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Research Article

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF PROCESSABLE POLYAZOMETHINES FOR HIGH TEMPERATURE APPLICATIONS

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ABSTRACT

New dithiazole-diamine monomer containing cyclohexylidene ring and pendant methyl group i.e. 1,1-bis [4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (BATMPC) was synthesized through various steps. The structure of new dithiazole amine monomer was confirmed by FT-IR, ^{1}H NMR and ^{13}CNMR Spectrometry. A series of polyazomethines containing cardo cyclohexane-thiazole unit have been incorporated by the polycondensation of a new diamine i.e. (BATMPC), with proportionate of aromatic dialdehydes. The impact of insertion of cardo cyclohexane, pendant methyl group and thiazole entity in the polyazomethine matrix with the dialdehydes [isophthalaldehyde (1,3 IPA) and terephthalaldehyde (1,4 TPA)], on solubility and thermal stability has been studied. All polyazomethines shown Tg in the range of 220-241°C and T_{10}% value of all thermally stable polyazomethines in nitrogen atmosphere was in between of 395-415°C These polyazomethines exhibited solubility in various polar aprotic solvents such as NMP, DMSO, DMAc, DMF etc. However, these polyazomethines were insoluble in common solvents such as DCM and $CHCl_3$. X-ray diffraction study confirms that all the polyazomethines are amorphous in nature having broad peak in the range of $2\theta=20°$. The UV absorption at 360 nm shows that there is a formation of imine (-C=N-) linkages in the polymer matrix which is helpful for the conduction of electron throughout. The structure-property correlation among these polyazomethines was studied, in view of their potential applications for high temperature applications.

Keywords: 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane, Pendant methyl group, Cyclohexane, Polyazomethines.

1. INTRODUCTION

Aromatic polyazomethines (polyimines) shows excellent thermal stability, good mechanical and conducting properties, which makes them favourable members for high temperature applications in the engineering [1]. In addition, polyazomethines exhibit desirable useful properties such as electronic, optoelectronic [2-5] and liquid crystalline [6-8], fiber forming and ability to form metal chelates [9-11]. These polymers also show leading role in gas sensing applications [12-16]. However, the main drawback of polyazomethines is their limited solubility in most common organic solvents [17-20], high molecular weight polymers are problematic to obtain, because the growing macromolecular chains precipitate out of the solution during polycondensation. Furthermore, their high melting temperature and insolubility makes them inflexible for processing by conventional techniques. Efforts devoted towards obtaining soluble and fusible polyazomethines include: insertion of flexible spacer between main chain aromatic rings [21, 22]; introduction of pendant groups, i.e. aromatic or alkyl substituents, insertion of methyl group into the polymer chain [23-25], introduction of structural irregularities such as kinks, bents, crankshaft-shaped units, etc. [26-28]. It is generally recognized that the presence of an alkyl group and ether linkage in the polymer backbone imparts segmental mobility to the polymer which enhances thesolubility and lowers the glass transition temperature.

The present study describes a successful synthesis of new semi-conjugated and processable aromatic polyazomethines for high temperature semiconducting applications by incorporation of thiazole unit, pendant methyl group and cardo cyclohexane moiety in the backbone. For this, a new aromatic diamine monomer havingthiazole unit, cardo cyclohexane moiety with ether linkage as well aspendant methyl group was designed and synthesized, which was subjected to high temperature polycondensation with isophthalaldehyde and terephthaldehyde.

2. MATERIAL AND MEASUREMENTS

2.1. Material

Isophthalaldehyde (IPA), terephthalaldehyde (TPA) were supplied by Sigma-Aldrich and used as received. Thiourea, 4-fluro acetophenone, O-cresol, 3-mercapto-propanoic acid (3-MPA) were purchased from spectrochem, S.D. fine and used as received. N,N′-dimethyl acetamide(DMAc) purchased from spectrochem and were dried over P_2O_5,distilled under reduced pressure and keptover 4Å molecular sieves. Solvents such as THF, DCM, methanol, ethanol and glacial acetic acid, were used as collected. K_2CO_3 and LiCl were dehydrated at 150°C in vacuum oven for 10 h.

2.2. Measurements

Fourier transform infrared (FTIR) spectrometry (Thermo Nicolet iS-10Mid Fourier transform infrared between wave numbers of 650-4000 cm^{-1}) was engaged to classify the functional groups of precursor and polymers. The ^{1}H-NMR scan was operated on 400 MHz Bruker spectrometer in dimethyl sulfoxide-d^6.Ultraviolet-visible(UV-Vis) spectra were recorded on a Shimadzu spectrophotometer in diluted DMAc solutions of 10^{-5}M concentration, using 10 mm quartz cells, at room temperature. The XRD analysis was drifting out by using X-ray diffractometer (ULTIMA IV Goniometer).Inherent viscosities of the PAMs were determined by an Ubbelohde suspended-level viscometer. Thermal behaviour of the CHPAMs was studied by TA SDT Q600 at a heating degree of 10°C/min under nitrogen atmosphere.

2.3. Experimental

2.3.1. Monomer Synthesis

2.3.1.1. Synthesis of 1, 1-bis(4-hydroxy-3-methyl phenyl) cyclohexane (I)

This bisphenol was synthesized as per reported procedure [29]. In 250 mL three necked flask equipped with HCl gas deep tube, reflux condenser and magnetic stirrer were placed 58.84g (0.6mol) of O-cresol and 9.8 g (0.1 mol) of cyclohexanone and 0.2 mL3-mercaptopropanoic acid. To this reaction mixture dry HCl gas was bubbled at room temperature. The reaction mixture became solid within 2 h. The solid reaction mixture was dissolved in ethyl acetate (600 mL) and neutralized by washing with aq. $NaHCO_3$ solution 3 X 200 mL, followed by washing with distilled water 2 X 200 mL. The organic layer was dried over magnesium sulfate, filtered and distilled off to obtain viscous liquid. Then upon addition of pet ether in viscous liquid, solid product was separated out. The product was washed with water then dried under vaccum. Finally the bisphenol was reprecipitated through methanol-water mixture; Yield: 20.72g (70 %), M.P.:130°C.

