

Synthesis and Characterization of Aromatic Polyazomethines Containing 1,2,4-Triazole Moiety.

A. B. Tamboli, N. A. Tupsamindar, N. N. Maldar*

School of Chemical Sciences, Solapur University, Solapur; Kegaon, Solapur- 413255 (India).

ABSTRACT: New aromatic polyazomethines containing 1,2,4-triazole moiety were synthesized by solution polycondensation of new aromatic diamine namely 3,5-bis (4'-amino phenyl) -4-(4''-methoxy-2''-pentadecyl phenyl)1,2,4-triazole (VII) and isophthalaldehyde(IPA) or terephthalaldehyde(TPA). Three Co-polyazomethines were also synthesized from diamine (VII) and various mole proportion of (IPA+TPA). Inherent viscosities of these polymers were in the range of 0.13 to 0.23dL/g in DMF indicating moderate molecular weight built up. Solubility of these polyazomethines was tested and these polymers dissolved in aprotic polar solvents such as DMF, DMAc, NMP, DMSO, due to presence of substituents methoxy and long alkyl chain i.e. pentadecyl group on pendant aromatic ring to the chain of polymer. Thermal stability of polymers was determined by Thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10⁰C/min. These polymers did not show any loss in weight upto 370⁰C whereas temperatures for 10% weight loss of the polymers were in the range of 398-425⁰C indicating good thermal stability. The glass transition temperatures (T_g) of these polyazomethines were determined by Differential Scanning Calorimeter (DSC) in nitrogen atmosphere at a heating rate of 10⁰C/min. The polymers showed lower glass transition temperatures, in the range of 110-125⁰C due to presence of long aliphatic pentadecyl group which acts as an internal plasticizer and it also avoids close packing of polymer chains. XRD analysis of the polymer structure showed the amorphous nature as evidenced by broad hollow in the region of 2θ of 10 to 35⁰. These polymers are being analysed further by conductivity measurement.

Keywords: pentadecyl chain, soluble -processable polyazomethines, 1,2,4-triazole moiety, thermal stability,

I. INTRODUCTON

Azomethine is formed by condensation of aromatic/aliphatic diamine with aromatic/aliphatic dialdehyde. The literature of polyazomethines is extensive¹⁻². A number of researchers have tried to synthesize high molecular weight polymers but failed due to poor solubility of aromatic polyazomethines in commonorganic reactionsolvent. Hence the preparation of high-molecular-weight polyazomethines is complicated by precipitation of the polymer during the polymerization process³. Various studies have been undertaken to overcome this limitation by modifying the polyazomethine structure; specifically, these studies have attempted to improve the solubility of the polymer by by introduction of flexible group, ether, ketone, aliphatic long chain,⁴⁻⁷ etc.

Aromatic polyazomethines exhibit extremely interesting properties which are associated mainly with their polyconjugated backbone. They have good thermal stability, chelate forming ability, semiconducting and good optoelectronics properties, thermotropic liquid crystalline behavior etc. Polyazomethines are generally infusible, and insoluble materials. As a result, only a few studies have reported⁸ Polyazomethines containing the nitrogen atom in the main chain with hybridization sp² has attracted a deal of interest due to the potential application of such materials in electronics, optoelectronics, and photonics, high-Performance properties⁹⁻¹² derived from high thermal stability and good mechanical strength.

In the present investigation we have synthesized new aromatic diamine namely 3,5- bis (4'-aminophenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII) and characterized by FT-IR, NMR (¹H, ¹³C), DEPT, spectroscopy and mass spectrometry. (VII) was utilized as building block to obtain various polyazomethines by polycondensation with isophthalaldehyde and terephthalaldehyde. These polyazomethines and co-polyazomethines were analysed by FT-IR, Viscosity, TGA-DSC, XRD, etc. to illustrate structure property relationship. Medium to high molecular weight polymers with good solubility in organic aprotic polar solvent, having lower T_g and good thermal stability were obtained.

II. EXPERIMENTAL

2.1 Materials:

3-Pentadecyl phenol, terphthaldehyde (TPA), isophthaldehyde (IPA), 10%Pd/C ,(all Aldrich make). Hydrazine hydrate, PCl₅, 4-Nitro benzoic acid, thionyl chloride (all s.d.fine chemical), were used as received.

Techniques

The FT-IR spectra of the monomers and polymers were recorded using Nicolet spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained with a Bruker Advance spectrometer at operating temperature of 25^oC using CDCl₃ and DMSO- d₆ as solvent. Inherent viscosities of polymers were measured at a polymer concentration of 0.5g/dL in DMF solvent at 30^oC using an Ubbelohde suspended level viscometer. Differential scanning calorimetry (DSC) were performed on a Mettler Toledo DSC STAR^x instrument at heating rate of 10^o/min under nitrogen. The glass transition temperature (T_g) was noted in DSC curves. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo STAR^x instrument at heating rate of 10^o/min under nitrogen. Wide angle X-ray diffraction (WAXD) was measured with a Rigaku ray diffractometer.

2.2 Monomer Synthesis:

4-Amino-3-pentadecyl anisole

i) 4-Nitro-3-pentadecyl phenol

3-Pentadecyl phenol (20g, 0.065mol) was dissolved in chloroform (75mL) over a period of 10 minutes, and (5.3g, 1.2 mmol) of fuming nitric acid (sp.gr.1.5) was added to it dropwise with stirring and cooling in an ice bath maintained at 5-10^oC. The solution was stirred for another 20 minutes at 10^oC. The reaction mixture was poured into water, the organic layer was separated by separating funnel. Chloroform solvent was removed by distillation using water aspirator, the residual mass solidified on cooling. After filtration and drying 23g of red orange solid was obtained. The crude solid, mixture of mononitro isomers of 3-pentadecyl phenol was dissolved in 150mL of petroleum ether (60-80^oC) and cooled overnight. About 10g of light tan powder of 4-nitro-3-pentadecyl phenol (I) was separated. This on further recrystallization from the pet. ether gave the desired product. Yield 8.0g (71%), m.p 70-71^oC.

