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Thermally stable methyl-substituted poly(azomethine-ether)s bearing cardo cyclopentylidene moiety

Sanjay S. Ankushrao[1,2], Anil A. Ghanwat[3], Suraj D. Jadhav[1,2] and Pradip D. Chavan[1,2]

Abstract

A new diether-diamine monomer, 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane (BAMPC), containing a cardo cyclopentane unit and a pendant methyl substituent, was synthesized through a multistep procedure. The structure of the methyl-substituted diether-diamine monomer was confirmed using FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry. Polycondensation of BAMPC with aromatic dialdehydes, including terephthalaldehyde and isophthalaldehyde, produced a series of co-poly (azomethine-ether)s incorporating cardo cyclopentane units in the polymer backbone. The influence of the cardo cyclopentane structure and pendant methyl group on the solubility and thermal stability of the resulting co-poly (azomethine-ether)s was examined. The polymers exhibited glass transition temperatures (Tg) in the range of 165-178°C and thermal degradation temperatures (T_d) between 456 and 486°C, indicating thermal stability. The polyazomethines were soluble in polar aprotic solvents such as DMF, NMP, DMAc, and DMSO at ambient temperature or upon heating. X-ray diffraction analysis indicated that SPAM-2, SPAM-3, SPAM-4, and SPAM-5 exhibited amorphous characteristics with a broad diffraction peak around $2\theta \approx 20°$, whereas SPAM-1 showed semicrystalline behaviour. The inherent viscosities of the co-poly (azomethine-ether)s ranged from 0.20 to 0.39 dL g^{-1}.

Keywords

polymer, co-poly(azomethine-ether)s, cyclopentane

Introduction

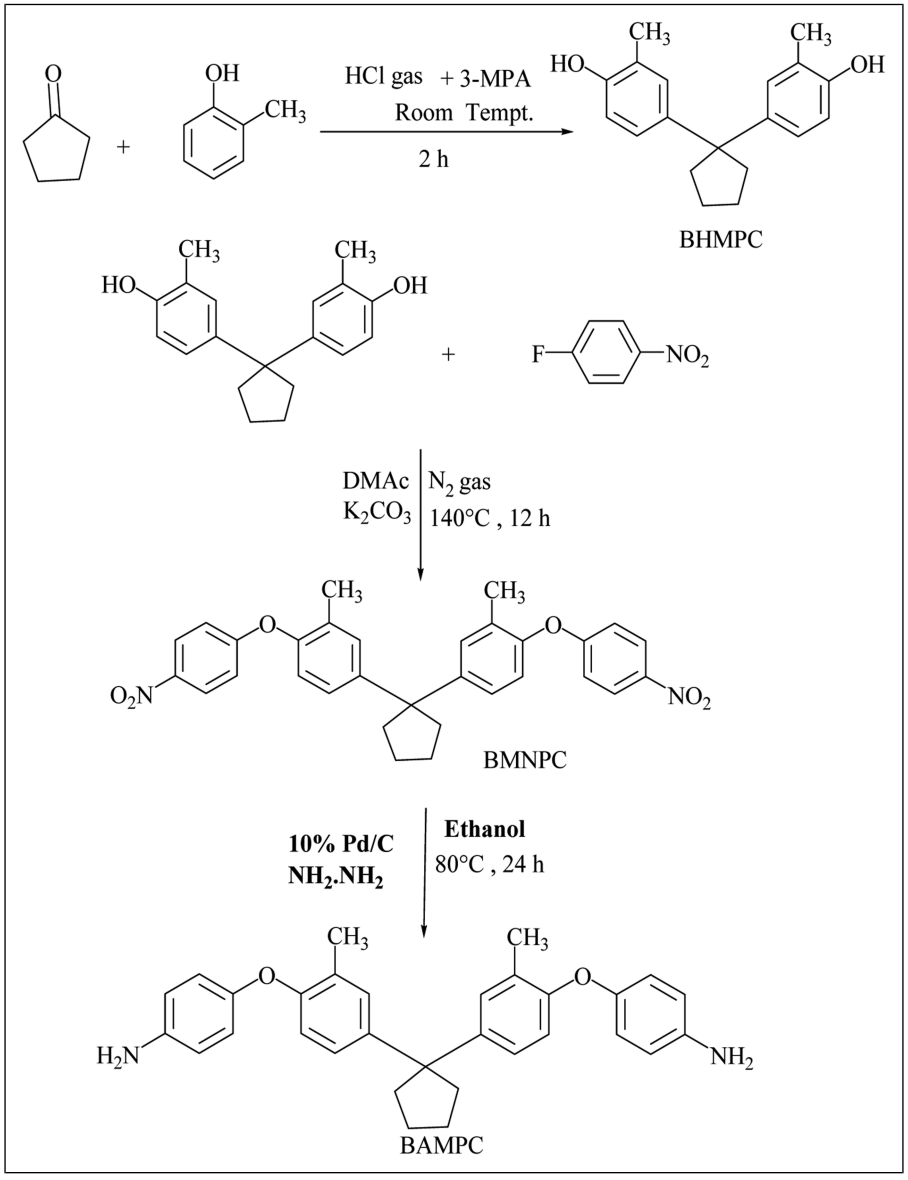
Polymers containing (-CH = N-) linkages in the main chain are referred to as polyimines or poly (Schiff base) s and are commonly known as polyazomethines. These conjugated polymers have attracted attention because of their mechanical strength,[1] thermal stability,[2] photoconductivity,[3] and optical properties.[4] Owing to these characteristics, polyazomethines have been investigated for applications in semiconductors, battery electrodes, advanced functional materials, electro-optical switching devices, energy storage and conversion systems, displays,[5–7] and electroluminescent (EL) devices.[8] The first polyazomethine was reported in 1923 through the polycondensation of terephthalaldehyde and benzidine.[9] Since then, several conjugated aromatic polyazomethines incorporating different structural units on both sides of the imine (CH = N) linkage have been reported.[10–12] Polyazomethines can be synthesized through methods such as solution polycondensation, chemical vapor deposition,[13–15] and oxidative polymerization.[16]

Despite these properties, many polyazomethines are infusible and exhibit limited solubility, which restricts their practical applications. To address these limitations, several modified polyazomethines have been developed, including poly (azomethine-ester)s,[17] poly (azomethine-ether)s,[18] poly (azomethine-carbonate)s,[19] poly (amide-azomethine-ester)s,[20] poly (acrylate-azomethine)s,[21] thermosetting polyazomethines,[22] and poly (azomethine-sulfone)s.[23–26] These modifications aim to improve solubility, reduce melting temperature, and introduce additional properties

[1]Department of Chemistry, Vivekanand College (An Empowered Autonomous Institute), Kolhapur, India
[2]Department of Chemistry, Shivaji University, Kolhapur, India
[3]School of Chemical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur, India

Corresponding author:
Sanjay S. Ankushrao, Department of Chemistry, Vivekanand College (An Empowered Autonomous Institute), Kolhapur 416003, India.
Email: sanjayankushrao21@gmail.com

Data Availability Statement included at the end of the article.



Scheme 1. Synthesis of BAMPC.

such as mesomorphic behavior.[27] Various strategies have been reported to enhance the solubility of polyazomethines. The incorporation of flexible alkyl or alkoxy substituents can improve solubility, although such modifications may reduce thermal stability.[28–30] The introduction of bulky substituents, including tetraphenylethylene, triphenylamine, and diphenylfluorene, has also been investigated.[31–33] In addition, copolymerization with electron-rich aromatic or heterocyclic units such as carbazole, thiophene, and fluorene has been explored to improve processability and solubility.[34–36]

Aromatic polyazomethines are commonly synthesized through solution or melt polymerization techniques. Interest in these polymers continues due to their combination of mechanical strength, thermal stability, optoelectronic properties, and semiconducting behavior.[37,38] However, their applications remain limited because of low solubility in common organic solvents and relatively low molecular weights. Furthermore, the limited availability of structurally diverse dialdehyde monomers restricts the structural modification of polyazomethines. Several strategies have therefore been proposed to improve solubility, including the incorporation of flexible alkyl or alkoxy substituents, although this may affect thermal stability.[39–41] The incorporation of bulky substituents such as tetraphenylethylene, triphenylamine, and diphenylfluorene has also been examined.[42] Copolymerization with electron-rich aromatic or heterocyclic units, including carbazole, thiophene, and fluorene, has also been reported.