2.3.1.2. Synthesis of 1,1-bis[4-(4-acetyl phenoxy)-3-methyl phenyl] cyclohexane (II)

This diketone intermediate was synthesized as per the reported procedure [30]. In a 500mL three neck round bottom flask equipped with calcium chloride guard tube, thermowell, N_2 gas inlet and magnetic stirrer, were placed 14.8 g 1,1-bis(4-hydroxy-3-methyl phenyl) cyclopentane (I) (0.05 mol) and 13.81g 4-fluoroacetophenone(0.1 mol) in 125 mL DMAc, then 13.82 g (0.1mol) of anhydrous K_2CO_3 was added. The resulting reaction mixture was refluxed for 12 h, allowed to cool at room temperature and precipitated the product from solution by addition of water. The product was isolated by filtration, washed with water and then methanol, and finally dried under vacuum. Recrystallized product in methanol; Yield: 24.18 g (93%), M.P.: 90°C.

2.3.1.3. Synthesisof 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (III) (BATMPC)

Into 100-mL single-neck round-bottom flask, diketone (II) (15.96 g, 0.03mol), thiourea (13.68 g, 0.18 mmol) and iodine (7.62 g, 0.09 mol) were dissolved in 125 mL THF. The mixture was stirred and refluxed for 48 h. Cooled the clear solution, transferred to another beaker containing cold sodium acetate solution and stirred for 3 h. The crude product was filtered, washed with THF and finally with pet ether-ethyl acetate (8:2) mixture. Dried the product under vaccum for 10h; Yield: 17.38 (90%), MP: 225°C. **IR**: 3350 cm^{-1} (-NH_2 stretching), 3108, 2932, 2855, 1617, 1246, 835 cm^{-1} **^{1}H NMR (400MHz, $CDCl_3$), δ (ppm):** 6.9-7.8 (Aromatic Protons), 6.8 (thiazole ring proton), 2.5(Methyl protons), 1.5, 2.0 (Cyclohexane ring protons). **^{13}C NMR (100MHz,**

CDCl3), δ (ppm):169.87 (NH_2 attached C), 157.86, 150.91, 144.46, 130.37, 129.88, 128.70, 127.68, 126.05, 119.46, 117.03, 116.18, 101.31, 44.68, 36.40, 25.70, 22.54 and 16.10.

2.4. Polyazomethines Synthesis

In a 100-mL three-neck round-bottom flask, a mixture of diamine (BATMPC) (0.644g 1 mmol) and 3 mL of dry DMAc containing 5% lithium chloride (0.150 g) was stirred under nitrogen gas to get transparent solution of diamine. Then, 0.134 g of dialdehyde was added (TPA/IPA/(TPA+ IPA) and stirred at room temperature for overnight in N_2 atmosphere. Finally, the polymerization mixture was heated at 140°C for 4 h. On cooling, the polymer mixture was gradually poured into water while stirring was continued, and precipitate of the resulting polymer was filtered off. Rinsed with water and resulting brown product was obtained in high yield, dried under vacuum at 80°C for 8 h to produce CHPAMs. The polyazomethines CHPAM-1 to CHPAM-4 were synthesized with various diamines by a similar procedure. All the polyazomethines gave better yield between 97-99%.

IR Spectrum

CHPAM 1: 3025, 2910, 1640, 1590, 1497, 1230, 1155, 830 cm^{-1}

CHPAM-2: 3030, 2905, 1641, 1595, 1492, 1235, 1155, 835 cm^{-1}

CHPAM-3: 3040, 2915, 1645, 1600, 1492, 1240, 1157, 832 cm^{-1}

CHPAM-4: 3045, 2913, 1642, 1585, 1480, 1240, 1156, 831 cm^{-1}

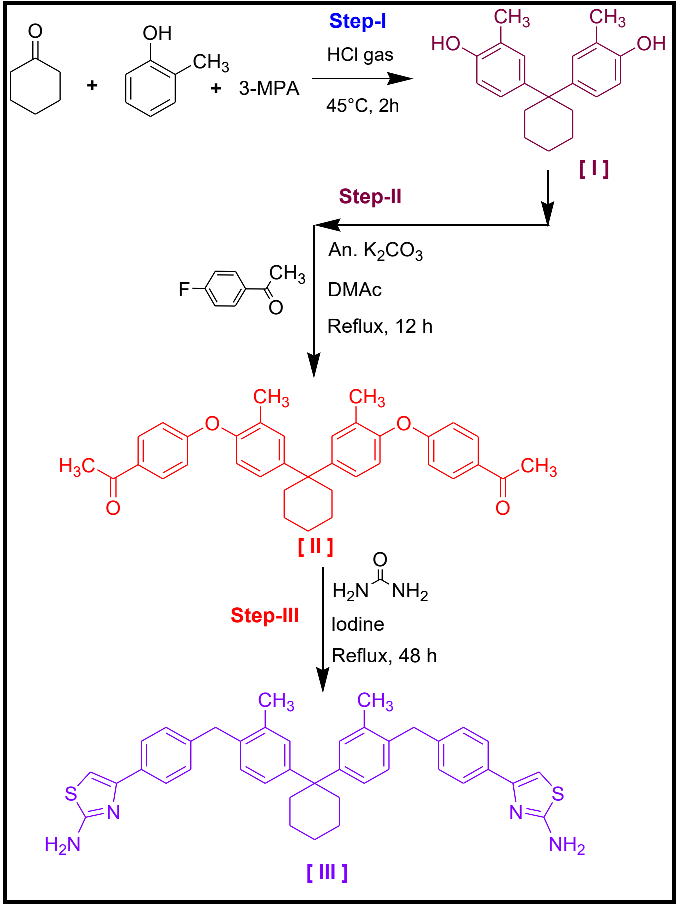
3. RESULTS AND DISCUSSION

3.1. Monomer Synthesis and Characterization

In the presented work, dithiazole amine monomer containing cyclohexylidene moiety, viz. BATMPC has been synthesized and used as building blocks for preparation of thiazole containing polyazomethines. The new dithiazole amine, 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (III) was synthesized starting from O-cresol and cyclohexanonein three steps as shown in Scheme 1.

