



SOLUBLE AND PROCESSABLE HEAT RESISTANT POLY(ETHER-AMIDE)S CONTAINING CYCLOPENTYLIDENE MOIETY

S. S. Ankushrao^{*1}, A. A. Ghanwat², V. N. Kadam¹, J. N. Mahindrakar¹, P. H. Salunkhe¹

¹Department of Chemistry, Vivekanand College (Autonomous), Kolhapur, Maharashtra, India

²School of Chemical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur, Maharashtra, India

*Corresponding author: sanjayankushrao@gmail.com

ABSTRACT

A new series of poly(ether-amide)s were synthesized by using direct Yamazaki's phosphorylative polycondensation of novel diacid 1,1-bis[4-(4-carboxy methyl phenoxy) phenyl] cyclopentane (BCMPP) with various aromatic diamines such as ODA, MDA, p-PDA, SDA etc. These novel polymers were characterized by FT-IR spectroscopy, solubility, inherent viscosity, thermal analysis and XRD studies. Inherent viscosities of these polymers were in the range 0.20 to 0.40 dL/g indicating moderate molecular weight built-up. These polymers exhibited excellent solubility in various polar aprotic solvents such as NMP, DMSO, DMAc, DMF etc. These polymers were also soluble in pyridine and Conc. H₂SO₄. The X-Ray diffraction patterns of polymers revealed that introduction of cardo moiety containing ether linkage would disturb the chain regularity and packing, leading to amorphous and semicrystalline nature. Thermal analysis by TGA disclosed excellent thermal stability of polymers. The structure-property correlation among these poly(ether-amide)s was studied, in view of these polymer's potential applications as processable high temperature resistance materials.

Keywords: 1,1-bis[4-(4-carboxy methyl phenoxy) phenyl] cyclopentane, poly(ether-amide)s, Solubility, Viscosity, Thermal stability

1. INTRODUCTION

Aromatic polyamides attract much interest because of their thermal and chemical resistances as well as their high strength and high modulus in fiber form. However these materials suffer poor processability due to their limited solubility, extremely high glass transition temperatures and infusibility caused by the high crystallinity and stiffness of polymer backbones and that make them very difficult to be processed by spin coating or thermoforming techniques [1, 2]. Much effort has been made to create structurally modified aromatic polymers having increased solubility and processability with retention of their high thermal stability. It is known that the solubility of polymers is often increased when flexible bonds such as [-O-, -SO₂-, -CH₂-, -C(CF₃)₂], bulky pendent groups (such as t-butyl, adamantyl and naphthyl), large pendent groups or polar constituents such as heterocyclic segments are incorporated into the polymer backbone which alters crystallinity and intermolecular interactions [3-5]. Recently, there have been some reports concerning the incorporation of cardo and pendant groups into polymeric frameworks [6-8]. If

the cardo or pendant moiety is carefully chosen, it is possible to promote solubility without affecting thermal and mechanical properties to any greater extent [9-17]. In the literature study we observed that synthesis of different polyamides containing pendant or cardo moieties such as cyclohexylidene, t-butyl, adamantyl, naphthyl as well as insertion of flexible bonds such as -O-, -SO₂-, -CH₂-, -C(CF₃)₂ in the main chain with improved solubility and thermal properties [18-32]. In the present study, synthesis and characterization of six new polyamides SPA-1 to SPA-6 containing cyclopentylidene moieties in the main chain is reported from the Yamazaki's phosphorylative polycondensation reaction of 1,1-bis[4-(4-carboxy methylene phenoxy)phenyl] cyclopentane (BCMPP) and 4,4'-diamino diphenyl ether, 4,4'-diamino diphenyl methane, 4,4'-diamino diphenyl sulfone, 1,4-phenylene diamine, 1,1-bis(4-(4'-aminophenoxy)phenyl)cyclopentane, 1,3-bis(4-amino phenoxy)benzene by using N-methyl-2-pyrrolidone (NMP), triphenylphosphite and pyridine as condensing agents. These polymers have a cyclopentylidene ring as cardo moiety and -O- as well as

-CH₂- flexible linkages in the main chain for improving solubility in organic solvents without much sacrificing thermal stability. Therefore preparation of soluble and processable polyamides has been a major research interest. It is highly desirable that these polymers be soluble in some specific organic solvents to facilitate processing, however they should retain resistance to common solvents during their use.

