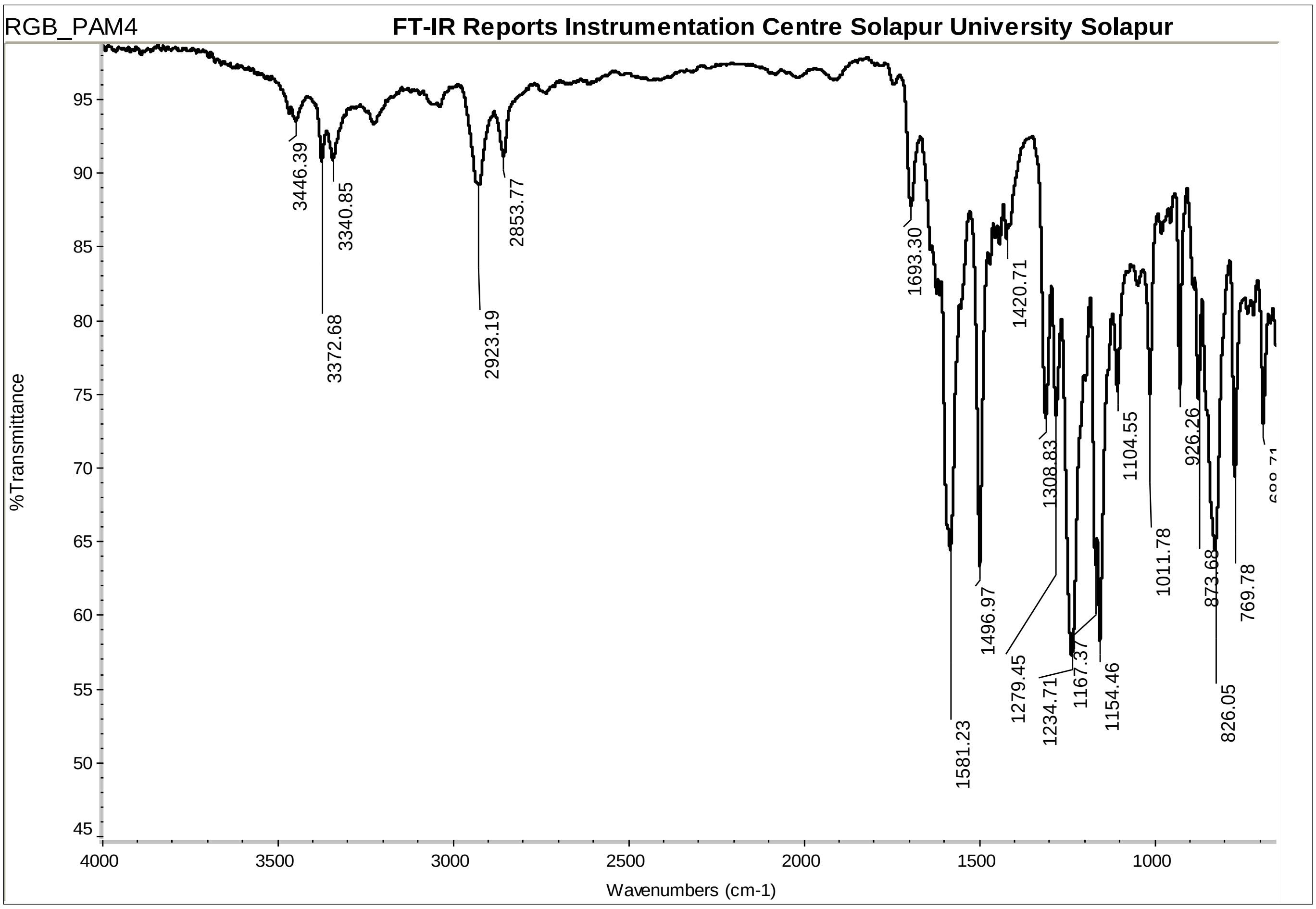


Fig 3: FT-IR Spectrum of PAM-4

A solubility behavior of these poly (ether – azomethine)s was tested quantitatively in various solvents and results are given below in Table No. 2. A 3% solution of polymer in solvent was taken as criterion for solubility. It was observed that the polymers were easily soluble in aprotic solvents such as DMAc, NMP, DMSO, DMF, Pyridine and m – cresol. The better solubility of polyazomethines as expected can be attributed to the introduction of pendant cyclohexylidene cardo moiety in the polymer backbone.