Structural modification of polyazomethines is commonly achieved by synthesizing new diamine monomers followed by polycondensation with commercially available dialdehydes such as terephthalaldehyde (TPA) and isophthalaldehyde (IPA). These approaches primarily aim to improve solubility and evaluate the resulting thermal behavior. In this context, a new series of co-poly (azomethine-ether)s was prepared using a newly synthesized methyl-substituted diamine in combination with commercially available IPA and TPA dialdehydes.

Experimental methods

Materials

All solvents and chemicals were purified before use according to standard procedures unless otherwise stated. 3-Mercaptopropanoic acid, 10% Pd/C, terephthalaldehyde, and isophthalaldehyde were obtained from Sigma-Aldrich and used as received. Potassium carbonate (K_2CO_3) was dried under vacuum at 150°C for 6 h prior to use. N,N-Dimethylformamide (DMF) was purified by vacuum distillation over P_2O_5, while N,N-dimethylacetamide (DMAc) was purified by vacuum distillation over barium oxide. Cyclopentanone and 4-fluoronitrobenzene were purchased from Spectrochem. *o*-Cresol and hydrazine hydrate were obtained from S.D. Fine Chemicals and used without further purification.

Synthesis of new methyl substituted diether-diamine monomer

Synthesis of 1, 1-bis (4-hydroxy 3-methyl phenyl) cyclopentane (BHMPC). In a 250 mL three-necked round-bottom flask equipped with a dry HCl gas inlet tube, reflux condenser, and magnetic stirrer, o-cresol (64.80 g, 0.60 mol), cyclopentanone (8.4 g, 0.10 mol), and 3-mercaptopropanoic acid (0.2 mL) were introduced. Dry HCl gas was passed through the reaction mixture at room temperature. The reaction mixture gradually solidified within approximately 2 h. The resulting solid was dissolved in ethyl acetate (600 mL) and neutralized by washing with aqueous $NaHCO_3$ solution (3 × 200 mL), followed by washing with distilled water (2 × 200 mL). The organic layer was dried over anhydrous magnesium sulfate, decanted, and the solvent was removed by distillation to obtain a viscous liquid. Addition of petroleum ether to the viscous liquid resulted in the formation of a solid product. The solid was washed with water, dried under vacuum, and subsequently reprecipitated from a methanol–water mixture to obtain the purified bisphenol.[43]

Yield: 15.10 g (65%).

M.P.:140°C.

Synthesis of 1, 1-bis [4-(4-nitro phenoxy)-3-methyl phenyl] cyclopentane (BMNPC). In a 500 mL three-necked round-bottom flask equipped with a calcium chloride guard tube, thermowell, nitrogen inlet, and magnetic stirrer, 1,1-bis(4-hydroxy-3-methylphenyl)cyclopentane (BHMPC) (11.28 g, 0.04 mol) and 4-fluoronitrobenzene (12.56 g, 0.08 mol) were dissolved in 60 mL of *N,N*-dimethylformamide (DMF). Anhydrous potassium carbonate (K_2CO_3) (11.04 g, 0.08 mol) was then added to the reaction mixture. The mixture was refluxed for 8 h under a nitrogen atmosphere. After completion of the reaction, the mixture was allowed to cool to room temperature, and water was added to precipitate the product. The precipitated product was collected by filtration, washed with water followed by ethyl acetate, and dried under vacuum.[44]

Yield: 22.86 g (98%),

M.P.: 270°C.

IR: 3062 cm-1 (Aromatic -CH stretch), 2959, 2870 cm-1 (Aliphatic -CH stretch) 1505, 1346 cm-1 (-NO_2 stretching), 1256, 1178 cm-1 (C-O-C stretching).

Synthesis of 1, 1-bis [4- (4-amino phenoxy)-3-methyl phenyl] cyclopentane (BAMPC). In a 250 mL single-neck round-bottom flask equipped with a calcium chloride guard tube and a magnetic stirrer, 1,1-bis [4-(4-nitro-3-methylphenoxy) phenyl]cyclopentane (BMNPC) (13.10 g, 0.025 mol), 10% Pd/C (0.284 g), and hydrazine hydrate (13.5 g) were introduced in 100 mL of a 75:25 ethanol and N, N-dimethylacetamide mixture. The reaction mixture was refluxed for 10 h, and the progress of the reaction was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was filtered while hot to remove the catalyst. The filtrate was then poured into 500 mL of water under vigorous stirring, resulting in the formation of a light-yellow product. The precipitated product was collected by filtration, washed with ethanol, and dried. The resulting BAMPC was recrystallized from a DMAc-water system.[45]

Yield: 9.86 g (85%),

M.P.: 160°C.

IR: 3464, 3377 cm-1 (-NH2 stretching), 3010, 2957, 2869, 1276, 1165 cm-1

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):

δ 7.11 (d, J ≈ 2 Hz, 2H, H_h), 7.00 (dd, J ≈ 8.4, 2 Hz, 2H, H_i), 6.80 (dt, J ≈ 9.6, 2.8 Hz, 4H, H_d), 6.73 (m, 6H, H_e, H_g), 3.54 (s, 4H, H_c), 2.25 (m, 10H, H_b, H_f), 1.8-1.6 (m, 4H, H_a).

^{13} C NMR (100 MHz, $CDCl_3$), δ (ppm): 153.93, 149.80, 143.28, 141.84, 129.79, 127.84, 125.26, 119.77, 116.75, 116.27, 54.64, 38.94, 23.02, 16.55.

Synthesis of poly (azomethine-ether)s from 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

In a 100 mL three-necked round-bottom flask equipped with a reflux condenser, magnetic stirrer, calcium chloride guard

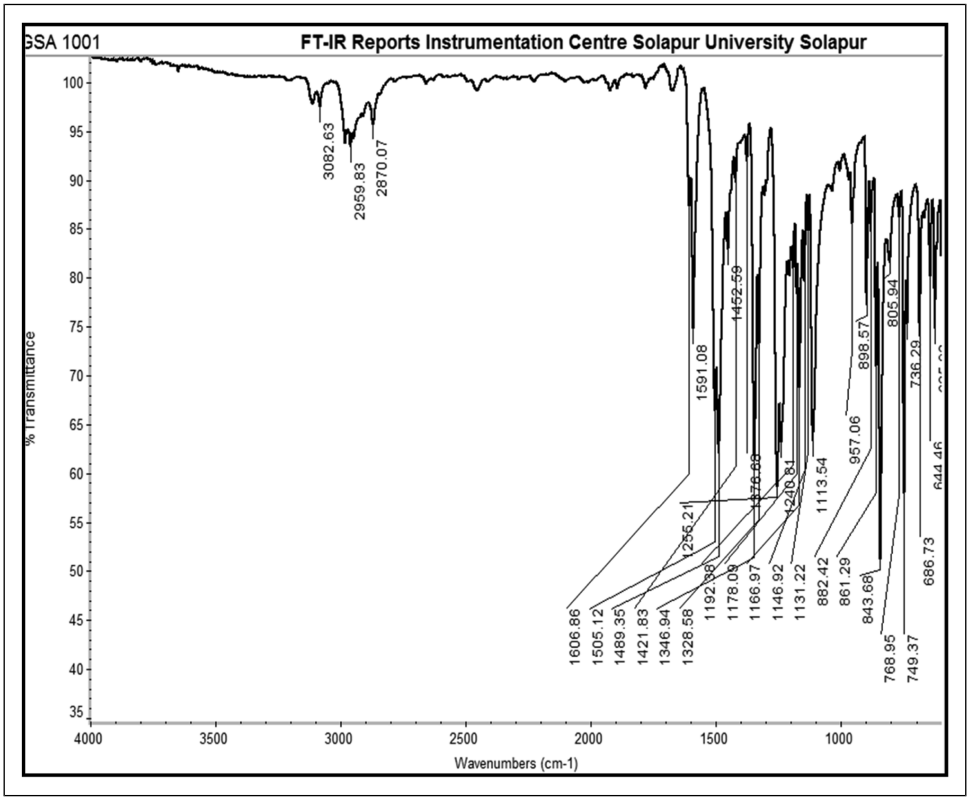


Figure 1. FT-IR spectrum of BMNPC.