Analysis found: C 72.45% , H 10.33% , N 4.07% ,

Analysis Calculated for C₂₁H₃₅NO₃ : C 72% , H 10.05% , N 4.02% .

ii) 4-Nitro-3-pentadecyl anisole

In one neck round bottom flask equipped with magnetic stirrer. a mixture of dichloromethane (50mL), water (50mL), the 4-nitro-3-pentadecyl phenol (3.63g 10mmol), sodium hydroxide (0.7g 15mmol), the alkylating agent dimethyl sulphate (2.5mL) (20-30mmol), and benzyltributylammonium bromide (0.1g-1 mmol), was agitated with stirrer at room temperature for 12 hrs. The organic layer was then separated and the aqueous layer was extracted twice with dichloromethane. The organic extract was washed with 2 M ammonia solution to remove residual dimethyl sulphate, the solvent was evaporated and the solid 4-nitro-3-pentadecyl anisole (II) was purified by crystallization from methanol. Yield 2.9g (85%), m.p. 49^oC. ¹H NMR (in CDCl₃) (ppm), 0.96 (q, 3H), 1.45 (t, 26 H), 2.5 (t, 2H), 3.8 (s, 3H), 6.7 (d, 1H), 7.9 (d, 1H), 7.2 (s, 1H), 7.9 (d, 1H).

iii) 4-Amino-3-pentadecyl anisole

In three neck round bottom flask (250 mL) equipped with magnetic stirrer, reflux condenser, calcium chloride guard tube, and placed 4-nitro-3-pentadecyl anisole 3.63g (0.01mol), then 10% Pd/C(0.2g), ethanol (50 mL) and heat this reaction mixture at 80^oC. Then hydrazine hydrate (8 mL), was added to reaction mixture dropwise and continue heating reaction mixture at 80^oC for 8 hrs. Reaction mixture was cooled to room temperature and poured into the ice cold water to precipitate solid (III), which was filtered, washed with plenty of water, and crystallized from ethanol. Yield 2.4 g, (80%), m.p. 44^oC. ¹H NMR (in CDCl₃) (ppm), 0.96 (q, 3H), 1.45 (t, 26H), 2.5 (t, 2H), 3.5 (s, 2H), 3.8 (s, 3H), 6.7 (dd, 2H), 7.2 (s, 1H).

iv) Synthesis of bis (4-Nitro benzohydrazide).

4-Nitrobenzoyl chloride (20.0 g, 0.108 mol), hydrazine hydrate (8.5g, 0.17 mol), and NMP (250 mL) were introduced into a two-neck 500mL flask and stirred at room temperature for 5hrs..The product was precipitated by pouring reaction mixture into excess of distilled water. Solid was collected by filtration, washed with ethyl acetate, and dried in a vacuum oven to obtain white crude product bis (4-Nitro benzohydrazide) (IV) which was crystallized from ethanol. Yield 30g (95%). m.p. 296^oC. FT-IR (KBr, cm⁻¹): 3200 (-NH), 1347, 1515 (-NO₂), 1614 (-C=O).

v) Synthesis of 1,2-bis ((4-nitrophenyl) chloromethylene) hydrazine

A mixture of bis(4-Nitro benzohydrazide) 3.93g, 12 mmol) and phosphorus pentachloride (6.12g, 30 mmol) was dissolved in toluene and heated at 120 °C for 5 hrs. Then solvent was removed under vacuum, and the residue was poured into distilled water. The solid was collected by filtration, dried and recrystallized from (ethanol and dichloromethane) (3:1) to afford the yellow solid (V) (2.59g, 60%). m.p. 188°C. FT-IR (KBr, cm⁻¹): 1590 (C=N), 1343, 1524 (-NO₂); ¹H-NMR (DMSO-d₆, ppm): 8.30-8.35 (m, 8H, ArH); Anal. Calcd. For C₁₄H₈N₄Cl₂O₄: C 45.80%, H2.20%, N 15.26%; Found: C45.83%, H 2.25%, N 15.22%.

vi) Synthesis of 3,5-bis (4'-Nitrophenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole.

In 250-mL three-neck flask fitted with an overhead stirrer were charged (III) (2.2g, 6mmol),(V) (2.4g, 7.2mmol), diisopropylamine (1.30g, 10mmol) and xylene (65mL). The flask was fitted with a reflux condenser and heated to reflux with stirring for 48 h. After cooling, the solvent was evaporated and the residue was washed with ethyl acetate. The crude product (VI) was recrystallized from ethanol. Yield 3.5g (70%) m.p. 120°C. FT-IR (KBr,cm⁻¹) 1593 (C=N), 1346, 1526 (-NO₂).

vii) Synthesis of 3,5-bis (4'-amino phenyl)-4(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII)

A mixture of (6.47g, 0.01mol) (VI),hydrazine hydrate (8 mL), ethanol (80 mL) , 10% Pd/C (0.2g) were refluxed for 24 hrs. The mixture was filtered to remove catalyst and the filtrate was poured into cold water to precipitate solid which was collected by filtration, dried, recrystallized from toluene to give (VII). Yield 4.7 g (80%), mp.103°C Anal. Calcd. for C₃₆H₄₉N₅: C 76.19%, H 8.64%, N 12.34%, Found: C75.82%, H8.54%, N 11.36%.

FT-IR (KBr, cm⁻¹): 3369, 3461 (NH₂).¹HNMR (CDCl₃,ppm), 0.96 (t,3H), 1.2 (q,26H), 2.03 (t,2H), 3.7 (s, 2H,NH₂), 3.8 (s, 3H), 6.6 (d,1H), 6.7 (s, 1H), 7.1(d,1H), 7.1(d,4H), 7.2(d,4H).

¹³C NMR, (CDCl₃, ppm) 14, 22, 28, 29, 30, 55, 112, 114, 115, 127, 129, 130, 141, 147, 154, 160.