The 1,1-bis(4-hydroxy-3-methylphenyl) cyclohexane(I) was synthesized by reacting *o*-cresol with cyclohexanone in the presence of 3-MPA as catalyst. The 1,1-bis[4-(4-acetyl phenoxy)-3-methylphenyl]cyclohexane(II) was obtained by reaction of (I) with 4-fluoroacetophenone and potassium carbonate in DMAc. Structure of (II) was confirmed by IR spectroscopy.

In the third step, diketone (II) undergoes ring closure with thiourea to give 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane (III)(BATMPC). Chemical elucidation of new diamine precursor BATMPC was confirmed by ^{1}HNMR, ^{13}C NMR and FTIR spectroscopy.



Scheme 1: Synthesis of 1,1-bis[4-(2-amino-thiazole)-3-methylphenyl] cyclohexane

The FTIR spectrum of the corresponding diamine monomer BATMPC supported the evidences of the successful achievement ofcomplete ring cyclization of thiazole monomer, as shown in Fig.1. The infrared spectrum showed characteristic absorption bands at 3350 cm^{-1} ($-NH_2$ stretch), 1617 cm^{-1} (>C=C< stretch), 1246cm^{-1} (>C-O-C< stretch), 3108cm^{-1} (aromatic -CH stretch), 2932, 2855 cm^{-1} (aliphatic -CH stretch).The proton-NMR spectra of BATMPC is shown in Fig. 2. The resonance peak were observed at 6.9-7.8 ppm (Aromatic Protons), 6.8 ppm (thiazole ring proton), 2.5 (Methyl protons), 1.5 ppm, 2.0 ppm (Cyclohexane ring protons). ^{1}H NMR analysis clearly indicated that diketone structure is completely transformed into diamine structure by cyclization.

Further ^{13}C NMR spectrum of BATMPC showed eighteen NMR signals to 18 types of different carbons atoms shown in Fig. 3. The NMR signals appeared at 169.87 ppm (NH_2 attached C), 157.86, 150.91, 130.37, 129.88, 128.70, 127.68, 126.05, 119.46, 117.03, 116.18 ppm (aromatic carbons), 144.46, 101.31ppm (thiazole C). The signal at 44.68, 36.40, 25.70, 22.54 ppm confirms presence of cyclohexane ring and signal at 16.10 ppm confirms presence of pendant methyl group in the monomer.

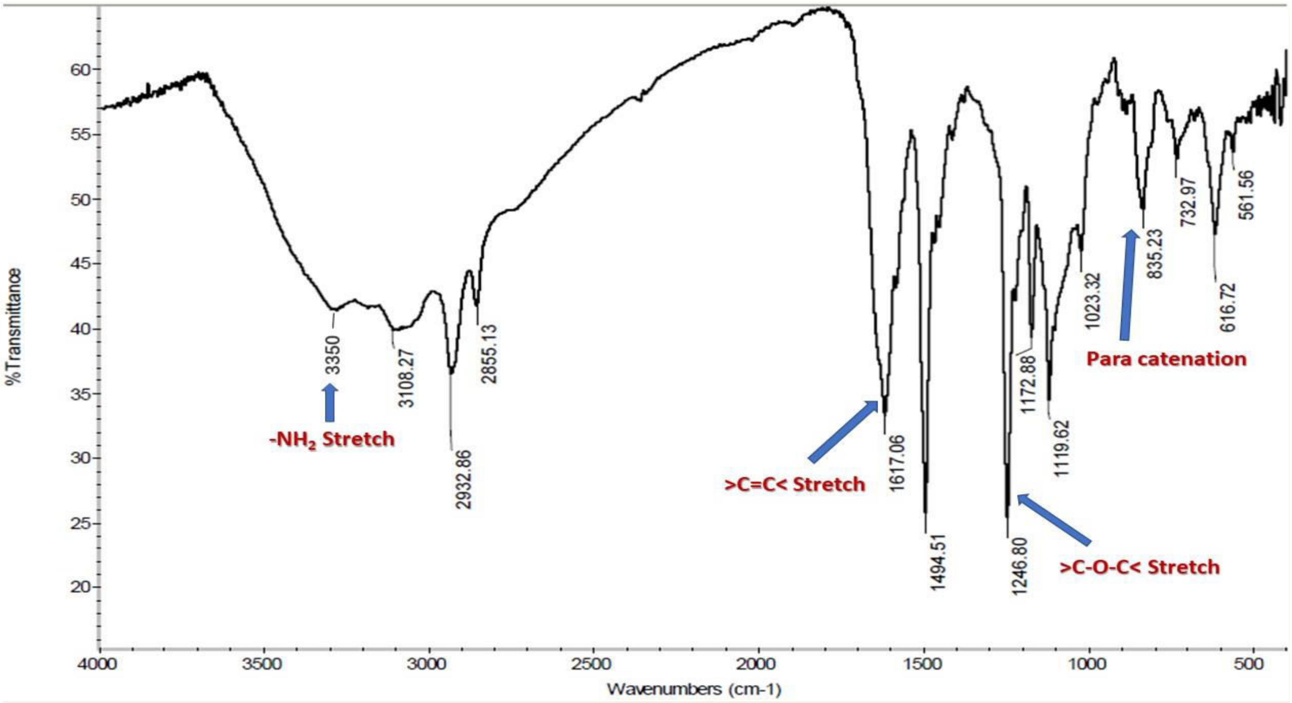


Fig. 1: FT-IR spectrum of 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane

