



Synthesis and Characterization of Novel Processable Poly (Ether-Azomethine)s Containing Naphthyl Moiety

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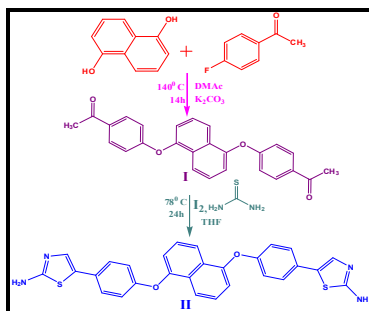
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ABSTRACT

A new diamine 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) was synthesized starting from 1,5- naphthol. New series of poly (ether-azomethine)s were synthesized from 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) with different compositions of dialdehydes such as isophthalaldehyde and terephthalaldehyde in *N,N*-dimethylacetamide (DMAc) with 5 wt% LiCl by the solution polycondensation method. Inherent viscosities of these polymers were in the range 0.29 to 0.44 dL g⁻¹, indicating formation of moderate molecular weights. These polymers exhibited good solubility in various polar aprotic solvent such as *N*-methyl-2-pyrrolidone (NMP) and H₂SO₄ etc. However, some polymers showed partial solubility in DMF, DMAc and THF etc. X-Ray diffraction pattern of polymers showed amorphous nature. Thermal stability was assessed by 10% weight loss temperature and the degradation temperature of the resultant polymers falls in the ranges from 396°C to 489°C in nitrogen. The glass transition temperature was in the range of 168-205°C. The structure-property correlation among these polyazomethines were studied; in view of their potential applications as high-performance polymers.

Graphical Abstract



Synthesis of 1, 5-bis (4-(2- aminothiazol-4-yl) phenoxy) naphthalene (II)

Keywords: 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II), processability, Viscosity, Thermal stability.

INTRODUCTION

The azomethine bond $-\text{CH} = \text{N}-$ is formed during polycondensation of aromatic and aliphatic diamines with aromatic and aliphatic dialdehydes. The literature of polyazomethines is extensive [1-4]. Many researchers have tried to synthesize high molecular weight polymers but failed due to poor solubility in common organic solvents. Polyazomethines are of interest because of their high thermal stability, good mechanical properties, which makes them favorable members for aerospace applications [5, 6]. Additionally, polyazomethines exhibit desirable useful properties such as electronic, optoelectronic [7, 8] and liquid crystalline [9, 11], fibers forming, ability to form metal chelates [12-14], energy allocations [15] and for semiconducting properties [16]. The first polyazomethines were reported by Adams and coworkers [17] in 1923. Suematsu and Morgan and coworkers have also reported the synthesis of some soluble, film- and fiber-forming polyazomethine [18]. It is established that the presence of ether linkages in the polymer backbone imparts segmental mobility to the polymer which enhances the solubility and lowers the glass transition temperature. To enhance the processability of aromatic polyazomethines, the present study describes a successful synthesis of new soluble and processable aromatic polyazomethines without much sacrifice of thermal stability by incorporation of aromatic naphthalene moiety and heterocyclic thiazole group into the polymer backbone. A new aromatic diamine monomer having aromatic naphthalene as well as heterocyclic thiazole group was designed and synthesized, which was subjected to polycondensation with various aromatic dialdehydes.

MATERIALS AND METHODS

Measurements: FTIR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer. NMR spectra were recorded on a Bruker 400 MHz spectrometer for ^1H spectrum and 100 MHz for ^{13}C spectrum measurements using (d_6 -DMSO). Inherent viscosity of polymers was measured with 0.5% (w/v) solution of polymer in N, N-dimethylformamide at $30 \pm 0.1^\circ\text{C}$ using an Ubbelohde Suspended Level Viscometer. Solubility of polyamides was determined at concentration of 3% (w/v) in different solvents at room temperature or on heating. Dried polymer powder was used for X-ray measurements. Differential scanning calorimetry (DSC) measurements were made on a Mettler Toledo Instrument at a heating-cooling rate of $10^\circ\text{C min}^{-1}$ under nitrogen. The T_g was taken at the middle of the step transition in the second heating run. Thermogravimetry (TGA) was measured on a Mettler Toledo Instrument. A heating rate of $10^\circ\text{C min}^{-1}$ was used for the determination of the decomposition temperature (T_d) at a 10% weight loss under nitrogen environment. X-ray diffraction patterns of polymers were obtained on a RigakuDmax 2500 X-ray diffractometer.