2. MATERIALS AND MEASUREMENTS

2.1. Materials

All the reagents such as 4, 4'-Oxydianiline; 4, 4'-methylenedianiline; 4, 4'-Sulfonyl dianiline were purchased from Sigma Aldrich and used as received. The p-Phenylene diamine was purified by recrystallization in ethanol. The monomers 1, 3-bis (4-aminophenoxy) benzene (BAPB) and 1, 1-bis(4-(4-aminophenoxy)phenyl)cyclopentane (BAPC) were prepared in the laboratory as per procedure reported.⁹ Cyclopentanone, Phenol, 4-fluoro nitrobenzene were purchased from Spectrochem and used as received. N, N-dimethyl formamide was vacuum distilled from P₂O₅; N, N-dimethylacetamide was purified by vacuum distillation from barium oxide. Commercially available Sulfur was also purified by refluxing with calcium oxide for 30 min and reprecipitated with HCl. Pyridine was refluxed with solid potassium hydroxide pellets, fractionally distilled and stored over Linde type 4 Å Molecular sieves, N-Methyl-2 pyrrolidone (NMP) was dried by azeotropic removal of water with benzene for 6 h, distilled under reduced pressure and stored over Linde type 4 Å Molecular sieves. Morpholine was dried with potassium hydroxide and fractionally distilled. Potassium carbonate (K₂CO₃) was dried under vacuum at 150°C for 6 h. Lithium chloride was dried under vacuum at 150°C for 6 h. Glacial acetic acid, Conc. hydrochloric acid used as received.

2.2. Measurements

Inherent viscosity measurements were carried out with a 0.5% (w/v) polymer solution in N, N-Dimethyl formamide (DMF) at 30°C with an Ubbelohde suspended level viscometer. ¹H NMR spectra were recorded on a Bruker AV III 400 MHz instrument [the reference was 0 ppm with tetramethylsilane (1H)]. An IR spectrum was recorded with a Thermo Nicolet IS- 10 FTIR spectrometer. Differential scanning calorimetry (DSC) measurements were made on a Mettler Toledo Instrument at a heating-cooling rate of 10°C /min 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°C /min was used for the determination of the decomposition temperature (Td) at a 10% weight loss under nitrogen environment. X-ray diffraction patterns were obtained on Ultima-IVX-ray diffractometer.

3. EXPERIMENTAL

3.1. Monomer Synthesis

3.1.1. Synthesis of 1, 1-bis(4-hydroxy phenyl) cyclopentane (I)

In a 500 mL round bottom flask equipped with a thermowell, a condenser and a magnetic stirrer were placed 141 g (1.5mol) of phenol and 21 g (0.25mol) of cyclopentanone. To this solution 100 mL of conc. HCl and 50 mL of glacial acetic acid were added. Resulting reaction mixture was stirred for 8 h at 45°C and kept overnight at room temperature. Then pink color product was isolated by filtration and washed with hot water till it is free from phenol and acid. A crude bisphenol(I) was purified by dissolving in minimum quantity of 2M NaOH at room temperature and the resulting solution was filtered to remove the gummy product. The filtrate was acidified with conc. HCl to yield the precipitate. The precipitated product was filtered, washed with water till free from acid and dried. Finally the crude bisphenol was reprecipitated from methanol-water mixture to get faint pink shining crystals.

Yield: 28.6 g (45.03 %), M.P: 168-170°C, **IR**: 3582, 3387, 3299, 2967, 2865, 1633, 1592, 1449, 1373, 1251, 1178, 1083, 835, 735, 681cm⁻¹

3.1.2. Synthesis of 1, 1-bis [4-(4-acetyl phenoxy) phenyl] cyclopentane (II)

In a 500 mL three neck round bottom flask equipped with calcium chloride guard tube, thermowell, N₂ gas inlet and magnetic stirrer, were placed 12.7 g bisphenol (I) (0.05 mol) and 13.814 g 4- fluoroacetophenone (0.1 mol) in 125 mL N,N-dimethyl acetamide (DMAc), then 13.821 g of anhydrous K₂CO₃ 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 finally dried under vacuum. The crude product was recrystallized from methanol.