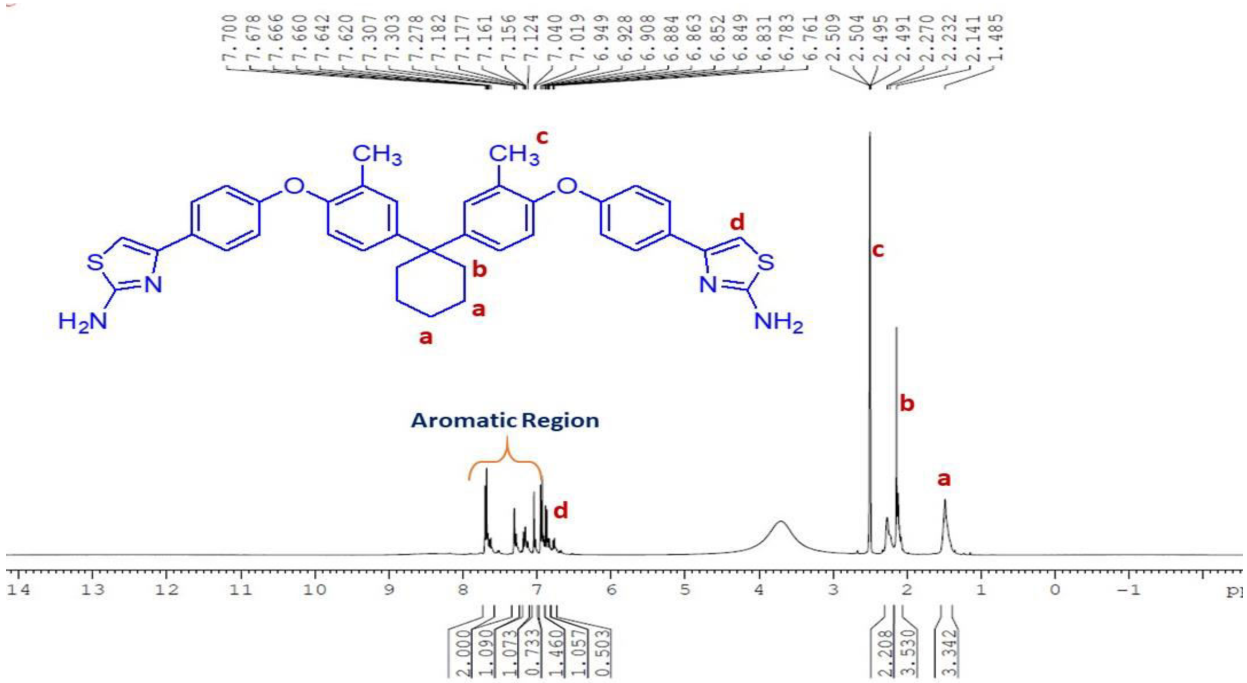


Fig. 2: ^{1}H NMR spectrum of 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane

3.2. Polymer Synthesis and Characterization

As presented in Scheme 2, a series of four new CHPAMs were synthesized from new diamine precursor, i.e.1,1-bis[4-(2-aminothiazole)-3-methyl-phenyl] cyclohexane (BATMPC) with varying mole ratios of IPA + TPA by a high-temperature solution polycondensation method [29]. Yields and inherent viscosities are shown in Table 1. The synthesised CHPAMs were proved by FTIR spectra.

The vibrational assignments of various cyclohexane-thiazole-based polymers are reported in Fig. 4. The stretching vibrations of -C=N- (azo linkages) absorption bands are typically located at 1640 cm^{-1}. The loss of stretching vibrations at 1700 and 3400-3150 cm^{-1} specified that total dialdehyde and diamine functionality had proceeded to produce with great molecular framework of CHPAMs. The stretching absorption at 1590 cm^{-1} is attributed to aromatic -C=C- stretching frequency of aromatic and thiazole unit which is well-constructed in polyazomethine. The stretching at 3025 cm^{-1} explains the aromatic C-H stretch of the polyazomethines chain.

Table 1: Yield and Viscosity of Polyazomethines (CHPAM-1 to CHPAM-4)

Polymer[a] Code	Monomers			Yield %	Inherent Viscosity dL/g [b]
	Diamine (III) mol %	TPC (X) mol%	IPC (100-X) mol %		
CHPAM-01	100	100	0	99	0.35
CHPAM-02	100	75	25	99	0.33
CHPAM-03	100	25	75	98	0.29
CHPAM-04	100	0	100	97	0.27

*[a]Polymerization was carried out with 1 mmol each of diamine and dialdehyde, [b]Inherent viscosity was measured at a concentration of 50mg/10 ml in **DMAc** at 30°C*