tube, and nitrogen inlet, 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane (BAMPC) (0.464 g, 0.001 mol) was dissolved in 3 mL of *N,N*-dimethylacetamide (DMAc) containing 5% lithium chloride (0.150 g). After the solution became clear, terephthalaldehyde (TPA) (0.134 g, 0.001 mol) was added to the flask, and the mixture was stirred overnight under a nitrogen atmosphere. The polymerization mixture was then heated at 140°C for 4 h. The resulting viscous mass was poured into a large excess of water to precipitate the polymer. The fibrous polymer was collected by filtration and washed several times with hot water to remove inorganic impurities. The polymer (SPAM-1) was dried under vacuum at 60°C overnight. The yield of the polymer was 99%, and the inherent viscosity measured in NMP was 0.39 dL g^{-1}.

Polyazomethines and co-polyazomethines (SPAM-2 to SPAM-5) were synthesized using varying molar ratios of terephthalaldehyde (TPA) and isophthalaldehyde (IPA) following a similar procedure.[46]

Results and discussion

To obtain processable polyazomethines, a new diamine monomer containing ether linkages, a cyclopentylidene cardo unit, and a pendant methyl group, namely 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane, was employed. To examine the influence of ether linkages, the cyclopentylidene cardo moiety, and methyl substitution on solubility behavior, a series of co-poly (azomethine-ether)s was synthesized through high-temperature solution polycondensation of 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane with commercially available aromatic dialdehydes, including terephthalaldehyde, isophthalaldehyde, and mixtures of terephthalaldehyde and isophthalaldehyde.

The resulting homo- and co-polyazomethines were characterized using inherent viscosity measurements, solubility studies, FT-IR spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Synthesis of 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

In the first step, cyclopentanone was reacted with *o*-cresol in the presence of dry HCl gas using 3-mercaptopropanoic acid as a catalyst to obtain the bisphenol, 1,1-bis(4-hydroxy-3-methylphenyl)cyclopentane (BHMPC). The obtained bisphenol was subsequently reacted with 4-fluoronitrobenzene in the presence of anhydrous K_2CO_3 to produce the intermediate dinitro compound, 1,1-bis [4-(4-nitrophenoxy)-3-methylphenyl]cyclopentane (BMNPC). The purified BMNPC was characterized by FT-IR spectroscopy Scheme 1.

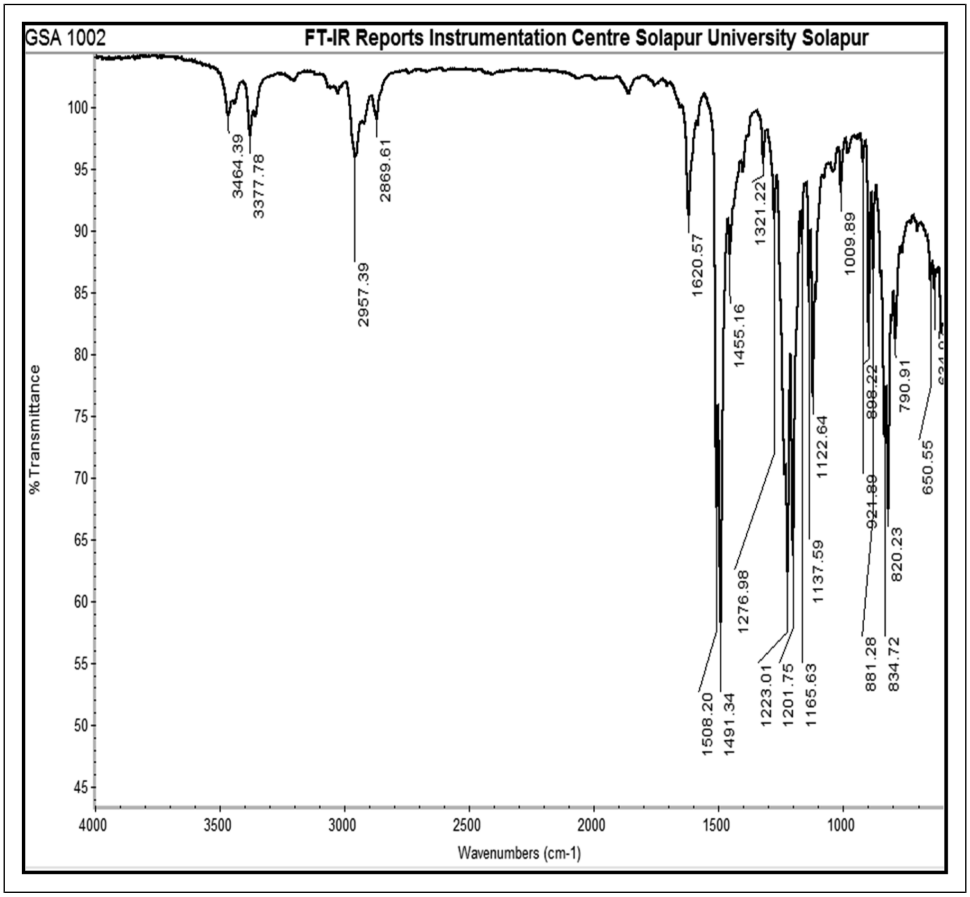


Figure 2. FT-IR spectrum of BAMPC.

The FT-IR spectrum of BMNPC (Figure 1) showed characteristic absorption bands at 1505 cm^{-1} corresponding to asymmetric -NO_2 stretching and at 1346 cm^{-1} attributed to symmetric -NO_2 stretching vibrations. The absorption bands observed at 3062 and 2959 cm^{-1} were assigned to aromatic -CH stretching and aliphatic -CH stretching, respectively. Bands appearing at 1255 and 1178 cm^{-1} correspond to C-O-C stretching vibrations, indicating the presence of ether linkages in the dinitro compound.

In the subsequent step, BMNPC was reduced to the corresponding diamine, 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane (BAMPC), through catalytic hydrogenation using hydrazine hydrate in the presence of 10 wt.% Pd/C. The crude diamine was purified by recrystallization from a DMAc-water mixture and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

The FT-IR spectrum of BAMPC (Figure 2) showed characteristic N-H stretching absorption bands at 3464 cm^{-1} (asymmetric N-H stretching) and 3377 cm^{-1} (symmetric N-H stretching). Absorption bands observed at 1223 cm^{-1} and 1122 cm^{-1} correspond to C-O-C stretching vibrations, indicating the presence of ether linkages. The band at 3010 cm^{-1} was attributed to aromatic C-H stretching, whereas bands at 2957 and 2869 cm^{-1} correspond to aliphatic C-H stretching associated with the cyclopentane moiety.

The ^{1}H-NMR spectrum of 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane (BAMPC) is shown in Figure 3.

The ^{1}H NMR spectrum exhibits characteristic signals corresponding to both aromatic and aliphatic protons. The aromatic region (δ 6.64-7.28 ppm) contains multiple resonances attributable to protons of substituted benzene rings.

A doublet at δ ∼ 7.11 ppm (2H, 'H_h') with a small coupling constant (J ≈ 2 Hz) is characteristic of meta coupling, indicating these protons are positioned meta to adjacent protons. The signal at δ ∼ 7.00 ppm (2H, 'H_i') appears as a doublet of doublets with coupling constants of J ≈ 8.4 Hz and 2 Hz, confirming simultaneous ortho (strong) and meta (weak) coupling interactions within the aromatic system.