Materials: All the solvents/chemicals were purified before use by using standard procedures. The reagents such as 1, 5 Naphthalol, 4-fluoro acetophenone, Thiourea, Iodine, Terephthalaldehyde (TPA), Isophthalaldehyde (IPA) were purchased from Sigma Aldrich (USA) and used as received. DMAc was purified by vacuum distillation from barium oxide. Potassium carbonate (K_2CO_3) was dried under vacuum at 150°C for 6 h. Lithium chloride was dried under vacuum at 150°C for 6h.

Monomer Synthesis

Synthesis of 1, 5-bis (4-acetylphenoxy) naphthalene (I): In a 500 mL three neck round bottom flask equipped with calcium chloride guard tube, thermo well, N_2 gas inlet were placed 8g 1, 5-naphthol (0.05 mol) and 13.814 g 4-fluoroacetophenone (0.1mol) in 125 mL N, N-dimethyl acetamide (DMAc), then 13.821g of anhydrous K_2CO_3 was added. The resulting reaction mixture was refluxed for 5 h. The progress of reaction was studied by TLC method. After completion, reaction mixture was cooled to room temperature and water was added in it for precipitating the product from solution. Finally, the product was isolated by filtration, washed with water and finally dried under vacuum. Yield: 16.60 g (83.83 %), M. P: 144°C . IR: 3033, 2974, 1696, 1594, 1403, 1222, 1071, 1062, 815, 774 cm^{-1} .

Synthesis of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II): In a 100 mL three neck round bottom flask added compound (I) 0.508 g (0.001 mol) and iodine 0.252 g (0.003mol), thiourea 1.2 g (0.006mol) and the mixture was stirred in THF at reflux for 48 h. Then poured the solution with stirring in water, the yellow solid was obtained. Product (II) was recrystallized in ethanol. Yield: 11.80 g (81.49 %), M.P.: 165°C. **IR:** 3300, 3275, 3091, 3010, 1607, 1509, 1376, 1219, 1157, 1014, 827,781 cm^{-1} . **$^1\text{H NMR}$ ($\text{d}_6\text{-DMSO}$):** δ = 7.92 (dd, 2H), 7.87 (dd, 4H), 7.5 (t,2H),7.34 (dd 4H), 7.12 (dd,2H) , 6.23 (s, 2H), 4.71 (s,4H), **$^{13}\text{C NMR}$ ($\text{d}_6\text{-CDCl}_3$):** δ = 173.18, 156.38, 153.02, 131.08, 130.17, 128.24, 126.24, 118.69, 118.50, 117.40, 114.27, 100.20. **Mass Spectra m/e ($m+1$) = 509.**

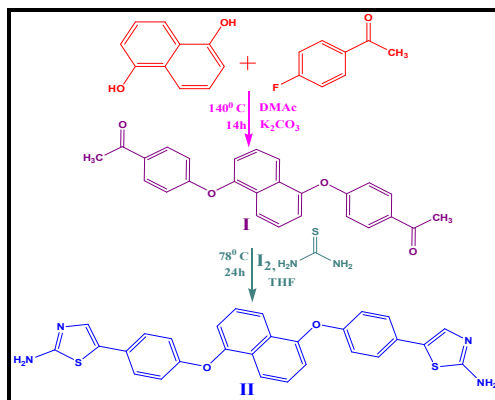
Polymer Synthesis

Synthesis of poly (ether-azomethine)s from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy)naphthalene (II): In a 100 mL three neck round bottom flask equipped with reflux condenser, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0.508 g 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) (1 mmol), in 3 mL N, N-dimethylacetamide (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 (PAM-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 0.44 dL g^{-1} . The polyazomethines and co-polyazomethines PAM-2 to PAM-5 were synthesized with varying mol proportion of TPA and IPA by similar procedure.

RESULTS AND DISCUSSION

A new diamine monomer bearing naphthyl Moiety, viz. 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) have been synthesized and used as building blocks for synthesis of new series of poly (ether-amide)s. These poly (ether-amide)s were characterized by IR, inherent viscosity, solubility, thermal study and XRD.

Synthesis of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II): New thiazole amine 1, 5-bis (4-(2- aminothiazol-4-yl) phenoxy) naphthalene (II) was successfully synthesized in several steps starting from 1, 5-naphthol (Scheme-1).