Yield: 21.7 g (88.97 %), M.P.: 90-92°C, **IR**: 2972, 2868, 1985, 1591, 1497, 1452, 1355, 1321, 1243, 1169, 1159, 1107, 1012, 957, 880, 848, 828, 768, 712 cm^{-1}

3.1.3. Synthesis of 1, 1-bis [4-(4-thioacetomorpholide phenoxy) phenyl] cyclopentane (III)

In a 100 mL round bottom flask equipped with reflux condenser and magnetic stirrer were placed 9.8 g (0.02 mol) of diketone (II); 1.84 g (0.06 mol) of sulphur and 5.227 g (0.06 mol) of morpholine (5.2 mL). The resulting reaction mixture was stirred initially under gentle reflux until the evolution of hydrogen sulphide subsides and more vigorously for 14 h at 140°C. The reaction mixture was allowed to cool and 90 mL ethanol was added to obtain buff colored product which was filtered, washed with excess of ethanol and dried.

Yield: 11.0g (79.47%), M.P.: 90°C, **IR**: 2930, 2861, 1684, 1494, 1453, 1240, 1169, 1160, 1029, 1013, 957, 879, 868, 849, 839 cm^{-1} .

3.1.4. Synthesis of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane(IV)(BCMP)

In a 500 mL round bottom flask equipped with reflux condenser, magnetic stirrer were placed 10.38g (0.015mol) of (III) and 200 mL ethanolic 10% NaOH solution, the reaction mixture was refluxed with stirring for 14 h. Then most of the ethanol was distilled out under reduced pressure. To this residual product 200 mL hot water was added and filtered. The filtrate was acidified by 1:1 HCl. The precipitated product was filtered, washed thoroughly with hot water and dried. Then product was dissolved in Sodium bicarbonate solution and reprecipitated from 1:1 HCl. Filtered product and washed thoroughly with water, dried under vacuum.

Yield: 7.0 g (89.39 %), M.P.: 110 - 114°C, **IR**: 3500-3260, 2959, 2873, 1707, 1593, 1500, 1408, 1240, 1170, 878, 826, 540 cm^{-1} . **¹H NMR (DMSO, δ):** 7.27-6.83 δ (m, 16H), 3.5 δ (s, 4H), 2.23 δ (4H), 1.62 δ (4H). **¹³CNMR (DMSO, δ):** 173, 156, 154, 143, 131, 129, 128, 119, 117, 54, 40, 38, 22 δ .

3.2. Synthesis of poly(ether-amide)s

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 0.522 g (1mmol) 1,1-bis[4-(4-carboxy methylene phenoxy) phenyl]cyclopentane (IV), 0.200g (1mmol) 4,4'-

diaminodiphenyl ether (ODA), 0.115g lithium chloride [5 wt % based on solvent N-methyl pyrrolidone (NMP) and pyridine mixture] and 0.744g (0.63mL, 2.4mmol) triphenyl phosphite (TPP), 0.5mL pyridine and 2mL NMP. The mixture was stirred well and temperature was slowly raised to 100°C over a period of 30 min. The mixture was heated at 100°C for 3h under nitrogen. After cooling the resulting viscous solution was poured into 200 mL of methanol under vigorous stirring. The precipitated polymer (SPA-1) was filtered, washed with methanol and dried. The polymer was purified by dissolving in N, N-dimethylacetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol and dried under vacuum at 100°C for 6 h. The yield was 100% and the viscosity of polymer in DMAc was 0.20 dL/g.

The polyamides SPA-2 to SPA-6 were synthesized with varying diamines by similar procedure.

IR(SPA-1): 3269, 3194, 3035, 2954, 2916, 2873, 1658, 1598, 1490, 1235, 1170, 1014, 875, 831, 756, 692, 557 cm^{-1}

IR(SPA-4): 3290, 2953, 2840, 1674, 1591, 1400, 1309, 1250, 1149, 1107, 875, 835, 758, 690, 553 cm^{-1}

IR(SPA-5): 3309, 2980, 2919, 2865, 1669, 1601, 1543, 1405, 1300, 1183, 1013, 962, 875, 796, 692, 668 cm^{-1}

4. RESULTS AND DISCUSSION

The main objective of this study was focused on improving the solubility of the novel polyamides through the design and synthesis of new diacid monomer. Therefore, for the preparation of a flexible diacid with built-in methylene linkage and ether linkage a series of reactions were performed. Hence in the present work, diacid containing cyclopentylidene moiety, viz. 1, 1-bis[4-(4-carboxy methylene phenoxy)phenyl] cyclopentane (IV) have been synthesized and used as building blocks for preparing poly (ether-amide)s.