The resonance at δ ∼ 6.80 ppm (4H, 'H_d') is observed as a doublet of triplets. This pattern arises from two closely spaced triplets (6.820-6.806 ppm and 6.796-6.782 ppm). The fine splitting within each triplet corresponds to J ≈

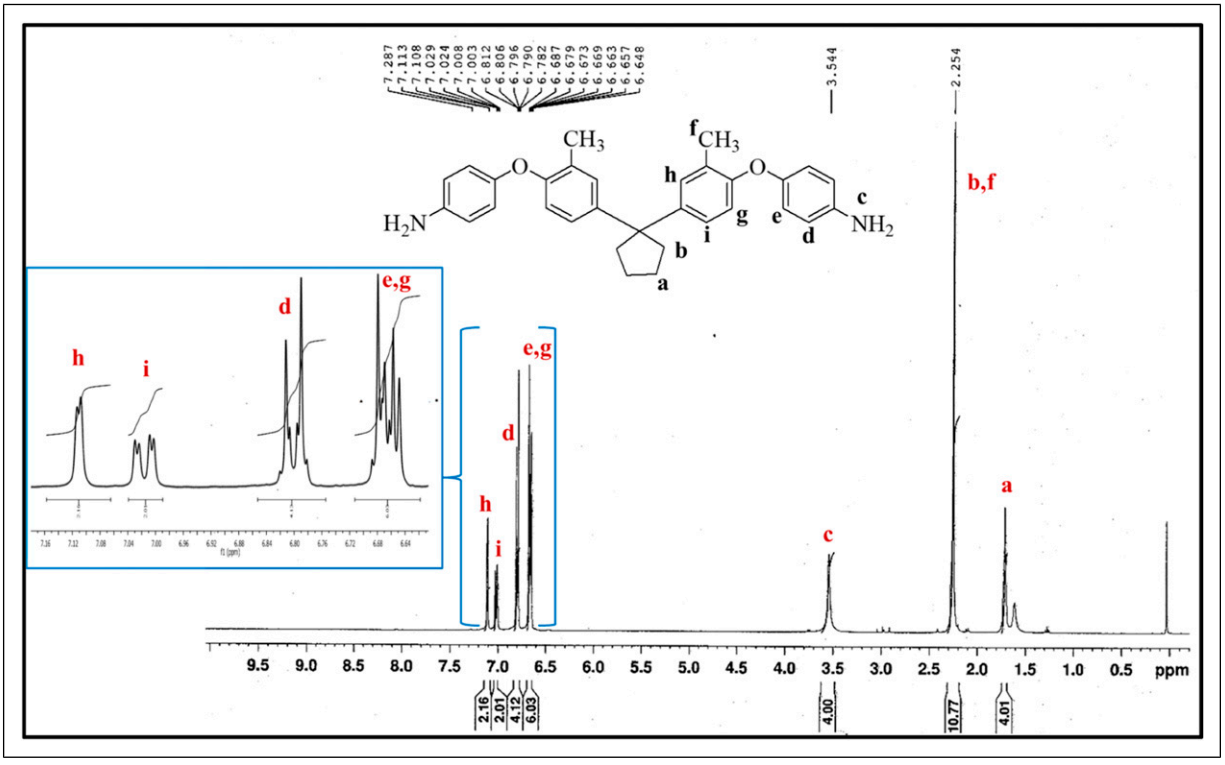


Figure 3. ^{1}H NMR spectrum of BAMPC.

2.8 Hz, attributed to unresolved long-range (meta and para) couplings, while the separation between the triplet centers (J ≈ 9.6 Hz) is due to ortho coupling. This splitting pattern supports interaction with one ortho proton along with weaker long-range couplings, consistent with a substituted aromatic system.

A multiplet in the range δ ~ 6.70-6.85 ppm (6H, 'H_e' and 'H_g') arises from overlapping aromatic signals. Although

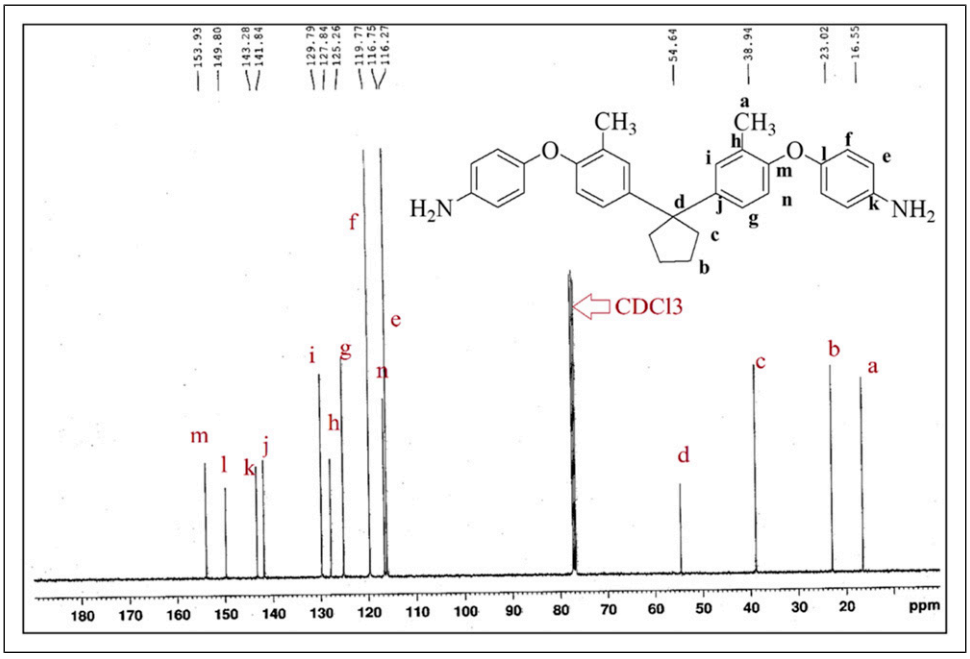


Figure 4. ^{13}C NMR spectrum of BAMPC.

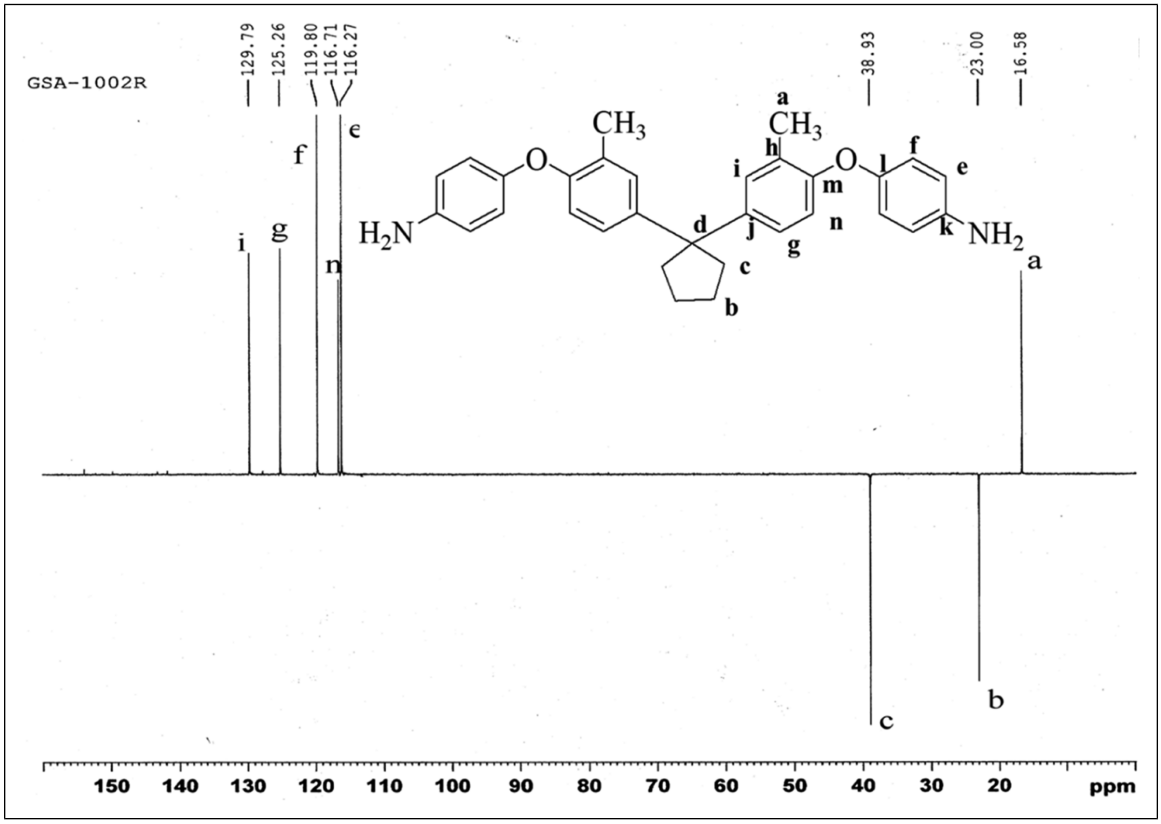


Figure 5. DEPT-135 spectrum of BAMPC.