Scheme 1. Synthesis of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II)

The 1, 5-bis (4-acetylphenoxy) naphthalene (I) was obtained by reacting 1, 5-naphthol with 4-fluoroacetophenone and potassium carbonate as catalyst in DMAc. The structure of (I) was characterized by infrared spectroscopy. The infrared spectrum (Fig. 1) showed medium strong absorption bands at 3033 and 2974 cm^{-1} showing the presence of aliphatic C-H stretching vibration. Spectrum also shows absorption near 1403 cm^{-1} due to C-H bending vibration. Absorption at 1696 cm^{-1}

¹ of carbonyl (C=O) stretching adsorption indicated acetyl carbonyl moiety. The absorption band in the region 1222 and 1071 cm^{-1} show C-O-C stretch.

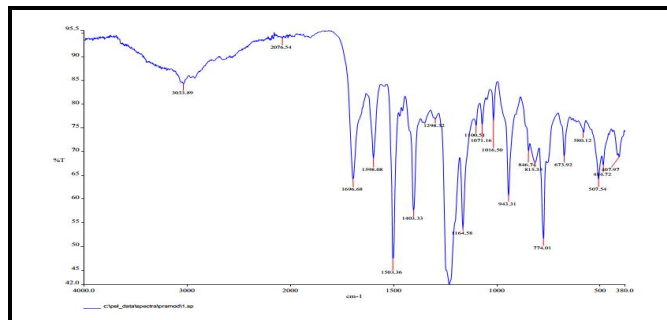


Figure 1. FT-IR spectrum of 1, 5-bis (4-acetylphenoxy) naphthalene (I).

The new thiazole amine monomer 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) was confirmed by IR, NMR (¹H and ¹³C) and mass spectroscopy. FT-IR spectrum of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) (Fig.2.) exhibited N-H stretching absorption bands at 3253 cm^{-1} (asymmetric N-H stretching) and 3075 cm^{-1} (symmetric N-H stretching) and C-O-C stretching at 1236 cm^{-1} and 1151 cm^{-1} . Band at 3015 cm^{-1} is due to aromatic C-H stretching of naphthyl moiety and very broad absorption bands near 3320 cm^{-1} was corresponding to N-H stretch of -NH₂ group.

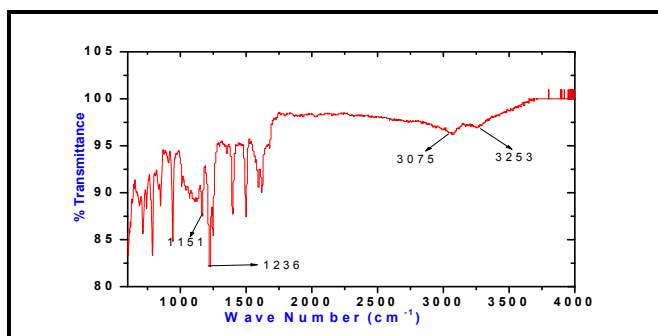


Figure 2. FTIR spectrum of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II).

The proton NMR spectrum of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) (Fig. 3) showed the NMR singlet at 4.71 δ (4H) corresponding to amine (-NH₂) proton. The signals in the range of 7.34 and 7.12 δ of (8H) are attributed to the aromatic protons of phenylene rings whereas signal at 7.92, 7.87 and 7.5 δ (6H) are assigned to naphthalene proton. The NMR signal appears at 6.23 δ (2H), singlet attributed to methylene of -CH attached to Thiazole ring. The ¹³C NMR spectrum (Fig. 4) of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy)naphthalene (II) 12 NMR signals corresponding to 12 different types of carbons. The amine attached carbon appeared at 173.18 δ for (C-NH₂); whereas quaternary carbons showed signals at 156.38, 153.02, 130.17 and 128.24 δ . The CH carbons appeared at 131.08, 126.24; 118.69, 118.50, 117.40, 114.27 δ whereas CH carbon bind with sulphur showed NMR signals at 100.02 δ .

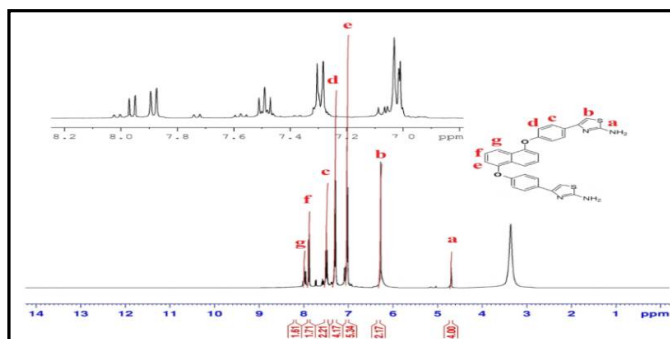


Figure 3. $^1\text{H-NMR}$ of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II).