2.3 Polymer Synthesis:

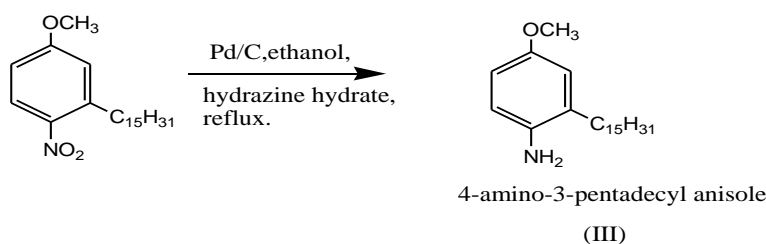
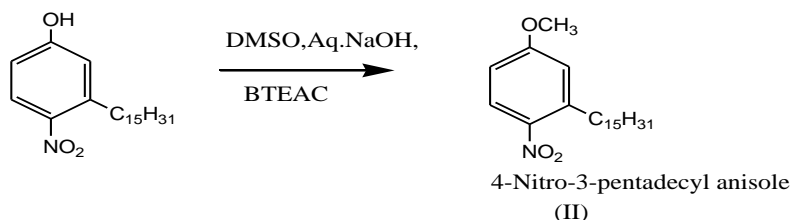
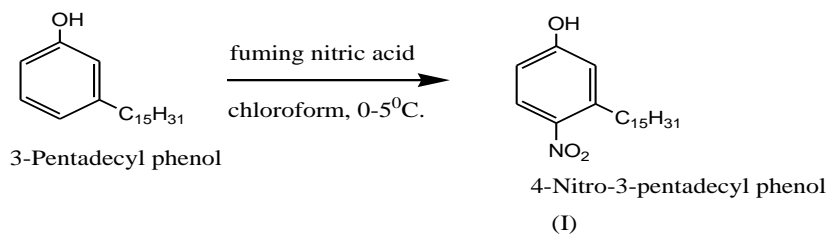
In dry three neck 100mL round bottom flask equipped with nitrogen gas inlet, magnetic stirrer, calcium chloride guard tube, were placed 0.587 g (1mmol) of 3,5-bis (4'-amino phenyl)-4-(4''-methoxy 2''-pentadecyl phenyl) 1,2,4-triazole (VII) dissolved in 4mL m-cresol and cooled in ice bath. Then (0.136 g 91 mmol) of isophthalaldehyde (IPA), was added in small amount over a period of 10 minutes. Stirred the reaction mixture for 24 hr. at room temperature. The viscous mixture was poured into 300 mL methanol polymer precipitates out, it was filtered, washed with hot water, dried in vacuum oven at 80°C for 6 hr. Yield (0.652 g)95%. Similarly all other polyazomethines were prepared.

III. RESULT AND DISCUSSION

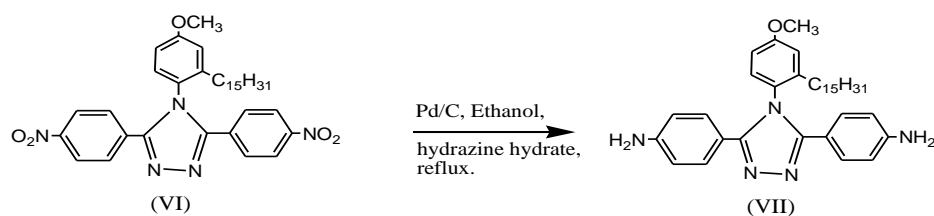
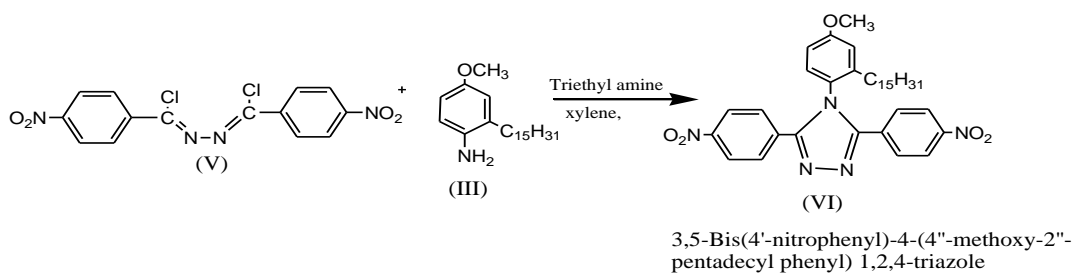
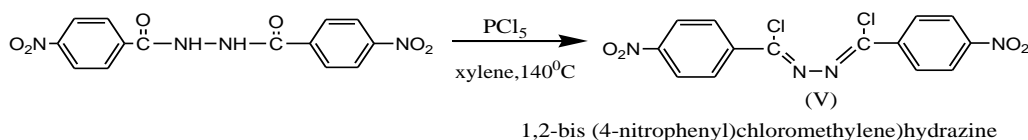
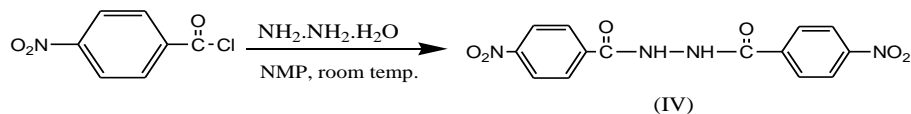
Aromatic polyazomethines exhibit good thermal stability, but show less solubility in common solvents so it becomes difficult for processing and modification. To overcome these limitations of aromatic polyazomethine polymers there is need of incorporation of pendent flexible moiety, into the backbone of polymer. In the present investigation, we have synthesized new aromatic diamine 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole containing long chain aliphatic group i.e. pentadecyl moiety for improving solubility of polyazomethine. Similarly co-polyazomethines were synthesized by using different mol% of two isomericphthalaldehyde (IPA)/TPA.

3.1. Monomer Synthesis:

The aromatic diamine (VII) was synthesized from 3-pentadecyl phenol and characterized by FT-IR, NMR (¹³C, ¹H) and mass spectrometry.



Scheme 1 Synthesis of 4-amino -3-pentadecyl anisole (III).



Scheme 2 Synthesis of 3,5-bis(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII).

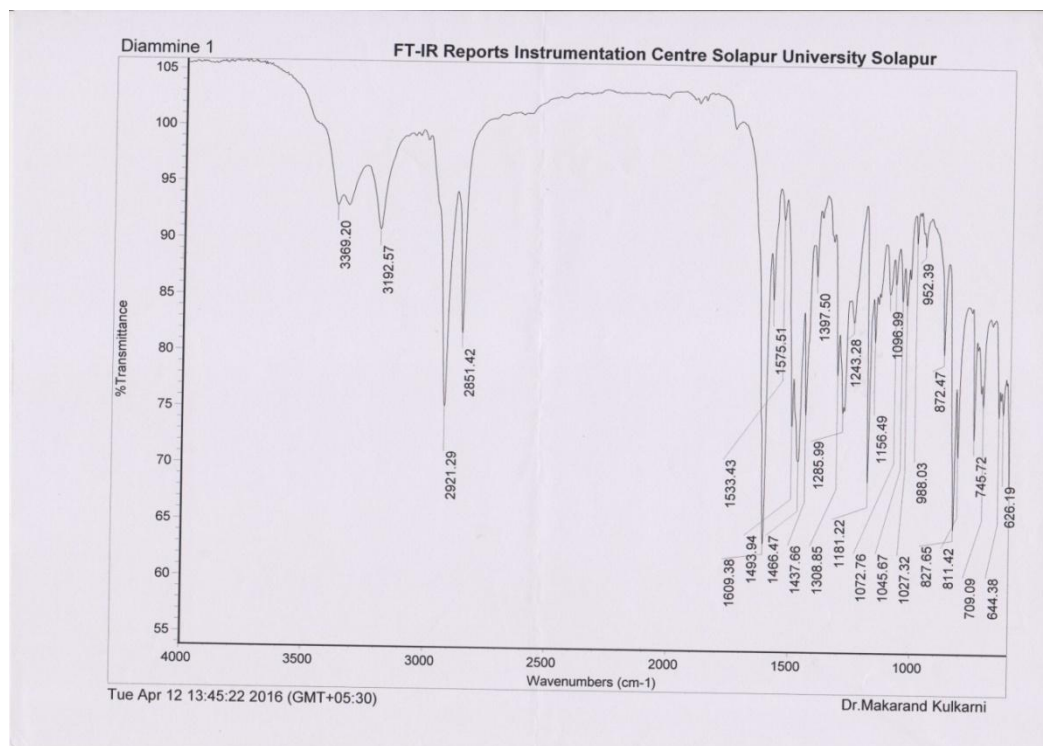


Fig. 1. FT-IR spectrum of 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII).