the two phenyl rings are chemically non-equivalent due to asymmetric substitution, the ortho protons adjacent to the ether linkage (-O-) experience similar electronic environments. The + R (electron-donating resonance) effect of oxygen increases electron density at the ortho positions, resulting in shielding and an upfield shift; consequently, these signals overlap and appear as a combined multiplet.

In the aliphatic region, the multiplets at δ 1.6-1.8 ppm assigned to the cyclopentyl methylene protons ('H_a'). A single intense singlet at δ ~ 2.25 ppm corresponds to the methyl protons ('H_b' and 'H_f') due to their close ppm values, resulting in overlapping signals. A sharp singlet at δ ~ 3.54 ppm is assigned to the -NH_2 protons ('H_c'), confirming terminal amine functionality with minimal hydrogen bonding. Overall, the spectral data are consistent with the proposed structure and confirm the successful formation of the BAMPC monomer.

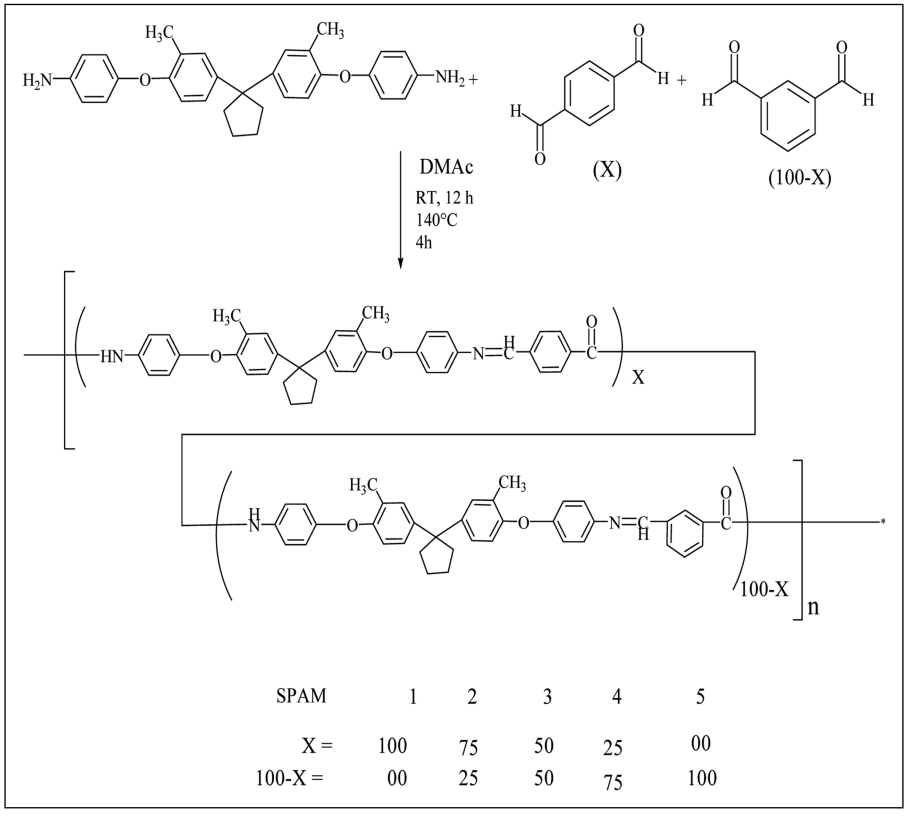
The ^{13}C-NMR spectrum of BAMPC with the corresponding assignments is shown in Figure 4. The spectrum displayed fourteen signals, indicating the presence of fourteen different carbon environments in the molecule. Signals at 127.84, 125.26, 119.77, 116.75, and 116.27 δ correspond to aromatic CH carbons. Signals at 153.93, 149.80, 143.28 (C-NH_2), 141.84, 129.79, and 54.64 δ were attributed to tertiary carbons. The CH_2 carbons of the cyclopentylidene ring appeared at 38.94 and 23.02 δ, confirming the presence of the aliphatic cyclopentylidene unit. The signal observed at 16.55 δ was assigned to the methyl carbon attached to the aromatic ring.

The DEPT spectrum (Figure 5) further supports the structure of the amino compound. Quaternary carbons were absent in the spectrum, while signals corresponding to CH and CH_3 carbons appeared in the positive region at 129.79, 125.26, 119.80, 116.71, and 116.27 δ, and at 16.58 δ for the methyl carbon. The CH_2 carbons appeared in the negative region at 38.93 and 23.0 δ.

The mass spectrum of BAMPC (Figure 6) exhibited a molecular ion peak at m/z 465, which corresponds to the molecular weight of the BAMPC monomer.

Synthesis of poly (azomethine-ether)s from 1, 1-bis [4-(4-amino phenoxy)-3-methyl phenyl] cyclopentane

A series of methyl-substituted homo- and co-poly (azomethine-ether)s were synthesized, as shown in Scheme 2, through high-temperature solution polymerization of BAMPC with the dialdehydes TPA and/or IPA in DMAc containing LiCl. Lithium chloride was added to facilitate the removal of water generated during the



Scheme 2. Synthesis of co-poly (azomethine-ether)s (SPAM-1 to SPAM-5).

polycondensation reaction. The polymerization proceeded smoothly, resulting in highly viscous solutions. The resulting polymers were precipitated by pouring the viscous reaction mixture into water.

The inherent viscosities of the polymers were measured in NMP and were found to range from 0.20 to 0.38 dL g^{-1}. The corresponding data for these poly (azomethine-ether)s are summarized in (Table 1).

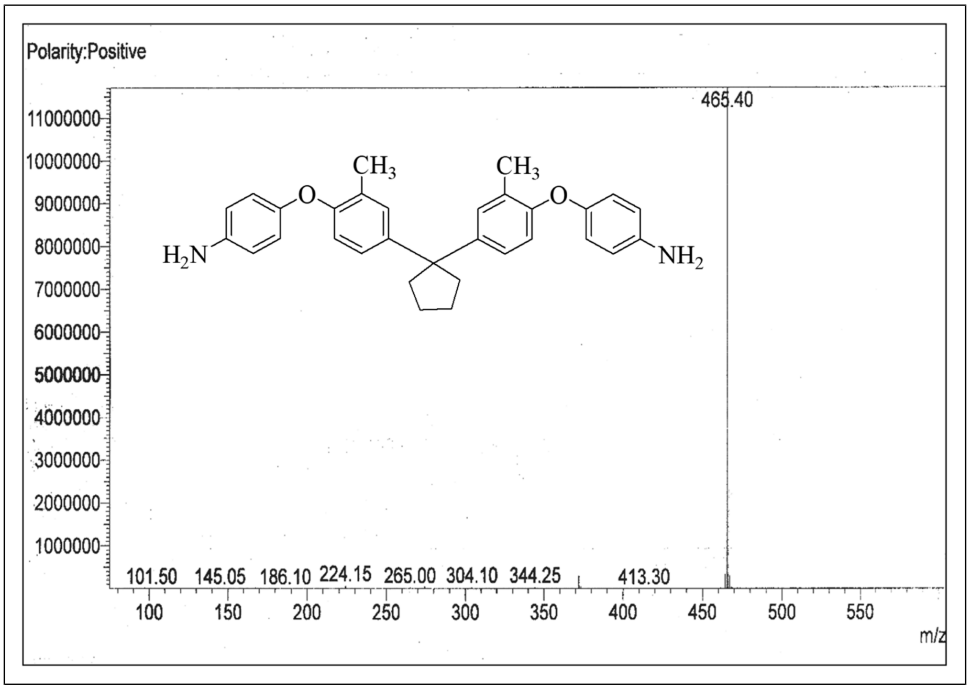


Figure 6. Mass spectrum of BAMPC.