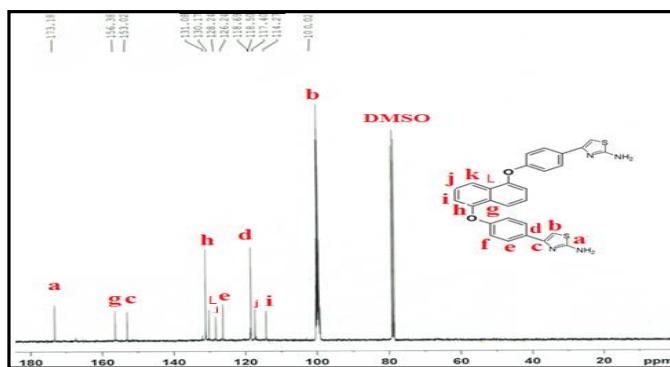


Figure 4. $^{13}\text{C-NMR}$ of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II).

The mass spectrum of 1, 5-bis (4-(2- aminothiazol-4-yl) phenoxy) naphthalene (II) (Fig. 5) showed molecular ion peak at m/e ($m+1$) at 509 corresponding to molecular weight of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II)

From all the above spectral characterization data, it confirmed that, 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) diamine monomer was formed. A series of co-poly(ether-azomethine)s were synthesized as outlined in (Scheme 2.) by elevated temperature solution polymerization of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II) with dialdehydes TPA and/or IPA in DMAc containing LiCl. Lithium chloride was used to absorb water formed during the polycondensation. The polymerization preceded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous solutions in water.

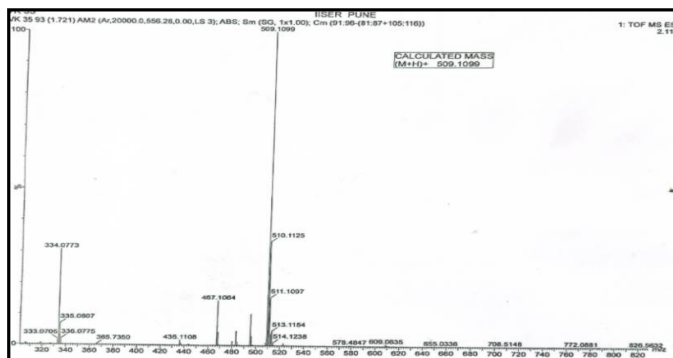
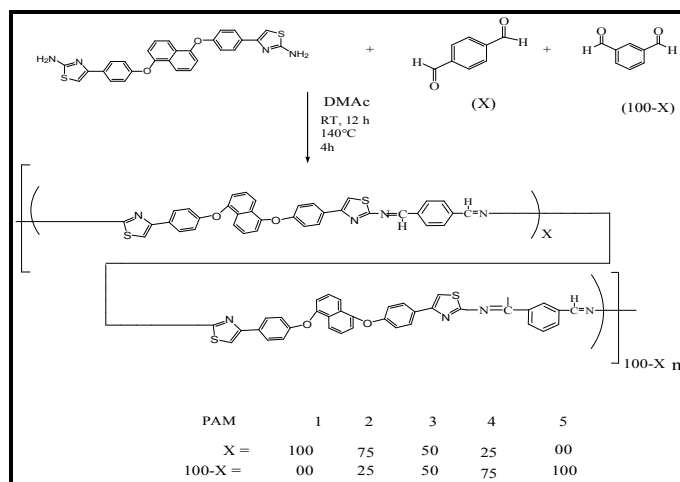


Figure 5. Mass spectrum of 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy) naphthalene (II).



Scheme 2. Synthesis of poly (ether-azomethine)s obtained from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy) naphthalene (II) and aldehyde.

The yield and viscosity obtained are presented in table 1. The inherent viscosities of all these polymers were determined in NMP and ranged from 0.29 to 0.44 dLg⁻¹. The data of these poly (ether-azomethine)s are presented in table 1.