The structure of (VII) was confirmed by FT-IR spectroscopy. FT-IR spectrum of VII showed absorption bands at 3330-3400 cm^{-1} (NH_2) and stretching at 1593 cm^{-1} shows ($-\text{C}=\text{N}$), indicating the complete cyclization of dihydrazide into 1,2,4-triazole and also complete reduction of nitro group into amino group function in the monomer (VII). The absorption band at 1200-1252 cm^{-1} showed the presence of methoxy ether linkage.

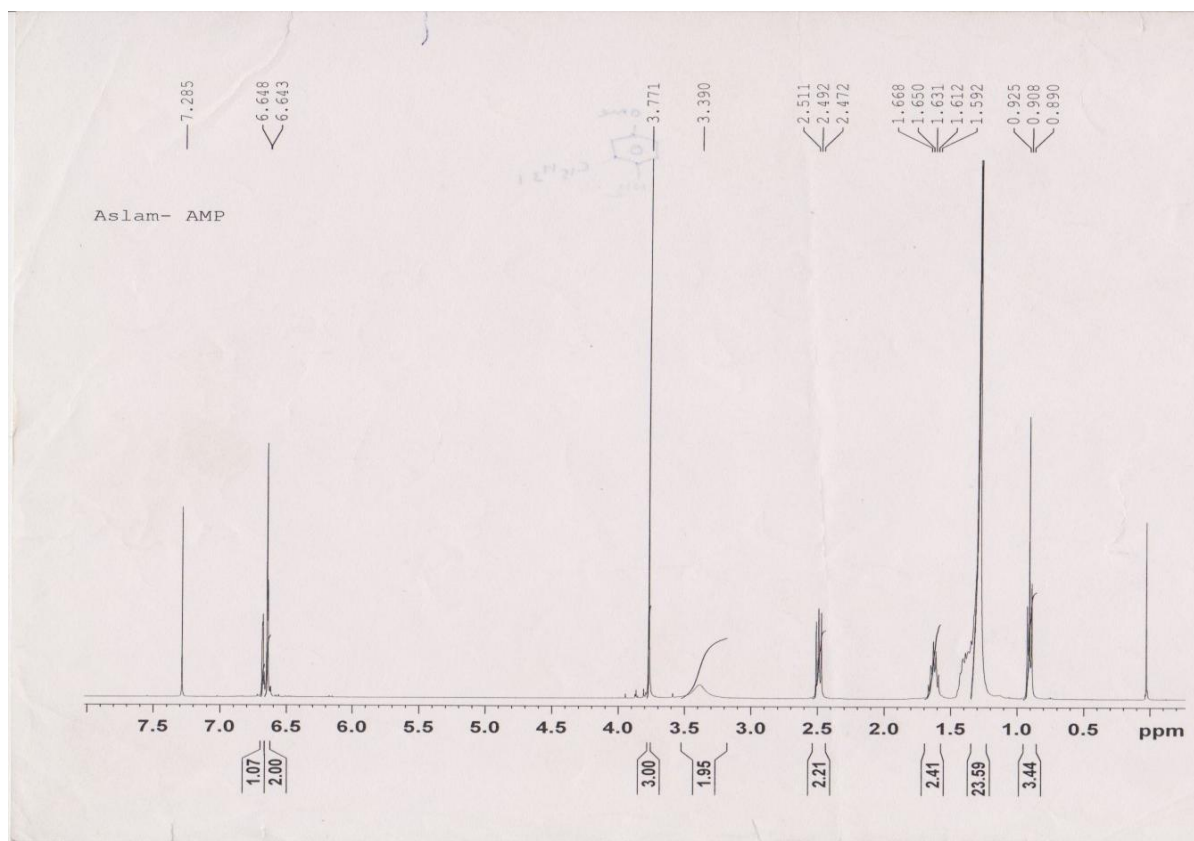


Fig. 2. ^1H NMR spectrum of 4-amino 3-pentadecyl anisole.