Table 1. Yield and Viscosity of co-poly (azomethine-ether)s.

	Monomers				
polymer Code	Diamine BAMPC mol %	TPA mol%	IPA mol%	Yield %	Inherent viscosity dL/g[a]
SPAM-1	100	100	0	99	0.39
SPAM-2	100	75	25	98	0.28
SPAM-3	100	50	50	97	0.33
SPAM-4	100	25	75	98	0.20
SPAM-5	100	0	100	99	0.24

[a]Inherent viscosity was measured at a concentration of 0.5 % (W/V) in NMP at 30°C.

Structural characterization. The polymers were characterized by infrared spectroscopy. The FT-IR spectrum of poly (azomethine-ether) SPAM-1 (Figure 7) showed a characteristic absorption band at 1624 cm^{-1} corresponding to CH = N stretching of the azomethine linkage. Sharp bands observed at 1229 and 1121 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the C-O-C ether linkage. The bands appearing at 2970 and 2865 cm^{-1} correspond to asymmetric and symmetric aliphatic C–H stretching vibrations. The band at 827 cm^{-1} indicates para-substituted aromatic ring linkage. The absence of characteristic N–H and aldehyde C = O bands in the FT-IR spectrum indicates complete consumption of terminal amine and aldehyde groups, confirming successful polymerization and the formation of a well-condensed polyazomethine structure.

The FT-IR spectrum of poly (azomethine-ether) SPAM-3 (Figure 8) exhibited a characteristic absorption band at 1623 cm^{-1} attributed to CH = N stretching. Bands observed at 1229 and 1156 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of the C-O-C ether linkage. Absorption bands at 2969 and 2846 cm^{-1} were assigned to asymmetric and symmetric aliphatic C-H stretching vibrations. The vibration at 832 cm^{-1} indicates para-linked aromatic rings. The disappearance of the characteristic N–H and aldehyde C = O absorption bands in the FT-IR spectrum suggests full consumption of terminal amine and aldehyde groups, thereby confirming successful polymerization and

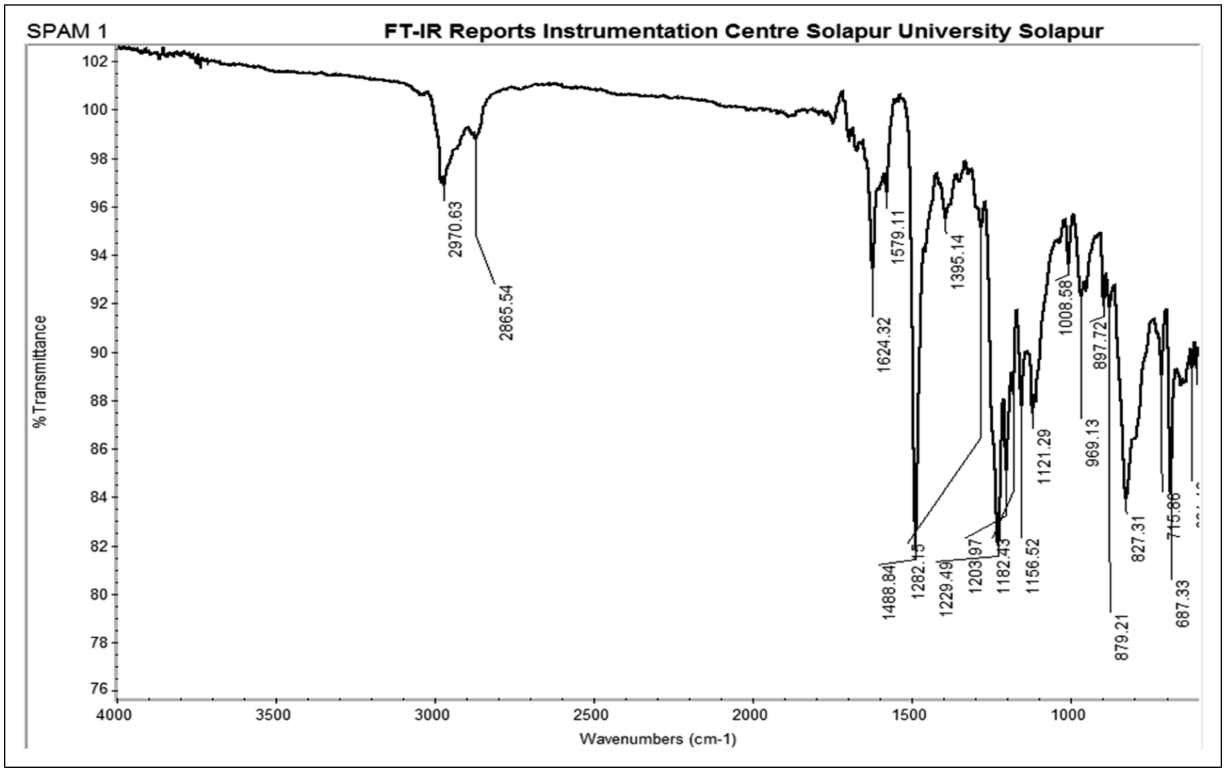


Figure 7. FT-IR spectrum of SPAM-1 polymer.