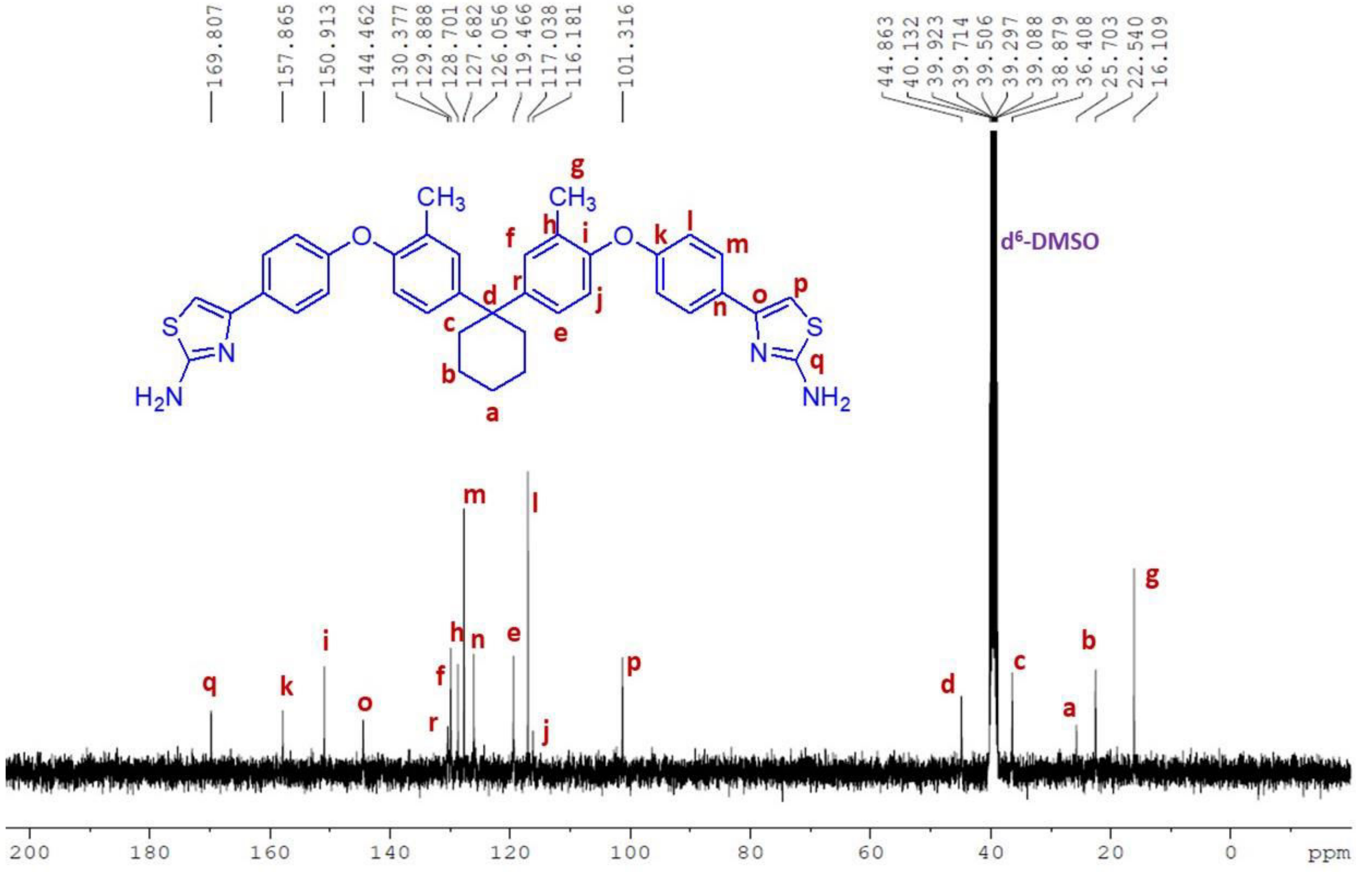
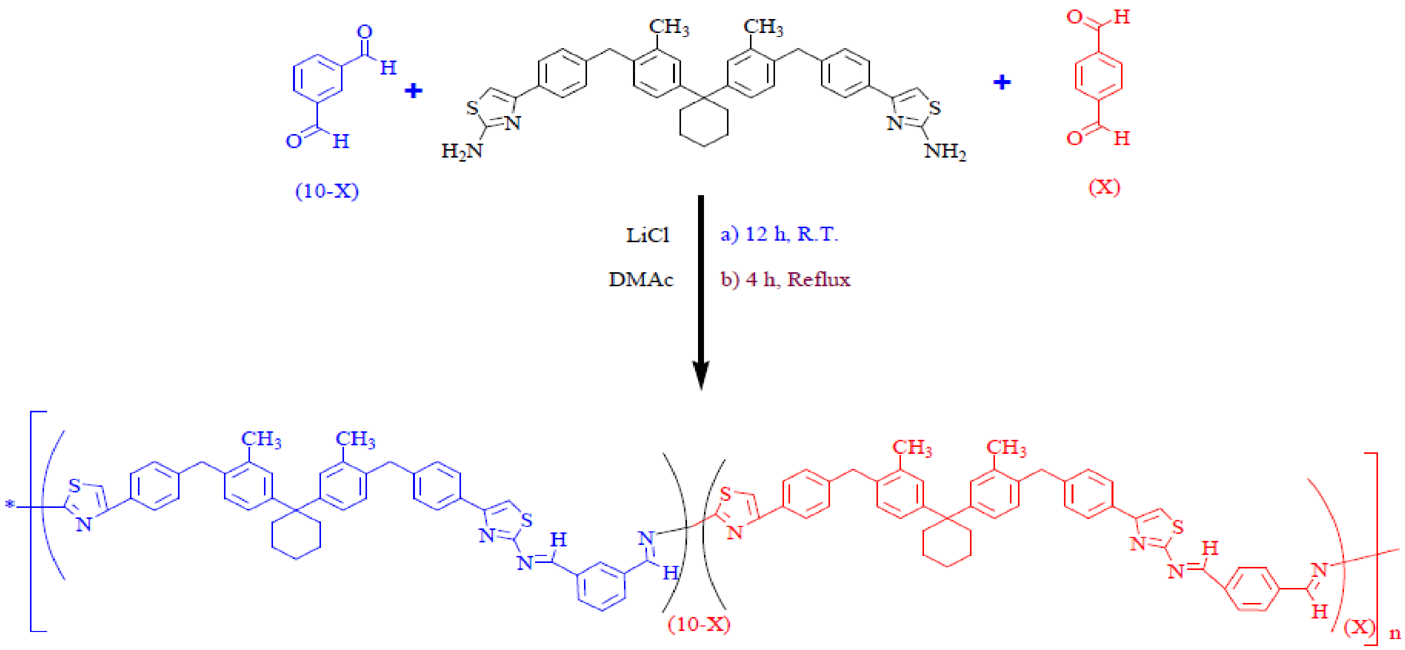