Table 1. Yield and viscosity of poly (ether-azomethine)s obtained from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy) naphthalene (II) and aldehyde

Polymer Code	Monomers			Yield %	Inherent Viscosity dLg ⁻¹
	Diamine Mol %	TPA Mol%	IPA Mol%		
PAM-1	100	100	0	99	0.44
PAM-2	100	75	25	98	0.39
PAM-3	100	50	50	97	0.33
PAM-4	100	25	75	98	0.29
PAM-5	100	0	100	99	0.31

^ainherent viscosity was measured at a concentration of 0.5dLg⁻¹ in NMP at 30°C.

The polymers were characterized by the infrared spectroscopy. The IR spectrum of poly (ether-azomethine) PAM-1, (Fig. 6) showed the characteristic absorption at 1621 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1242 and 1144 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 821 cm⁻¹ indicates para catenation of aromatic rings. The IR spectrum of poly (ether-azomethine) PAM-2, (Fig. 6) showed the characteristic absorption at 1618 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1249 and 1158 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The IR spectrum of poly (ether-azomethine) PAM-3, (Fig. 6) showed the characteristic absorption at 1627 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1255 and 1165 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The IR spectrum of poly (ether-azomethine) PAM-4(Fig. 6) showed the characteristic absorption at 1621 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1242 and 1165 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage. The IR spectrum of poly (ether-azomethine) PAM-5(Fig 6) showed the characteristic absorption at 1613 cm⁻¹ (CH = N stretching). The sharp bands occurring at 1246 and 1151 cm⁻¹ in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the(C-O-C) ether linkage.

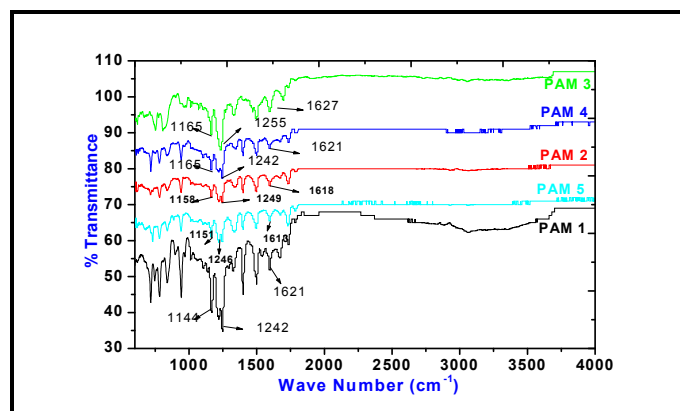


Figure 6. FT-IR spectrum of PAM- 1 to PAM- 5 obtained from 1, 5-bis (4-(2-aminothiazol -4-yl)phenoxy) naphthalene (II) and aldehyde

Properties of poly(ether-azomethines)

Solubility properties: Solubility characteristics of poly (ether-azomethine)s are summarized in table 2. It is observed that the entire poly (ether-azomethine)s PAM-1 to PAM-5 exhibited solubility in organic solvent N-methylpyrrolidone (NMP) and also shows partial solubility in solvents such as THF and DCM. All these Polyazomethines (PAM-1 to PAM-5) are insoluble in solvents such as DMF, DMAc and DMSO. Polymer PAM-1 synthesized from terphthaldehyde (TPA) exhibit less solubility due to its stiff structure attributed more close packing of polymer chains. But polyazomethine PAM-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 naphthyl moiety and ether linkages in the polymer backbone.

Table 2. Solubility behaviour of Poly (ether-azomethine)s obtained from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy) naphthalene (II) and aldehyde

Solvent	PAM-1	PAM-2	PAM-3	PAM-4	PAM-5
DMAc	--	+ -	+ -	++	+ -
DMSO	--	+ -	++	++	+ -
DMF	--	+ -	+ -	++	+ -
NMP	++	++	++	++	++
THF	+ -	+ -	+ -	+ -	+ -
DCM	++	++	++	+ -	+ -
m- Cresol	++	+	+	++	++
Pyridine	+	+	+	+	+
H ₂ SO ₄	++	++	++	++	++

(++) Soluble at room temperature, (+) soluble on heating, (+-) partially soluble, (--) insoluble,

^a Solubility measured at a polymer concentration of 3% (w/v)

Thermal properties: Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. Table 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.