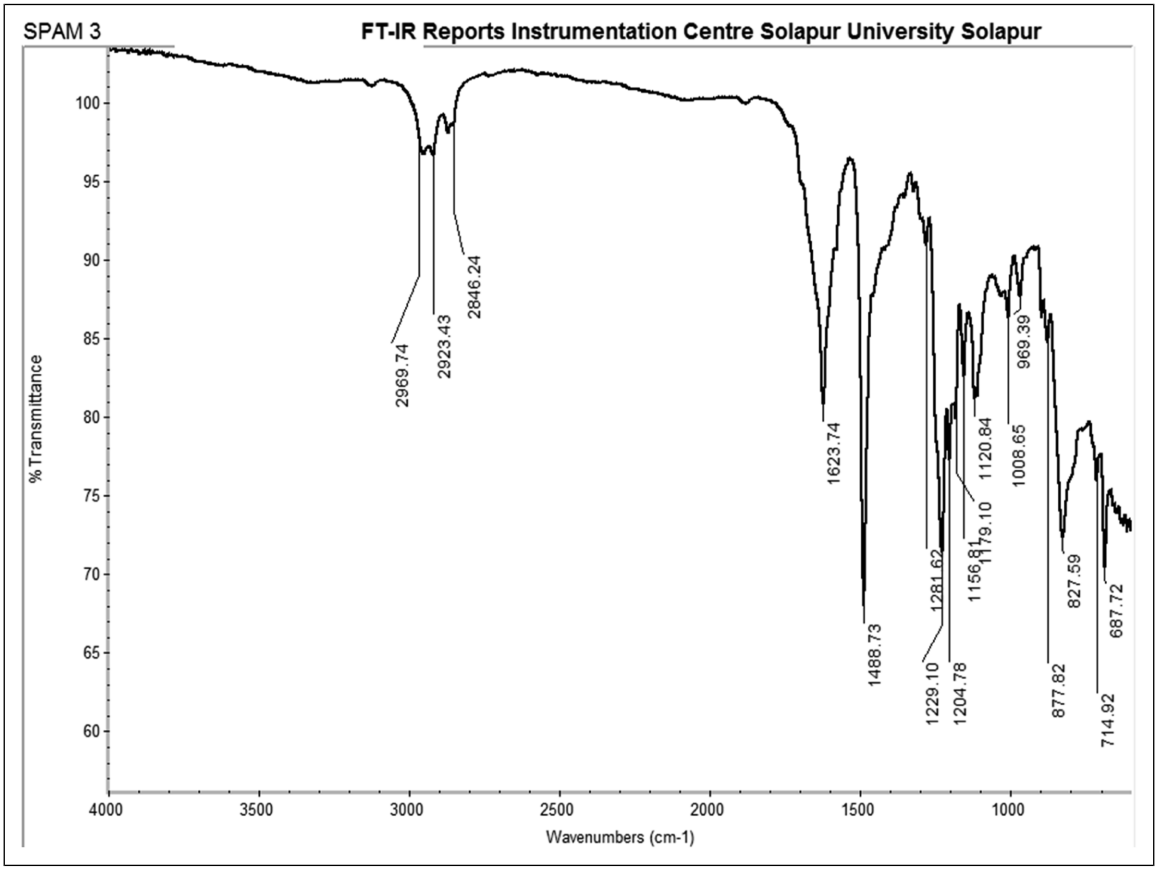


Figure 8. FT-IR spectrum of SPAM-3 polymer.

the formation of a highly condensed polyazomethine structure.

Similarly, the FT-IR spectrum of poly (azomethine-ether) SPAM-5 (Figure 9) showed a characteristic band at 1621 cm^{-1} corresponding to CH = N stretching. The bands at 1234 and 1122 cm^{-1} were attributed to asymmetric and symmetric stretching vibrations of the C-O-C ether linkage. Absorption bands at 2970 and 2872 cm^{-1} correspond to asymmetric and symmetric aliphatic C-H stretching vibrations. The band at 835 cm^{-1} indicates para-catenation of the aromatic rings. Further, the appearance of a weak, broad absorption band in the range of 3300–3500 cm^{-1}, which is attributed to the N–H stretching vibration of terminal amine groups. Additionally, a weak but sharp band observed around 1686 cm^{-1} corresponds to the C = O stretching of terminal aldehyde groups, confirming the presence of end functionalities in the polymer. These characteristic absorptions confirm the incomplete end-group conversion and validate the expected polyazomethine structure with identifiable terminal functionalities.

Solubility properties. The solubility characteristics of the methyl-substituted poly (azomethine-ether)s are

Table 2. Solubility behaviour of co-poly (azomethine-ether)s.

Polymer Code	Solvents							
	DMF	DMAc	DMSO	NMP	THF	$CHCl_3$	DCM	$C.H_2SO_4$
SPAM-1	–	–	–	+	±	–	+	+
SPAM-2	±	±	–	+	±	–	+	+
SPAM-3	±	±	–	+	±	–	+	+
SPAM-4	+	+	+	+	±	–	±	+
SPAM-5	±	±	±	+	±	–	±	+

+: Soluble; –: Insoluble on heating; ±: Sparingly soluble.

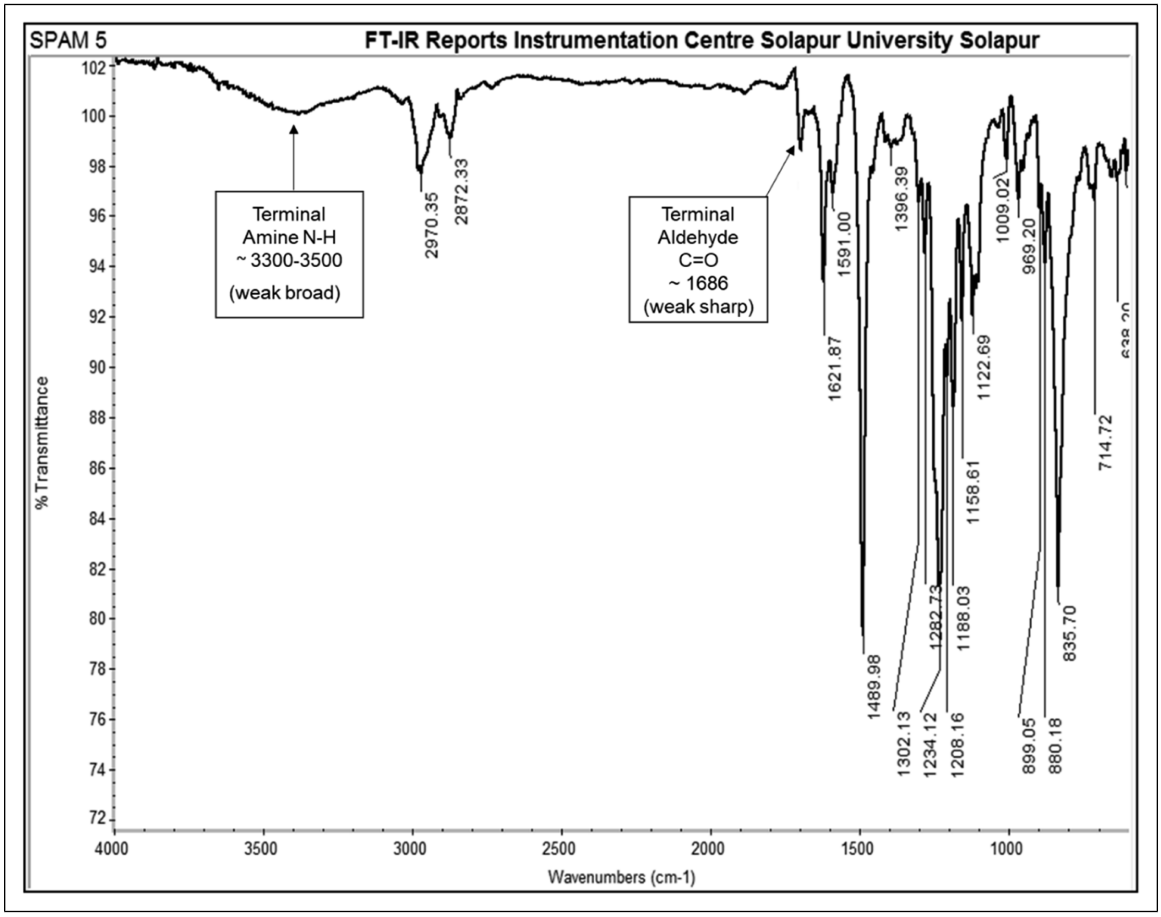


Figure 9. FT-IR spectrum of SPAM-5 polymer.

summarized in Table 2. Poly (azomethine-ether)s SPAM-1 to SPAM-5 showed solubility in N-methylpyrrolidone (NMP) and partial solubility in solvents such as THF and dichloromethane (DCM). These polyazomethines were insoluble in solvents including DMF, DMAc, and DMSO.

Polymer SPAM-1, synthesized from terephthalaldehyde (TPA), exhibited lower solubility, which may be associated with its relatively rigid structure leading to closer packing of the polymer chains. In contrast, polyazomethine SPAM-4 showed improved solubility in DMF, DMAc, NMP, and DMSO. The observed improvement in solubility can be attributed to co-polymerization of the diamine with TPA and IPA, as well as the presence of the cyclopentylidene cardo unit, pendant methyl substitution, and ether linkages within the polymer backbone.

Thermal properties. The thermal behaviour of the co-poly (azomethine-ether)s was evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Table 3 summarizes the thermal parameters, including glass transition temperature (Tg), initial decomposition temperature (T_i), temperature at 10% weight loss (T_d), and residual weight at 900°C.

The thermal stability of the methyl-substituted poly (azomethine-ether)s (Figure 10) was evaluated by thermogravimetric analysis at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. The temperature corresponding to 10% weight loss (T_d) was observed in the range of 456-486°C. These polymers, similar to other poly (Schiff

Table 3. Physical properties of co-poly (azomethine-ether)s.