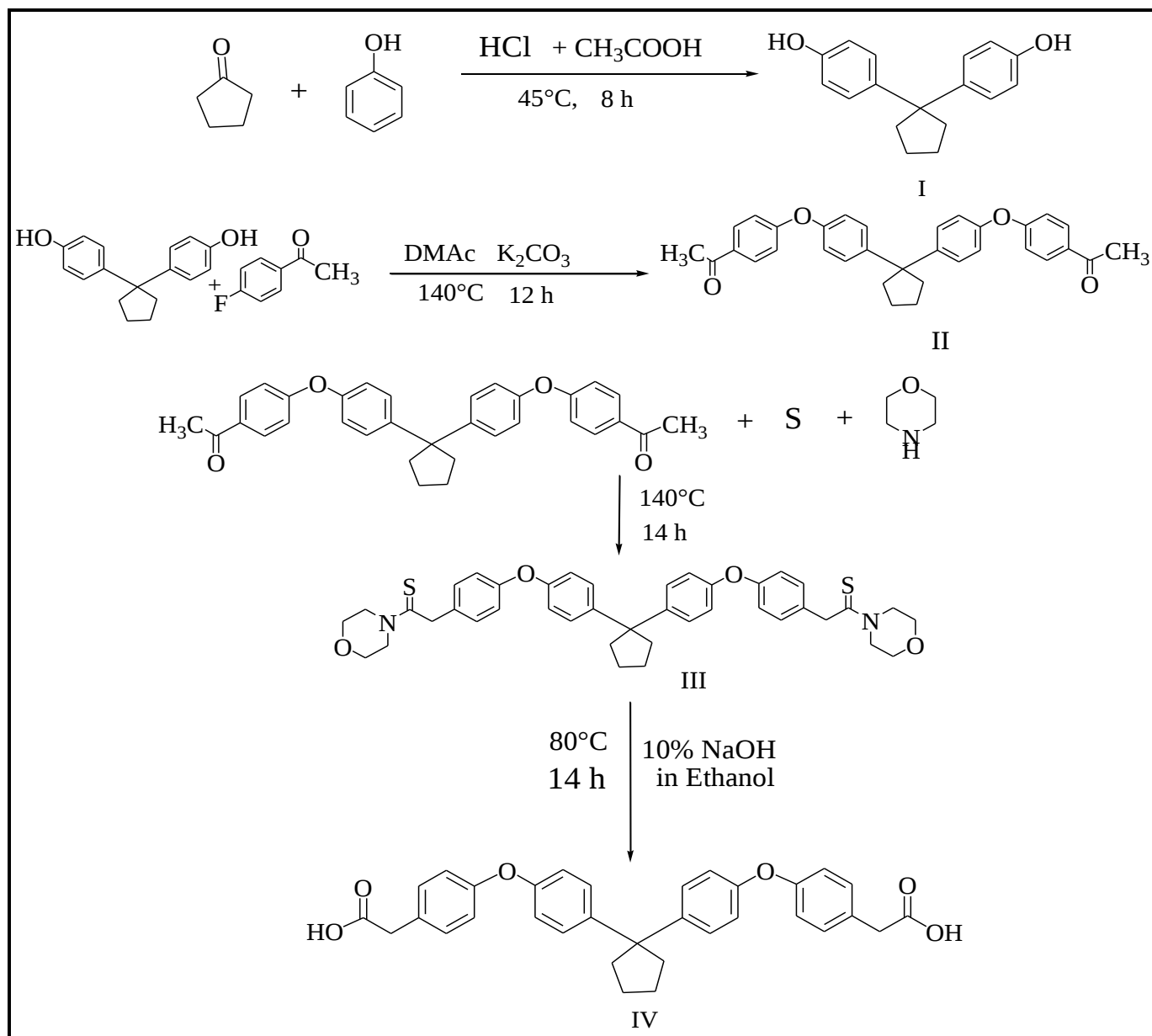
4.1. Monomer

The novel dicarboxylic acid, 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) was synthesized from phenol and cyclopentanone in several steps as shown in Scheme 1.