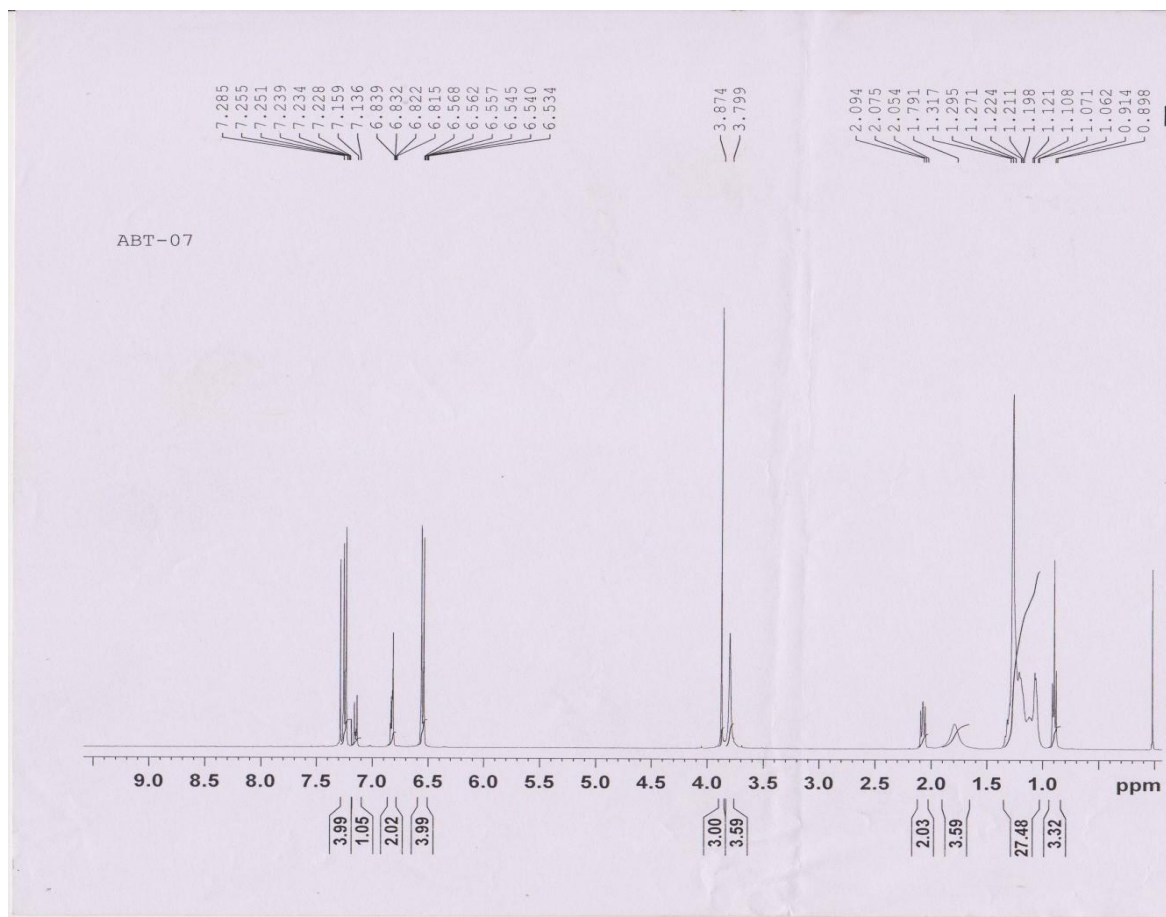


Fig. 3 ^1H NMR spectrum of 3,5- bis (4'-amino phenyl)4-(4''-methoxy-2''- pentadecyl phenyl) 1,2,4- triazole (VII).

The ^1H NMR (CDCl_3 , ppm), 0.96 (t,3H), 1.2 (q,26H), 2.01 (t,2H), 3.7 (s,2H, NH_2), 3.8 (s,3H), 6.6 (d,1H), 6.7 (s,1H), 7.1 (d,1H), 7.1 (dd,4H), 7.2 (d d, 4H),.

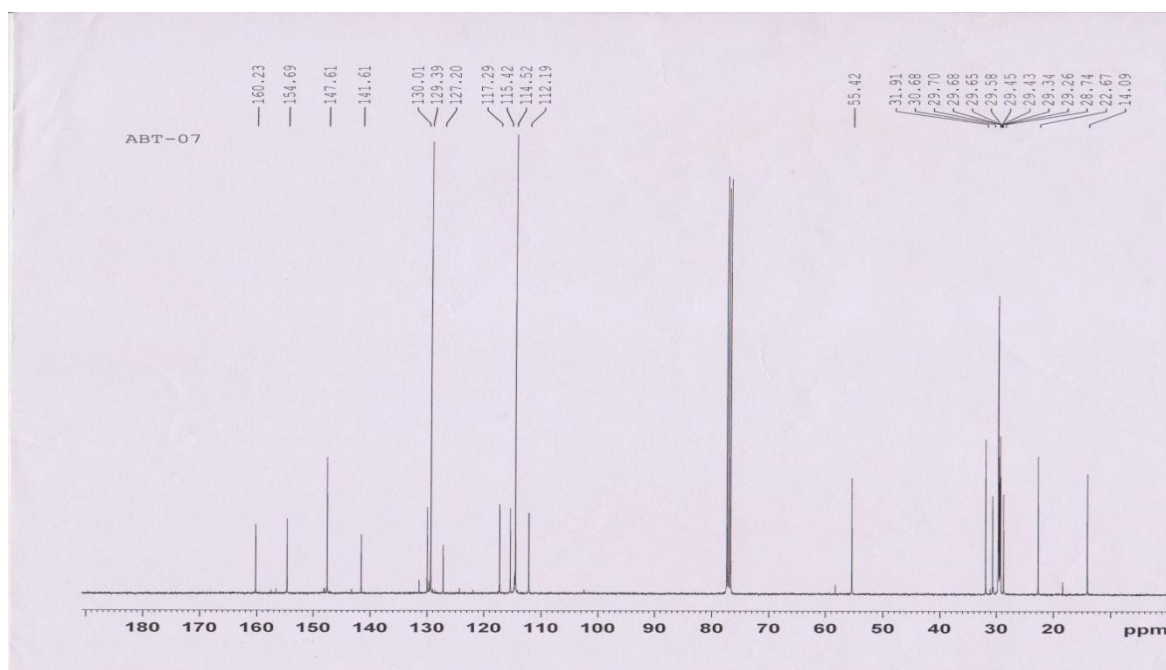


Fig.4 ^{13}C NMR spectrum of 3,5- bis (4'-amino phenyl)4-(4''-methoxy-2''- pentadecyl phenyl) 1,2,4- triazole (VII).

^{13}C NMR: The signal peaks at 154.2 and 154.2 ppm are the characteristic of triazole ring Carbon ($-\text{C}=\text{N}$). The ^1H NMR and ^{13}C NMR illustrated in fig.3, 4 and 5 showed methylene groups present in pentadecyl chain as well aromatic carbons. The ^{13}C peak at 147 ppm shows carbon atom directly attached with $-\text{NH}_2$, and 160 ppm shows methoxy carbon atom attached with $-\text{O}$ group.