Polymer Code	Thermal behaviour[a]			
	T_i °C	T_d °C	Tg °C	Residual weight % at 900°C
SPAM-1	416	486	178	18
SPAM-2	414	474	175	19
SPAM-3	410	456	170	18
SPAM-4	414	484	170	17
SPAM-5	409	470	165	16

[a]Temperature at which onset of decomposition was recorded by TGA at **a** heating rate of 10°C/min.
Tg- Glass transition temperature determined at second heating by DSC at a heating rate of 10°C/min.
T_d – Temperature of 10% decomposition.
T_i – Initial decomposition temperature.

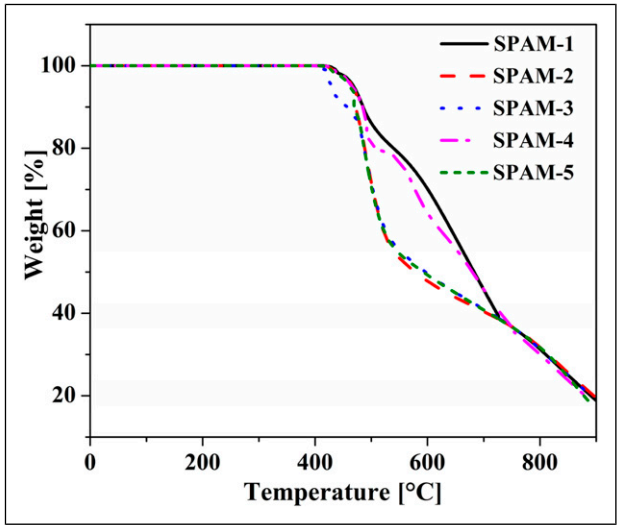


Figure 10. TGA curve of co-poly (azomethine-ether)s SPAM-1 to SPAM-5.

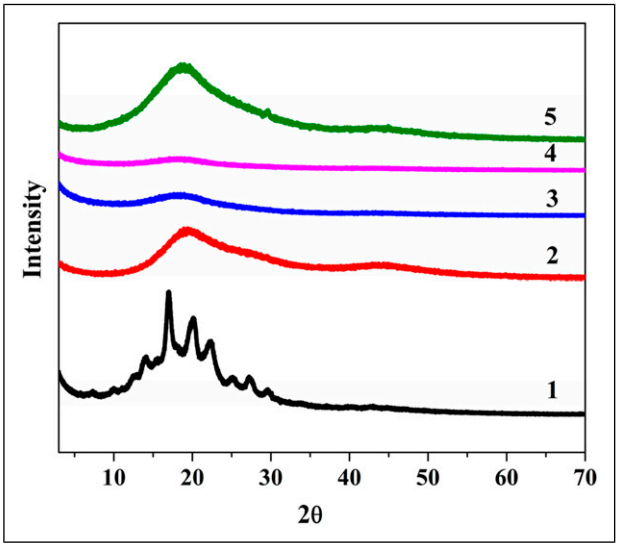


Figure 12. XRD curve of co-poly (azomethine-ether)s SPAM-1 to SPAM-5.

base)s, exhibited thermal stability under a nitrogen atmosphere, with 10% weight loss occurring only above 456°C. The initial decomposition temperatures (T_i) were in the range of 409-416°C. The residual weight at 900°C was found to be between 16% and 19%.

The DSC curves (Figure 11) show the glass transition temperatures (Tg) of the methyl-substituted poly (azomethine-ether)s. All polymers exhibited a Tg, indicating an amorphous or glassy morphology. This behaviour can be associated with the presence of cardo units, pendant methyl substituents in the polymer backbone, and copolymerization, which limit regular chain packing and reduce crystallinity. The Tg values of the polymers were observed in the range of 165-178°C. Polymer SPAM-5 showed a comparatively higher Tg than the other polymers, which can be attributed to the incorporation of terephthalaldehyde (TPA). The rigid structure of TPA promotes closer packing of polymer chains, leading to an increase in the glass transition temperature.

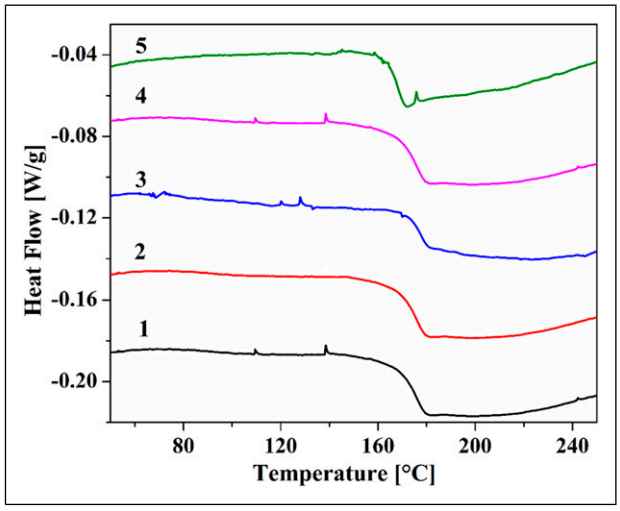


Figure 11. DSC curve of co-poly (azomethine-ether)s SPAM-1 to SPAM-5.

Wide-angle X-ray diffraction (WAXD) studies. The wide-angle X-ray diffraction (WAXD) patterns of the polymers showed a broad halo in the region of $2\theta \approx 20°$, indicating that the polymers predominantly exhibit an amorphous structure. The methyl-substituted poly (azomethine-ether)s were further examined using wide-angle X-ray diffraction, and the diffraction patterns of the polymers are presented in Figure 12. Among the polymers, SPAM-4 exhibited a highly amorphous nature. This behavior may be attributed to copolymerization of the diamine with IPA and TPA, along with the presence of the cyclopentylidene cardo unit, pendant methyl substitution, and ether linkages in the polymer backbone. These structural features can disrupt chain regularity and packing, leading to an amorphous morphology. In contrast, polymer SPAM-1 showed a semicrystalline nature, which may be associated with the presence of para-linked terephthalaldehyde units that facilitate closer packing of the polymer chains.

Conclusions

A methyl-substituted diether–diamine monomer, 1,1-bis [4-(4-aminophenoxy)-3-methylphenyl]cyclopentane (BAMPC), containing a cardo cyclopentane unit was synthesized through a multistep route, and its structure was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry. Polycondensation of BAMPC with

terephthalaldehyde and isophthalaldehyde produced a series of co-poly (azomethine-ether)s incorporating cardo cyclopentane units. The resulting polymers exhibited high thermal stability with glass transition temperatures (Tg) in the range of 165-178°C and decomposition temperatures (Td) between 456 and 486°C. The polymers were soluble in polar aprotic solvents such as DMF, NMP, DMAc, and DMSO at ambient temperature or upon heating. X-ray diffraction analysis indicated that SPAM-2, SPAM-3, SPAM-4, and SPAM-5 are predominantly amorphous with a broad diffraction peak around $2\theta \approx 20°$, whereas SPAM-1 exhibits semicrystalline behaviour. The inherent viscosities of the copolymers were in the range of 0.20-0.39 dL g^{-1} indicated moderate molecular weight. Future studies will examine the mechanical properties, film-forming ability, and performance of these polymers in high-temperature applications.

ORCID iDs

Sanjay S. Ankushrao https://orcid.org/0000-0003-2999-4208
Anil A. Ghanwat https://orcid.org/0000-0002-6053-0834
Suraj D. Jadhav https://orcid.org/0009-0008-6357-0840
Pradip D. Chavan https://orcid.org/0009-0007-9602-876X

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Author contributions

Sanjay S. Ankushrao: Conceptualization, Investigation, Writing-Original Draft, Methodology, Writing-Review & Editing.
Anil A. Ghanwat: Supervision, Visualization, Formal Analysis, Validation, Resources.
Suraj D. Jadhav: Software, Data Curation, Formal Analysis.
Pradip D. Chavan: Review, Resources.

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Data Availability Statement

The data will be made available on request.

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