Table 2: Solubility of Polyazomethines prepared by solution polycondensation method.

Polymer → Solvent ↓	**PAM-1**	**PAM-2**	**PAM-3**	**PAM-4**	**PAM-5**
DMAc	+ +	+ +	+ +	+ +	+ +
NMP	+ +	+ +	+ +	+ +	+ +
DMSO	+ +	+ +	+ +	+ +	+ +
DMF	+ +	+ +	+ +	+ +	+ +
m-Cresol	+ +	+ +	+ +	+ +	+ +
$CHCl_3$	--	--	--	--	--
DCM	--	--	--	--	--
H_2SO_4	+ +	+ +	+ +	+ +	+ +

+ +: Soluble, --: Insoluble

Thermal behavior of polymers (PAM) was evaluated by thermogravimetric and differential scanning calorimetry under nitrogen atmosphere. (Table 3) Incorporate the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), 10% weight loss temperature (T_{10}) maximum decomposition temperature (T_{max}) and residual weight at 900 °C.

Table 3: Thermal properties of polyazomethines prepared by solution polycondensation method.

Polymer Code	T_i^b (°C)	T_{10}^c (°C)	T_{max}^d (°C)	Residual wt% at 900°C	T_g^e (°C)
PAM-1	199	585	619	42	167
PAM-2	207	547	628	32	154
PAM-3	214	421	661	33	173
PAM-4	208	607	652	43	184
PAM-5	203	581	656	33	187

a. Thermogravimetric analysis were conducted at a heating rate of 10°C / min. under nitrogen.
b. Temperature at which weight loss initiated.
c. Temperature at which 10% weight loss was observed
d. Temperature at which maximum rate of weight loss was observed.
e. Determined by DSC measured at a heating rate 20°C / min.

TGA curves (Fig.4) of all poly(ether-azomethine)s showed more or less similar pattern of decomposition with no weight loss below 199°C. The T_i and T_{10} of these polyazomethines varied in the range 199 to 214 °C and 421 to 607 °C respectively. T_{max} values were between 619 to 661 °C and the char yield at 900 °C were in the range 32 to 42 °C. This showed that, these polyazomethines exhibited good thermal stability.

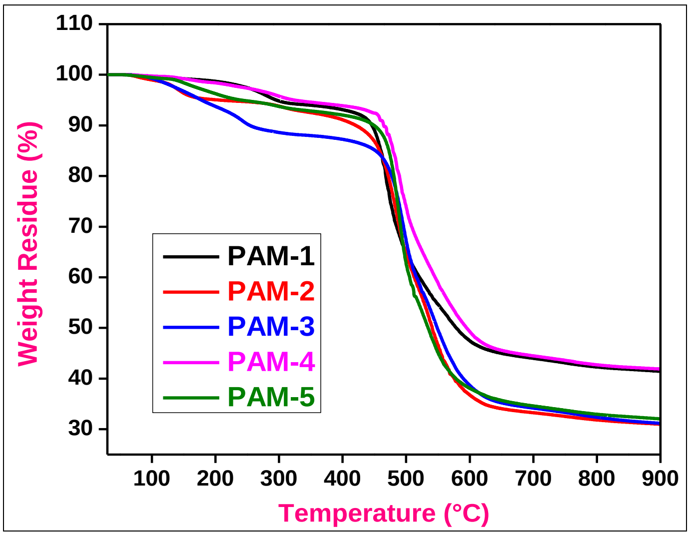


Fig 4: TGA Curves of PAM-1 to PAM-5

The DSC curves shown in (Fig.5) represent the T_g. values of poly(ether-amide- azomethine)s which were in the range 154 to 187 °C. The T_g values of azomethines PAM-5 synthesized from hexafluoroisopropylidine diamine 6–FDA was highest (187°C) and lowest T_g exhibited for polymer PAM-2 based on methylenedianiline- MDA.