Fig. 3:^{13}**C NMR spectrumof 1,1-bis[4-(2-aminothiazole)-3-methylphenyl] cyclohexane**



Scheme 2: Synthesis of Polyazomethines (CHPAM-1 to CHPAM-4)

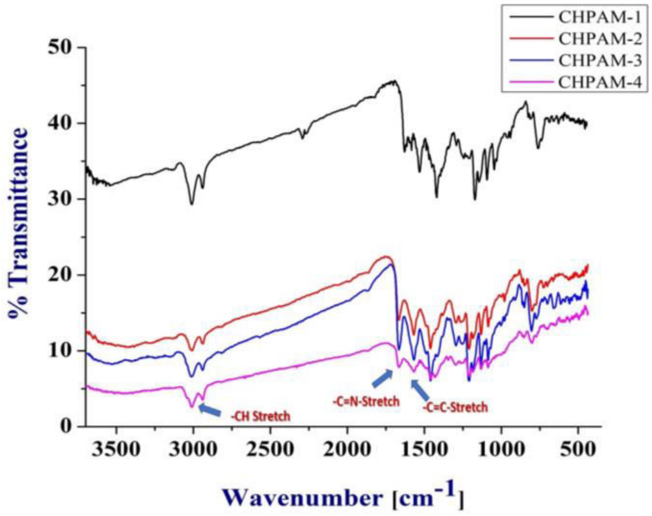


Fig. 4: FT-IR spectrum of Polyazomethines (CHPAM-1 to CHPAM-4)

3.2.1. Solubility and inherent viscosity

As shown in Table 2, solubility of CHPAMs was proved qualitatively in numerous organic solvents. All CHPAMs were dissolved at room temperature in DMAc and conc.H_2SO_4. These polymers are partly soluble in DMSO, NMP, pyridine and DMF. Moreover, they were totally insoluble in fewer active solvents such as DCM and chloroform.

As shown in Table 1, the resulting CHPAMs showed inherent viscosities in the range 0.27-0.35 dL/g, measured in DMAc at concentration of 0.50 dL/g at 30°C.

3.2.2. XRD analysis

The X-ray diffraction (XRD) technique has been used to check the crystallinity/amorphous nature of series of polyazomethines (Fig. 5) over in the 2θ range of 5°-90° [29]. Broad diffraction peaks at ~ 12° and ~ 20° (2θ) were detected which support the amorphous nature of CHPAMs. No more sharp peaks are detected which specifies amorphous nature of CHPAMs.

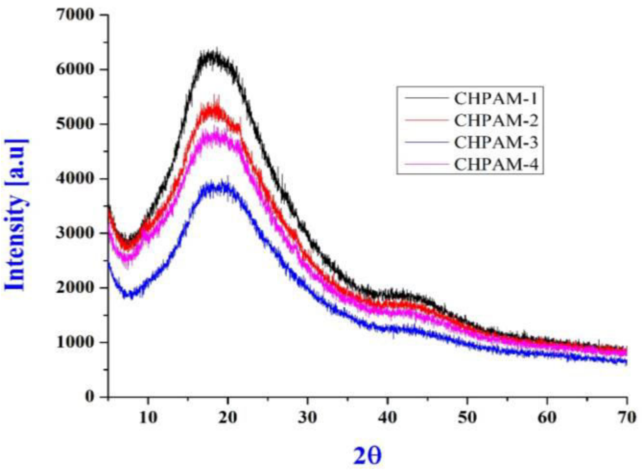


Fig. 5: XRD of Polyazomethines (CHPAM-1 to CHPAM-4)

From the observed arrangements, it is granted to confirm that considered material had an amorphous nature which was predicted and also in good compliance with the reported literature [31, 32].

Table 2: Solubility behaviour of Polyazomethines (CHPAM-1 to CHPAM-4)

Polymer Code	Solubility behaviour							
	DMF	DMAc	DMSO	NMP	DCM	$CHCl_3$	Pyridine	Conc. H_2SO_4
CHPAM-01	±	+	±	±	-	-	-	+
CHPAM-02	±	+	±	±	-	-	±	+
CHPAM-03	+	+	+	+	-	-	+	+
CHPAM-04	+	+	+	+	-	-	+	+

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

3.2.3. Thermal analysis

The thermal properties of the cyclohexane-thiazole-based CHPAMs were estimated by TGA and DSC in nitrogen atmospheres. The outcomes are outlined in table 3, and the representative TGA curves of the polyazomethines are displayed in Fig. 6. As presented in table 3, the strategy of polyazomethines with the merger of 1,4 and 1,3 linkages and cardocyclohexane-thiazole structure provides high thermal stability. Polymers CHPAM-01 to CHPAM-04 were in the range 380-415°C in nitrogen atmosphere. In addition, these polymers remained 31-49 % of original weight at 900°C in nitrogen atmosphere. Amongst these polyazomethines, the CHPAM-01 presented uppermost thermal stability with T10% at 415°C in compliance with the previous reports [31, 32]. Polyazomethines composed of more percentage of rigid backbone, i.e. para orientated (1,4 linkages, TPA) shows higher thermal stability than the meta oriented (1,3 linkages, IPA). This varying composition of polyazomethines (CHPAM-01 to CHPAM-04) is also clearly seen in the residual weight at 900°C.