The 1, 1-bis (4-hydroxy phenyl) cyclopentane (I) was synthesized by reacting phenol with cyclopentanone in presence of acid catalyst. The 1, 1-bis[4-(4-acetyl phenoxy)phenyl]cyclopentane (II) was obtained by

reaction of (I) with 4- fluoroacetophenone and potassium carbonate in DMAc. Structure of (II) was confirmed by infrared spectroscopy. The infrared spectrum of (II) (**Fig.1**) showed medium strong absorption bands at 2972 and 2868 cm^{-1} showing the presence of aliphatic C-H stretching corresponding to the in phase and out phase

vibration of cyclopentane ring and methylene groups. Spectrum also shows absorption near 1497 cm^{-1} due to C-H bending vibration. Absorption at 1685 cm^{-1} of carbonyl (C=O) stretching adsorption indicated acetyl carbonyl moiety.



Scheme 1: Synthesis of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (IV)

The 1, 1-bis [4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) was obtained by the Conrad Willgerodt reaction with Kindler variation.

The formation of intermediate thiomorpholide derivative (III) was confirmed by infrared spectroscopy. The infrared spectrum of (III) (**Fig.2**) showed medium strong absorption bands at 2930 and 2861 cm^{-1} , due to the

presence of aliphatic C-H stretching corresponding to the in phase and out phase vibration of cyclopentane unit and methylene group. Spectrum also shows absorption near 1497 cm^{-1} due to C-H bending vibration. The appearance of absorption at 1240 cm^{-1} (C=S) confirm formation of thiomorpholide.

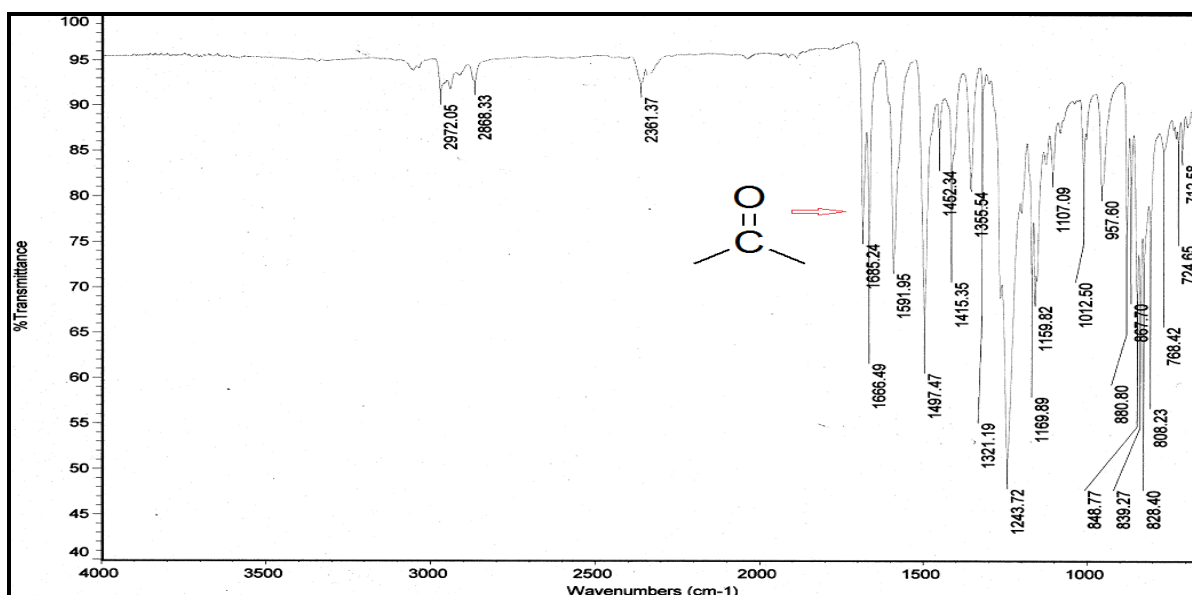


Fig. 1: FTIR of 1, 1-bis[4-(4-acetyl phenoxy) phenyl] cyclopentane (II)