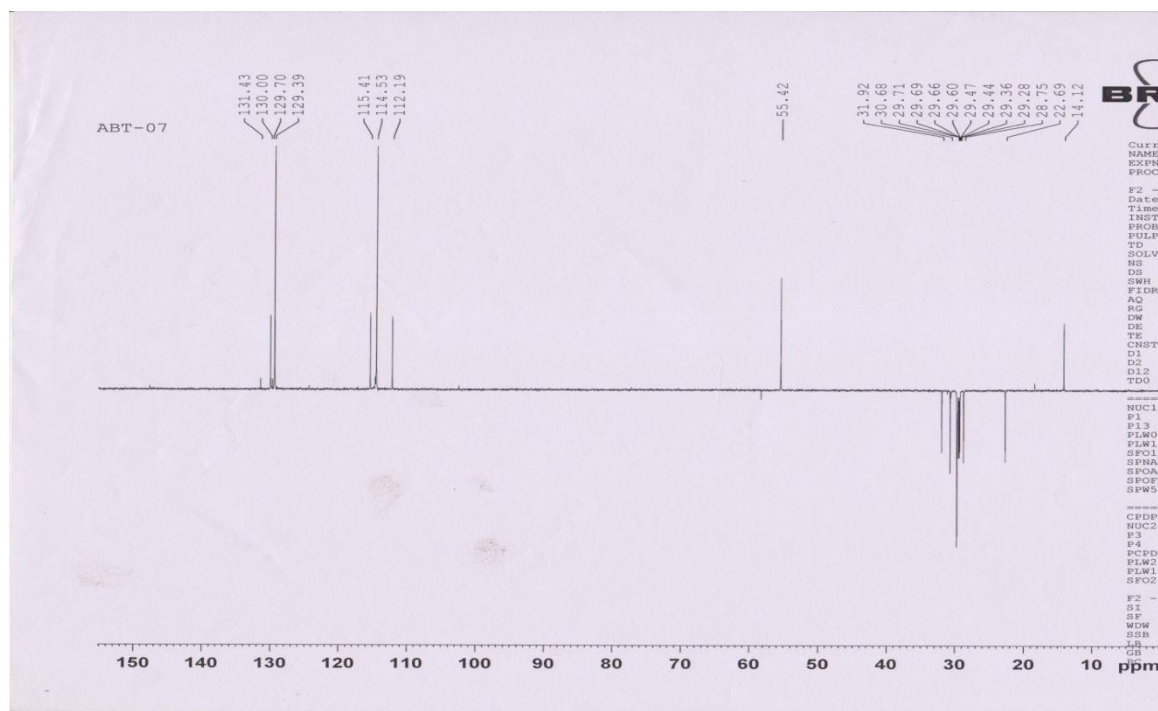


Fig. 5 ^{13}C NMR DEPT spectrum of 3,5- bis (4'-amino phenyl)-4-f(4''-methoxy-2''-pentadecyl phenyl) 1,2,4- triazole (VII).

The structure of (VII) was confirmed by ^{13}C NMR DEPT where the peak- CH_2 - appeared downside, $-\text{CH}$ -carbons remained upside and tertiary carbon peaks disappeared. DEPT (CDCl_3 , ppm) showed methylene group carbons in pentadecyl chain at 14, 22, 28, 29, 30,31,ppm. Mass spectrum of (VII) in Fig. 6. showed (M+1) strong base peak at 568 indicating molecular formula weight of 567, corresponding to $\text{C}_{36}\text{H}_{49}\text{N}_5\text{O}$.

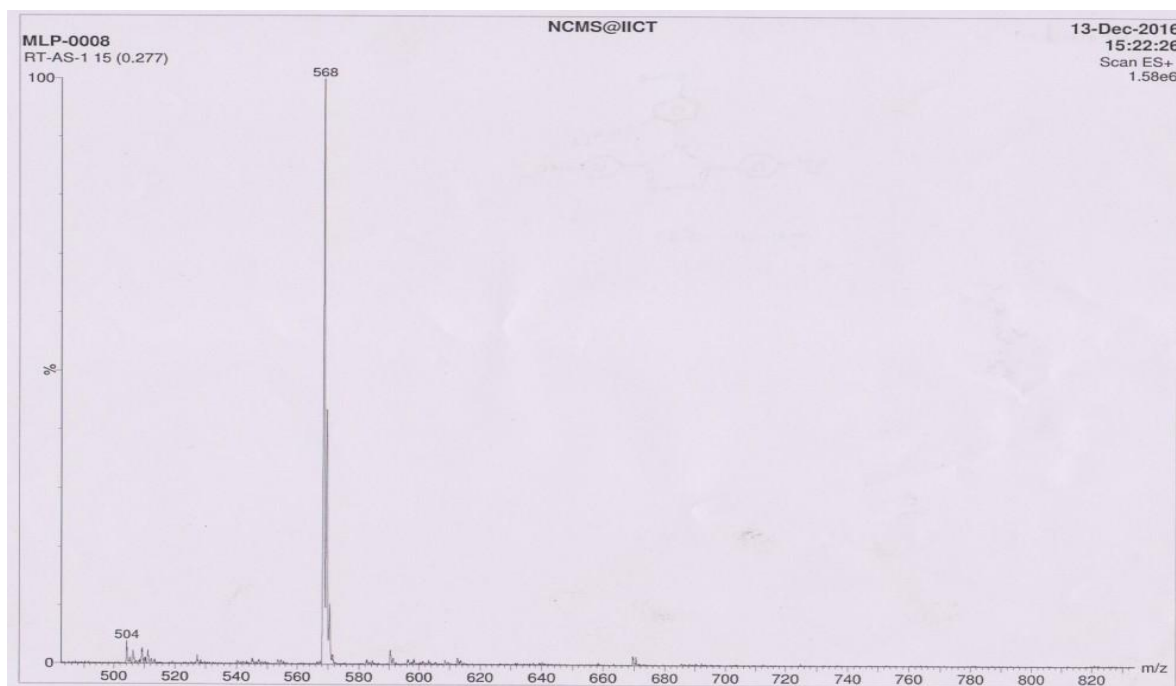
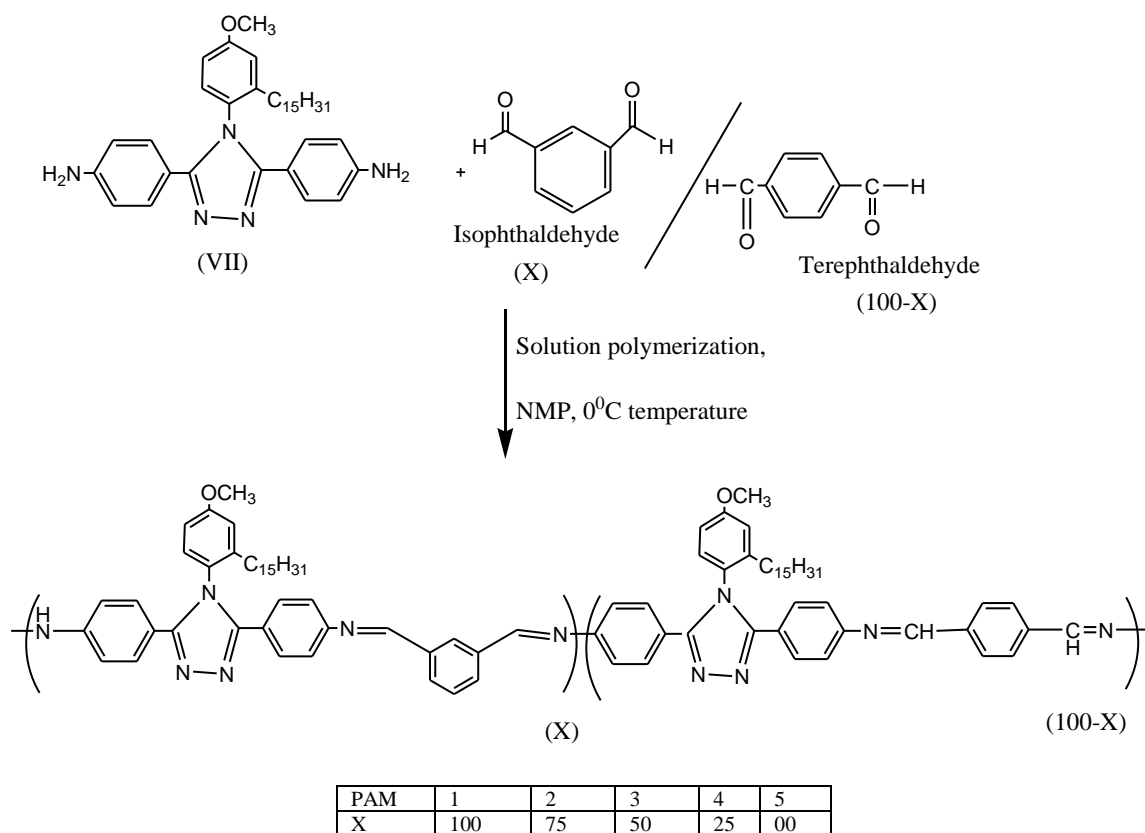