These polyazomethines gave the glass transition temperature (T_g) in between 220-241°C and are displayed in Fig. 7.

Table 3: Physical properties of Polyazomethines (CHPAM-1 to CHPAM-4)

Polymer Code	Thermal behaviour^b		
	T_d °C in N_2	T_g°C	Residual Wt % at 900°C
CHPAM-01	415	241	31
CHPAM-02	405	229	49
CHPAM-03	380	220	43
CHPAM-04	395	221	48

[b] *Temperature at which onset of decomposition was recorded by TG at aheating rate of 10°C/min. T_g-Glass transition temperature determined by DSC at a heating rate of 10°C/min, T_d-Temperature of 10 % decomposition*

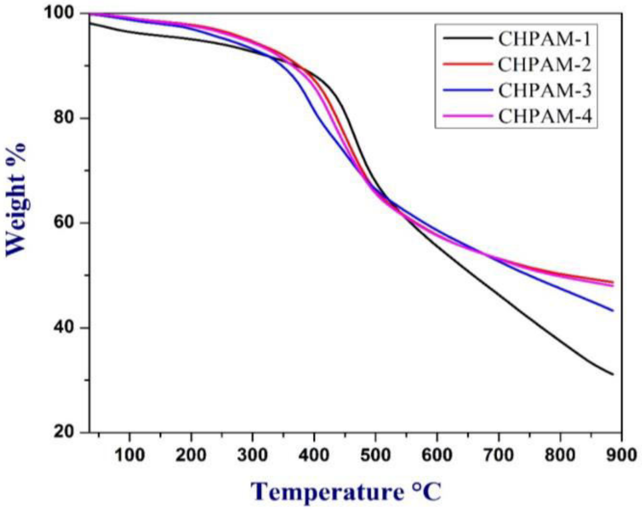


Fig. 6: TGAof Polyazomethines (CHPAM-1 to CHPAM-4)

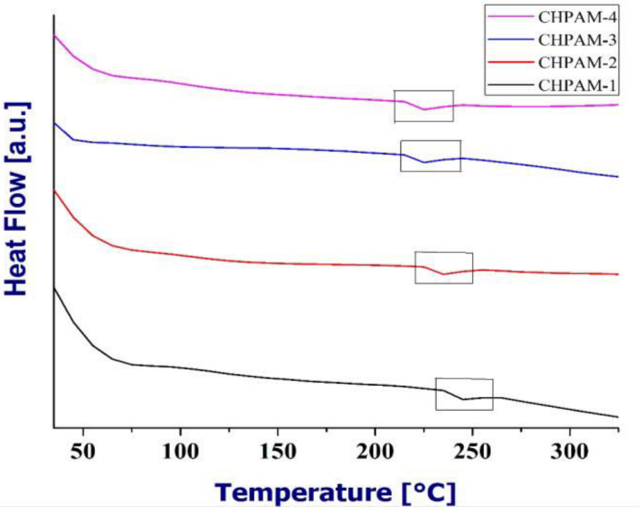


Fig. 7: DSC of Polyazomethines (CHPAM-1 to CHPAM-4)

The polymers CHPAM-1 and CHPAM-2 show the uppermost T_g value because of the presence of more percentage of rigid 1,4-benzene linkage (TPA) and a lower percentage of 1,3 benzene linkage (IPA), whereas the polymer CHPAM-4 gave the lowest Tg value due to the existence of cardo cyclohexane, pendant methyl group andmore percentage of 1,3 linkages.

3.2.4. Photophysical properties

The photophysical properties of the polyazomethines were investigated by UV-vis absorption spectroscopy in DMAC solutions (10^{-5} M). In solution, all polyazomethines presented at least two absorption bands (Fig. 8). The first absorption band in the range 352-360 nm is attributed to π–π* progression of aromaticring conjugations. The next most important absorption area is sighted around 463-471 nm owing to n–π* transition of imine conjugations. From this, it was confirmed that all the precursors or starting material totally vanished and increased electron shifting in the polymer backbone. These results are in good compliance with reported literature [33-37].

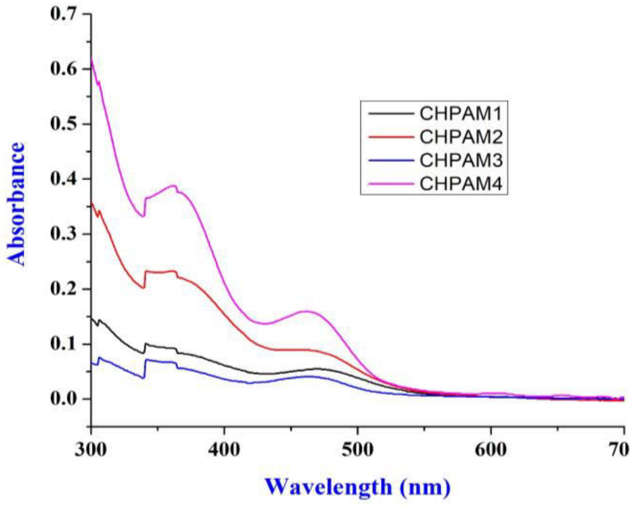


Fig. 8: UV-Visible spectrum of Polyazomethines (CHPAM-1 to CHPAM-4)

4. CONCLUSIONS

A series of CHPAMs were prepared by the high-temperature solution polycondensation of a novel diamine precursor 1,1-bis[4-(2-aminothiazole)-3-methyl phenyl] cyclohexane (BATMPC), with varying proportion of aromatic dialdehydes comonomer [1,3 linkage isophthalaldehyde (IPA) and 1,4 linkage terephthalaldehyde(TPA)]. Inherent viscosities of these CHPAMs were in between the 0.27 and0.35 dL/g indicating built-up of moderate molecular weights. These CHPAMs revealed solubility in many polar aprotic solvents without appreciable loss in thermal stability, so it is possible to process these polyazomethines in polar aprotic solvents. The existence of -CH=N- (azo linkage) in the CHPAMs framework was committed by UV-Vis spectra. The 10% weight loss in nitrogen range from 380ºC to 415ºC indicates that these polyazomethines are suitable for high temperature applications. The glass transition temperature of polyazomethines (220ºC to 241ºC) can allow processing of polymers above 220ºC. X-ray diffraction study shows amorphous nature of these polymers.