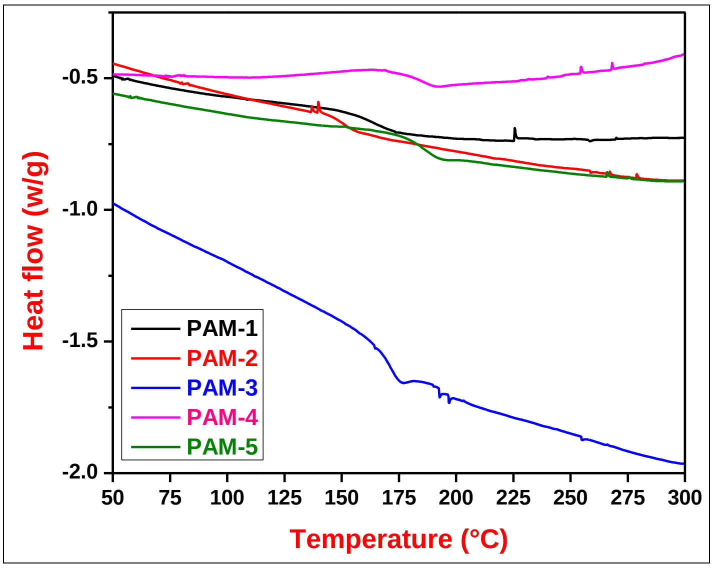


Fig 5: DSC Curves of PAM-1 to PAM-5

Poly(ether-azomethine)s were also characterized by wide angle X-Ray diffractograms-WAXD. The X-Ray diffraction pattern of all Poly(ether-azomethine)s are shown in (Fig.6). It was observed that, polyazomethines exhibited partly crystalline to amorphous nature peeks observed in the range 2θ = 10 to 30 °.

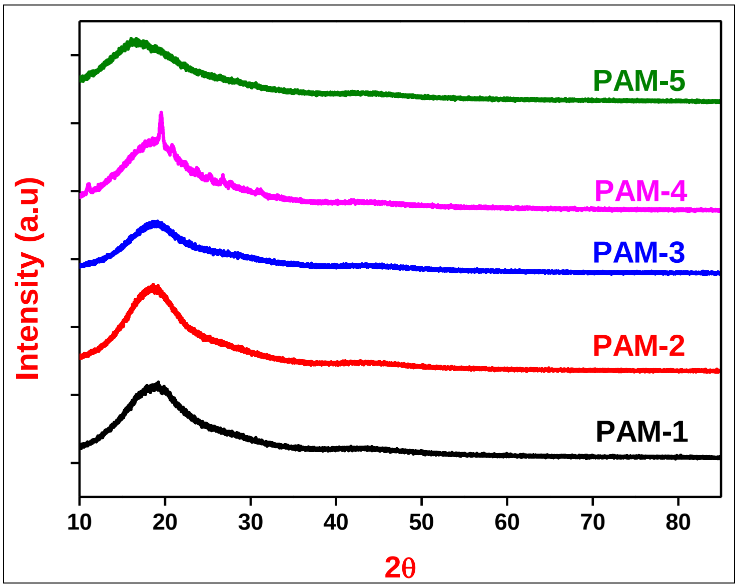


Fig 6: XRD Curves of PAM-1 to PAM-5

4. Conclusions

A novel aromatic dialdehyde monomer, 1,1[4-(4-benzaldehyde oxy)phenyl]cyclohexane (BBPC), containing an ether linkage, was synthesized. Various aromatic diamines featuring methylene, ether, and sulphonyl linkages were also prepared for the synthesis of aromatic polyazomethines. The structure of the monomer was confirmed using FT-IR, spectroscopy.

Aromatic poly(ether-azomethine)s were synthesized by the solution polycondensation method, involving a stoichiometric reaction between the novel aromatic dialdehyde (BBPC) and the aromatic diamines.

The resulting polyazomethines were characterized using a variety of techniques including FT-IR spectroscopy, inherent viscosity measurements, solubility tests, Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and X-ray Diffraction (XRD).

The inherent viscosities of the synthesized poly(ether-azomethine)s ranged from 0.22 to 0.45 dL/g, indicating a moderate molecular weight build-up in these polymers. Solubility tests revealed that the polyazomethines were soluble in aprotic polar solvents such as DMAc, DMSO, DMF, NMP, as well as in m-cresol and pyridine.

The glass transition temperatures (Tg) of the polyazomethines synthesized from BBPC and the diamines were found to be in the range of 154°C to 187°C.Thermal stability of the polymers, evaluated by TGA under a nitrogen atmosphere, showed that the polyazomethines possessed excellent thermal resistance, with no significant weight loss at high temperatures.

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