The thermal stability of poly (ether-azomethine)s outlined in (Fig. 7) was studied at a heating rate of 10°C min⁻¹ in nitrogen atmosphere by thermogravimetric analysis. T_d values were in the range of 396°C to 489°C. In general, these polymers are good thermal stability in nitrogen; 10% weight loss

Table 3. Physical properties of Poly (ether-azomethine)s obtained from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy) naphthalene (II) and aldehyde

Polymer	T _i (°C)	T ₁₀ (°C)	T _g (°C)	Residual Wt% at 900°C
PAM-1	313	396	168	49
PAM-2	364	436	174	48
PAM-3	383	451	185	50
PAM-4	402	478	194	52
PAM-5	425	489	205	53

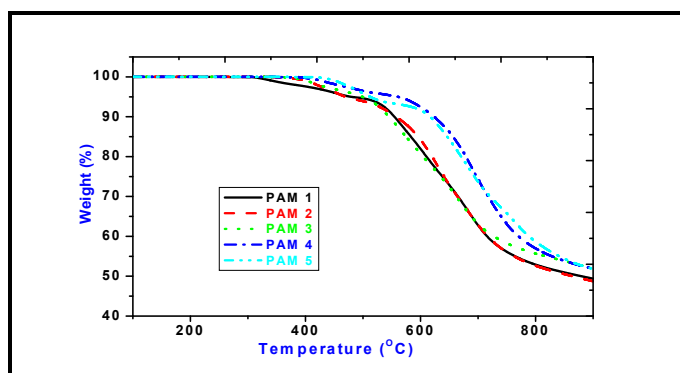
T_i – Initial decomposition temperature.

T₁₀ – Temperature of 10% decomposition.

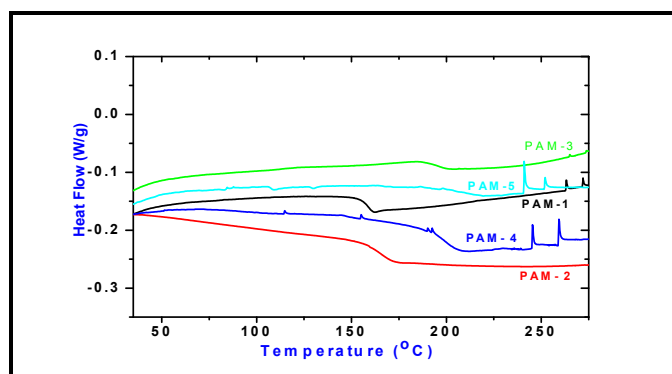
T_g- Glass transition temperature determined by DSC at a heating rate of 10°C min⁻¹.

^aTemperature at which onset of decomposition was recorded by TGA at a heating rate of 10°C min⁻¹.

only takes place when they are heated beyond 396°C in nitrogen. The initial decomposition temperature (T_i) was in the range of 313°C to 425°C. The residual weight at 900°C was in the range of 49-53%.

**Figure 7.** TGA curve of poly(ether-azomethine)s obtained from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy) naphthalene (II) and aldehyde

All the polymers show T_g in between 168-205°C. The higher T_g of PAM-1 compared to the T_g of other polymers is due to the usage of terphthaldehyde (TPA) which exhibits rigid structure attributed more close packing of polymer chains.

**Figure 8.** DSC of curve of poly (ether-azomethine)s obtained from 1, 5-bis (4-(2-aminothiazol-4-yl)phenoxy) naphthalene (II) and aldehyde.

X-Ray diffraction: 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. 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. 9) It is observed that, the all polymer is amorphous in nature. This may be attributed to the copolymerization of novel diamine with IPA and TPA, introduction naphthyl moiety of novel diamine monomer and ether linkages which may have disrupted the chain regularity and packing leading amorphous nature. But PAM-2 is crystalline in nature.

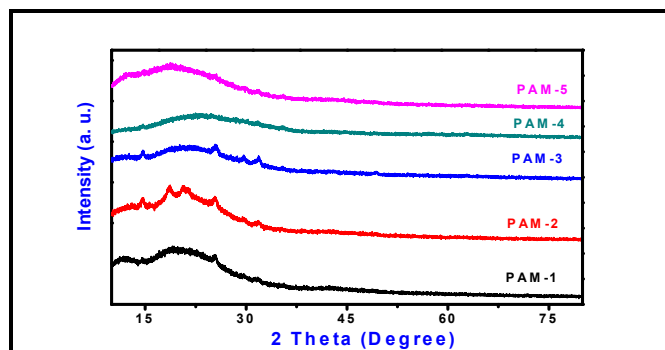


Figure 9. XRD curve of poly (ether-azomethine)s obtained from 1, 5-bis (4-(2- aminothiazol-4-yl)phenoxy)naphthalene (II) and aldehyde.