Fig. 6. Mass spectrum of 3,5- bis (4'-amino phenyl)-4-f(4''-methoxy-2''-pentadecyl phenyl) 1,2,4- triazole (VII).

3.2. Polymer synthesis:

The aromatic diamine 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole and isophthalaldehyde (IPA)/ terephthalaldehyde (TPA) co-polymerized to form polyazomethine as shown in scheme 3. Polymers were characterized by, FT-IR, solubility, inherent viscosity, TGA, DSC, and XRD.



Scheme: 3. Polyazomethine Polymer synthesis

The synthesis of co-poly(azomethine) from aromatic diamine 3,5-bis (4'-amino phenyl) -4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole and mixture of IPA/TPA, Yield of polymer, inherent viscosity of polymer and composition is shown in Table no. 1

Table no. 1. Composition, Yield, inherent viscosity of polyazomethines.

Sr. No.	Polymer code	Dialdehydes Mol%		Yield(%)	Inherent Viscosity η_{inh} dL/g
		IPA	TPA		
1.	PAM-1	100	00	97	0.23
2.	PAM-2	75	25	96	0.20
3.	PAM-3	50	50	98	0.13
4.	PAM-4	25	75	95	0.14
5.	PAM-5	00	100	96	0.15

- Polymerization was carried out with 1 mmol each of aromatic diamine and aromatic dialdehyde
- Aromatic diamine 3,5-bis (4'-amino phenyl) -4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII)
- Measured with 0.5% (w/v) polymer solution in DMF solvent.

The formation of polyazomethine was confirmed by FT-IR spectra. A representative IR spectrum of polyazomethine, PAM1 based on IPA, as shown in Fig.6., PAM1 showed characteristic absorption band of azomethine linkage (CH=N) at 1654 cm^{-1} . The disappearance of carbonyl band at around 1700 cm^{-1} due to monomeric dialdehyde and $-\text{NH}_2$ of amino group at $3400, 3387\text{ cm}^{-1}$ confirmed the formation of polyazomethine. Other characteristics absorption band at 2922 cm^{-1} (aliphatic CH), 3057 cm^{-1} (aromatic CH), 1230 and 1165 cm^{-1} (asymmetrical and symmetrical vibration of methoxy ether linkage) were also observed.

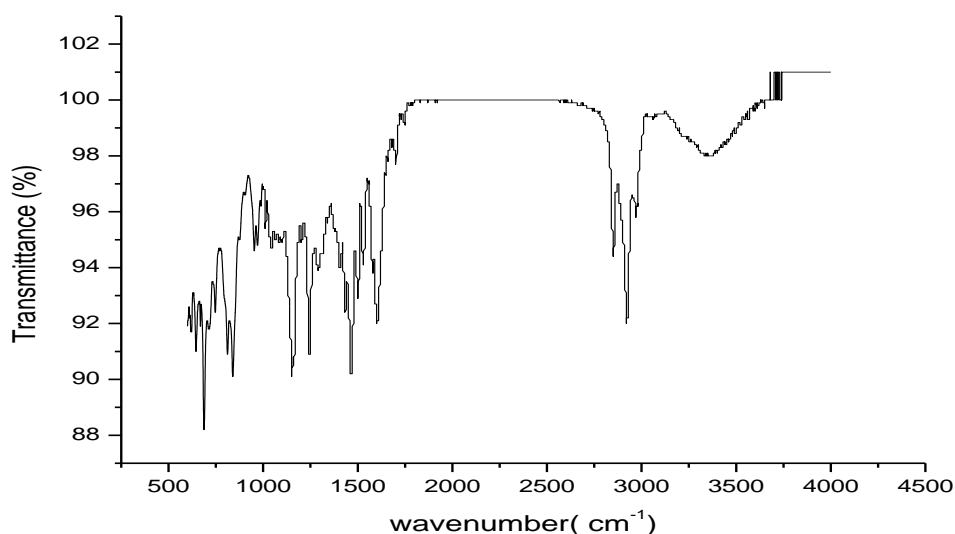


Fig.7.FT-IR spectrum of Polyazomethine (PAM-1)

Solubility behaviour of these poly(azomethine)s was tested qualitatively in various solvents and results are given in Table no. 2. It was observed that the polymers were soluble in aprotic polar solvents such as DMAc, NMP, DMSO, DMF, and m-cresol. The better solubility of these poly(azomethine)s as expected may be due to the presence of long aliphatic pentadecyl substituent on pendant phenyl ring which favours amorphous nature of polymer, as such from XRD data.

Table no. 2: Solubility of poly(azomethine)s

Polymer →	PAM-1	PAM-2	PAM-3	PAM-4	PAM-5
Solvent ↓					
DMAc	++	++	++	++	++
NMP	++	++	++	++	++
DMSO	++	++	++	++	++
DMF	++	++	++	++	++
m-Cresol	++	++	++	++	++
CHCl ₃	--	--	--	--	--

(++): soluble at room temperature, (--): insoluble

Thermal properties of polyazomethines were determined by thermogravimetric analysis and differential scanning calorimetry (DSC) at heating rate of 10°C/min. under nitrogen atmosphere. Initial decomposition temperature and temperature at 10% weight loss (T_{10}) were determined from thermograms and the data is given in Table no. 3. The TGA curves shown in (Fig. 8.) illustrate that the 10% weight loss of polyazomethines were in the range of 398-425°C indicating good thermal stability of polyazomethines. Glass transition temperatures (T_g) of polyazomethine were determined by differential scanning calorimetry (DSC) as shown in (Fig. 9) and the T_g of polyazomethine were in the range of 110-125°C, low glass transition temperatures of polyazomethines are probably due to internal plasticization effect of the long pentadecyl group pendant chain. These polyazomethine showed more solubility as compared to other aromatic polyazomethines^{13,14}.