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Conflict of interest

None declared

6. REFERENCES

1. Iwan A, Sek D. *Prog Polym Sci*, 2008; **33:**289-345.
2. Iwan A, Sek D. *Prog Polym Sci*, 2011; **36:**1277-325.
3. Salunkhe PH, Patil YS, Patil VB, Navale YH, Ubale VP, Dhole IA, et al. *J Polym Res*, 2018; **25:**147.
4. Mahindrakar JN, Patil YS, Salunkhe PH, Ankushrao SS, Kadam VN, Ubale VP, et al. *J Macromol Sci Part A*, 2018; **55:**658-667.
5. Patil YS, Mahindrakar JN, Salunkhe PH, Ubale VP, Ghanwat AA. *J Macromol Sci Part A*, 2018; **55:**572-581.
6. Jeevadason AW, Murugavel KK, Neelakantan MA. *Renew Sustain Energy Rev*, 2014; **36:**220-227.
7. Wan A. *Polimery*, 2010; **4:**253-266.
8. Iwan A. *Prace Instytutu Elektrotechniki*, 2011; **1:**157.
9. Iwan A, Schab-Balcerzak E. Liquid crystalline organic compounds and polymers as materials XXI century:From synthesis to applications, Transworld Research Network, Kerala, India, 2011.
10. Grigoras M, Catanescu C. *J Macromol Sci*, 2004; **44:**131-173.

11. Yang CJ, Jenekhe SA. *Chem Mater*, 1994; **6:**196-203.
12. Wetchakun K, Samerjai T, Tamaekong N, Liewhiran C, Siriwong C, Kruefu V, et al. *Sens Actuators B Chem*, 2011; **160:**580-591.
13. Santra S, Guha PK, Ali SZ, Hiralal P, Unalan H, Covington JA, et al. *Sens Actuators B Chem*, 2010; **146:**559-565.
14. Hakim M, Broza YY, Barash O, Peled N, Phillips M, Amann A, Haick H. *Chem Rev* 2012, **112:**5949-5966.
15. Shehada N, Brönstrup G, Funka K, Christiansen S, Leja M, Haick H. *Nano Lett*, 2015; **15:**1288-1295.
16. Li X, Le TM, Dutta RK, Qiao S, Chandran GT, Penner RM. *ACS Sens*, 2017; **2:**282-289.
17. Wang C, Shieh S, Le Goff E. *Macromol*, 1996; **29:**3147-3156.
18. Grigoras M, Catanescu C. *J Macromol Sci Part-C Polym Rev*, 2004; **44:**131.
19. Iwan A, Sek D, Rannou P, Kasperczyk J, Janeczek H, Mazurak Z, et al. *Synth Met*, 2004; **143:**331.
20. Catanescu M, Simionescu I. *Rev Roum Chim*, 2001; **46:**927.
21. Shao Y, Li Y, Zhao X, Ma T, Gong C, Yang F. *Euro Polym J*, 2007; **43:**4389-4397.
22. Choi H, Chung I, Hong K, Park E, Kim Y. *Polym*, 2008; **49:**2644-2649.
23. More A, Sane P, Patil A, Wadgaonkar P. *Polym Degrad Stab*, 2010; **95:**1727-1735.
24. Catanescu O, Grigoras M, Colotin G, Alina D, Nicolae H, Cristofor I. *Euro Polym J*, 2001; **37:**2213-2216.
25. Sadavarte N, Avadhani C, Wadgaonkar P. *High Perform Polym*, 2011; **23:**494-505.
26. Adell J, Alonso M, Barbera L, Pinol M, Serrano J. *Polym*, 2003; **44:**7829.
27. Jarraya I, Abid M, Abid S, Gharbi R. *J Macromol Sci Part A:Pure and Appl Chem*, 2013; **50:**931-939.
28. Kim H, Kim J, Kim K, Park K, Baek S, Ree M. *J Polym Sci Polym Chem*, 2004:**42:**825.
29. Ankushrao SS, Patil YS, Ubale VP, Maldar NN, Ghanwat AA. J *Macromol Sci Part A Pure and Appl Chem*, 2017; 54:411-417.
30. Ankushrao SS, Patil YS, Ubale VP, Maldar NN, Ghanwat AA. *Polym Sci, Ser B*, 2018; **3:**263-272.
31. Niu H, Huang Y, Bai X, Li X, Zhang G. *Mater Chem Phys*, 2004; **86:**33-37.
32. Jarzabek B, Weszka J, Domanski M, Jurusik J, Cisowski J. *J Non Cryst Sol*, 2008; **354:**856-862.
33. Lim WL, Oo CW, Choo YSL, Looi ST. 2015; **71:**5-22.
34. Dineshkumar S, Muthusamy A, Chitra P, Anand S. *J Adhes Sci Technol*, 2015; **29:** 2605-2621.
35. Cianga I, Ivanoiu M. *Eur Polym J*, 2006; **42:**1922-1933.
36. Marin L, Perju E, Damaceanu D. *Eur Polym J*, 2011; **47:**1284-1299.
37. Marin L, Harabagiu V, van der Lee A, Arvinte A, Barboiu M. *J Molec Struct*, 2013; **1049:**377-385.