APPLICATION

Based on results, future perspective will be to make composites of these polyazomethines with nanoparticles to improve electrochemical properties for applications such as supercapacitors, construction, sensors etc.

CONCLUSIONS

New series of poly(ether-azomethine)s were synthesized from obtained from 1, 5-bis (4-(2-amino thiazol-4-yl)phenoxy) naphthalene (II) and aldehyde with different compositions of dialdehydes such as isophthalaldehyde and terphthalaldehyde in N, N'- dimethyl acetamide (DMAc) with 5 wt% LiCl by the solution polycondensation method. Inherent viscosities of these polymers were in the range 0.29 to 0.44 dL g⁻¹, indicating formation of moderate molecular weights. These polymers exhibited good solubility in various polar aprotic solvent such as N-methyl-2-pyrrolidone (NMP) and H₂SO₄ etc. However some polymers showed partial solubility in DMF, DMAc and THF etc. X-ray diffraction pattern of polymers showed amorphous nature. Thermal stability was assessed by 10% weight loss temperature and the degradation temperature of the resultant polymers falls in the ranges from 396°C to 489°C in nitrogen. The glass transition temperature was in the range of 168-205°C. The structure-property correlation among these polyazomethines were studied; in view of their potential applications as high performance polymers.

REFERENCES

- [1]. G. F. D'Alelio, *Encycl. Polym. Sci. Technol.*, **1969**, 10, 659.
- [2]. R. J. Cotter and M. Matzner, *Org. Chem. (N.Y.)*, **1972**, 13B (1), 1.
- [3]. S. Banejee, S. K. Palit, and S. Maiti, *J. Polym. Mater.*, **1992**, 9, 219.
- [4]. P. W. Morgan, T. C. Pletcher, and S. L. Kwolek, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **1983**, 24(2), 470.
- [5]. S. S. Ankushrao, Y. S. Patil, V. P. Ubale, N. N. Maldar, A. A. Ghanwat., *Journal of Macromolecular Science, Part A Pure and Applied Chemistry*, **2017**, 54(6), 411-417.
- [6]. P. H. Salunkhe, S. S. Ankushrao, Y. S. Patil, J. N. Mahindrakar, V. N. Kadam, V. P. Ubale, A. A. Ghanwat *J. Macromol. Sci, Part A.*, **2018**, 55, 377-383.
- [7]. A. Iwan, D. Sek, *Prog. Polym. Sci.*, **2011**, 36, 1277-325.

- [8]. A. W. Jeevadason, K. K. Murugavel, M. A. Neelakantan, *Renew. Sustain. Energy Rev.*, **2014**, 36, 220-227.
- [9]. A. Wan, *Polimery*, **2010**, 4, 253-266.
- [10]. A. Iwan. *PraceInstytutuElektrotechniki*, **2011**, 1-57.
- [11]. A. Iwan, Schab-Balcerzak, E., Editors. Liquid crystalline organic compounds and polymers Asmaterials XXI century: From synthesis to applications. *In: Transworl Research Network, Kerala, India*, ISBN: **2011**, 978-81-7895-523-0.
- [12]. M. Grigoras, C. J. Catanescu, *Macromol. Sci.*, 2004, 44, 131-173.
- [13]. C. J. Yang, S. A. Jenekhe, *Chem. Mater.*, **1994**, (6), 196-203.
- [14]. C. Wang, S. Shieh, E. Le Goff, *Macromol.* **1996**, 29, 3147-3156.
- [15]. P. H. Salunkhe, Y. S. Patil, V. B. Patil, Y. H. Navale, I. A. Dhole, V. P. Ubale, N. N. Maldar, A. A. Ghanwat, *Journal of Polymer Research*, **2018**, 25, 127.
- [16]. Y. Saegusa, K. Sekiba, and S. Nakamura, *J. Polym. Sci. Part A: Polym. Chem.*, **1990**, 28, 3647.
- [17]. R. Adams, R. E. Bullock, and W. C. Wilson, *J. Am. Chem. SOC.*, **1923**, 46, 521.
- [18]. P. W. Morgan, S. L. Kwolek, and T. C. Pletcher, *Macromolecules*, **1987**, (20), 729.