Table no. 3. Thermal behavior of poly(azomethine)s

Polymer	T_g^a (°C)	T_i^b (°C)	Temperature (°C) at various weight loss%				
			10%	20%	30%	40%	50%
PAM-1	110	372	398	432	491	559	603
PAM-2	120	370	406	437	466	515	626
PAM-3	120	380	400	431	455	477	535
PAM-4	125	398	419	445	461	478	505
PAM-5	125	410	425	456	479	552	640

^aGlass transition temperature, ^bInitial decomposition temperature.

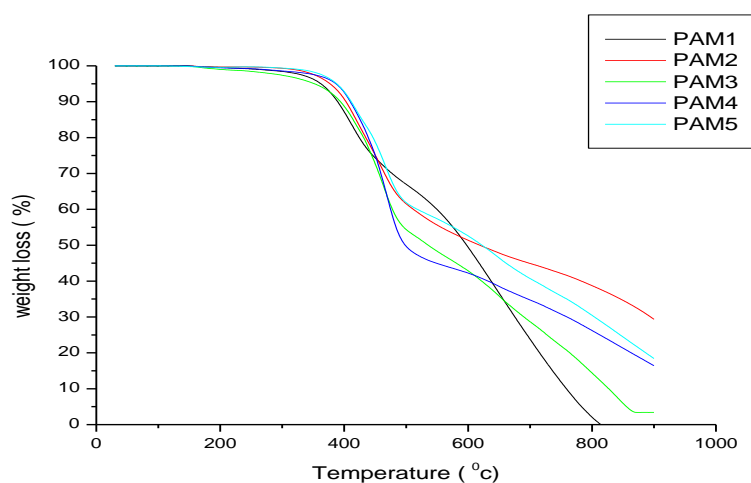


Fig. 8 TGA curves of Polyazomethines PAM-1 to PAM-5

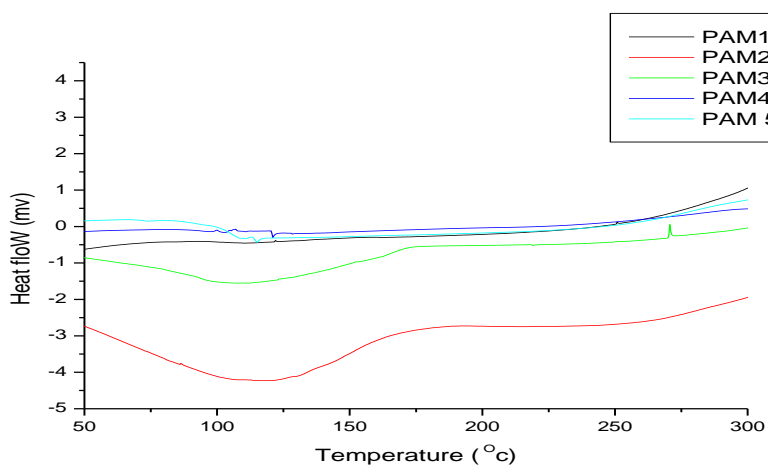


Fig.9. DSC curves of polyazomethines PAM-1 to PAM-5

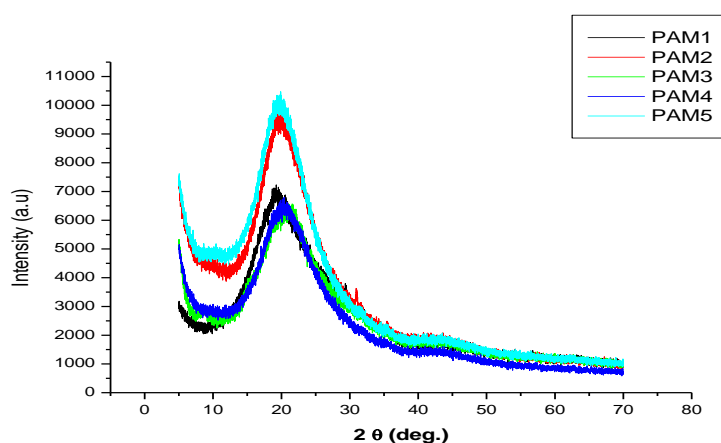


Fig. 10. XRD curves of polyazomethines PAM-1 to PAM-5

Polyazomethines were characterized by the wide angle X-ray diffractograms. The X-ray diffraction patterns of all polyazomethine are shown in Fig. 10. It was observed that, all polymers exhibited amorphous nature due to presence of aliphatic pentadecyl moiety on the long polymer main chain which causes disrupted packing leading to the amorphous morphology.

IV. SUMMARY AND CONCLUSION

- [1] Synthesis of new aromatic diamine containing pendant pentadecyl unit, methoxy group and 1,2,4-triazole moiety namely 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII) was synthesized and characterized by ¹H and ¹³C NMR, FT-IR spectroscopy, and mass spectrometry.
- [2] Polyazomethines were synthesized by solution polymerization of newly synthesized aromatic diamine 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII) with different proportion of aromatic dialdehyde namely isophthalaldehyde (IPA) and terephthalaldehyde (TPA). Inherent viscosities were in the range of 0.13 to 0.23 dL/g indicating moderate molecular weight of polymer.
- [3] The glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) in presence of nitrogen at the rate of 10°C/min. and T_g values were in the range of 110-125°C. Low glass transition temperatures due to presence of long aliphatic chain present on the long chain of polymer acting as an internal plasticizer.
- [4] Thermogravimetric analysis of polymers showed 10% weight loss at temperature 420 to 450°C indicating good thermal stability.
- [5] Poly(azomethine)s were soluble at room temperature in various aprotic polar solvents such as NMP, DMAc, DMSO, DMF, etc. due to the presence of long aliphatic pentadecyl pendant chain present on the long main chain of polymer, which favoured loose packing of polymer chains leading to the amorphous morphology.
- [6] The XRD patterns showed that the poly(azomethine)s have amorphous nature as indicated by the broad halos at 2θ range of 10 to 35°.

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