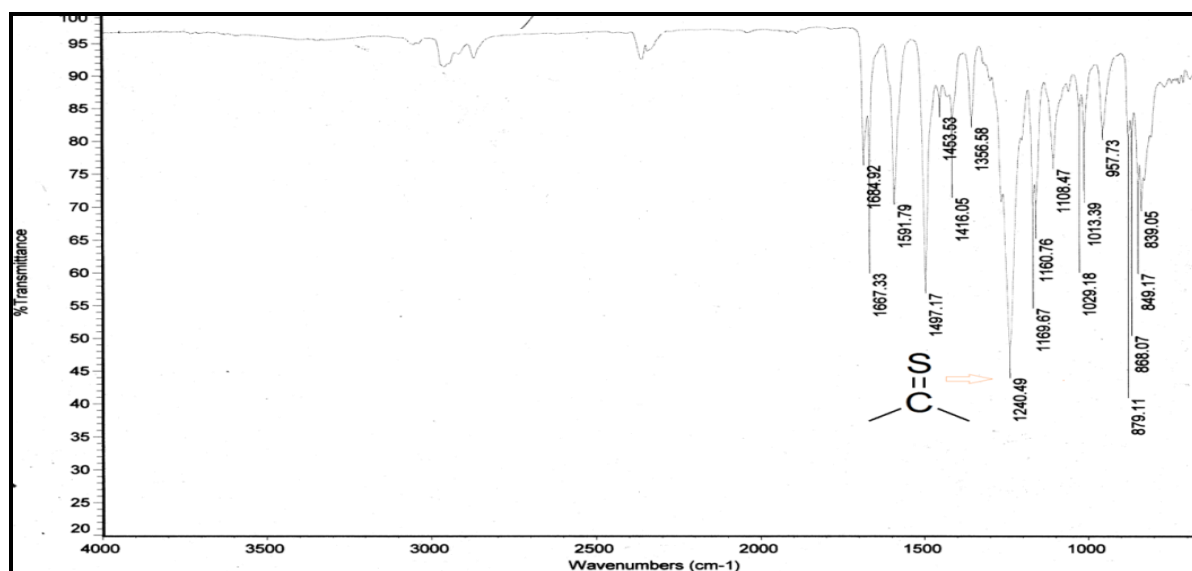


Fig. 2: FTIR of 1, 1-bis[4-(4-thioacetomorpholide phenoxy) phenyl] cyclopentane (III)

Thiomorpholide derivative on alkaline hydrolysis yielded the 1, 1-bis [4-(4-arboxy methylene phenoxy) phenyl] cyclopentane (IV). The structure of (IV) was confirmed by IR, NMR (^1H and ^{13}C) and mass spectroscopy.

The infrared spectrum of (IV) (**Fig.3**) showed absorption bands at $3500\text{--}3260\text{ cm}^{-1}$ (--COOH stretching) and 1707 cm^{-1} (C=O) indicating the presence of carboxyl group. IR spectrum also showed the absorption bands at 2959 and 2873 cm^{-1} corresponding to the in plane and out of plane stretching vibrations of the ($\text{--CH}_2\text{--}$) of the methylene group and cyclopentane unit.

The proton NMR spectrum (**Fig.4**) of (IV) showed the NMR singlet at $3.46\text{ }\delta$ corresponding to methylene (2H)

group of $\text{--CH}_2\text{COOH}$. The signals in the range of 7.27 to $6.79\text{ }\delta$ of (16H) are attributed to the aromatic protons of phenylene rings whereas signal at 2.21 and $1.63\text{ }\delta$ are assigned to cyclopentane proton.

The ^{13}C NMR spectrum(**Fig.5**)of (V) showed thirteen NMR signals corresponding thirteen types of different carbons of which carbonyl carbon appeared at $173.24\text{ }\delta$ for (C=O); whereas tertiary carbons showed signals at 156.01 ; 154.80 , 143.74 , 128.57 and $54.88\text{ }\delta$. The CH carbons appeared at 131.79 , 129.79 , 118.30 and $117.22\text{ }\delta$, whereas CH_2 carbon gave NMR signals at 40.53 , 38.76 , $22.86\text{ }\delta$ confirms the formation of diacid (V) monomer.

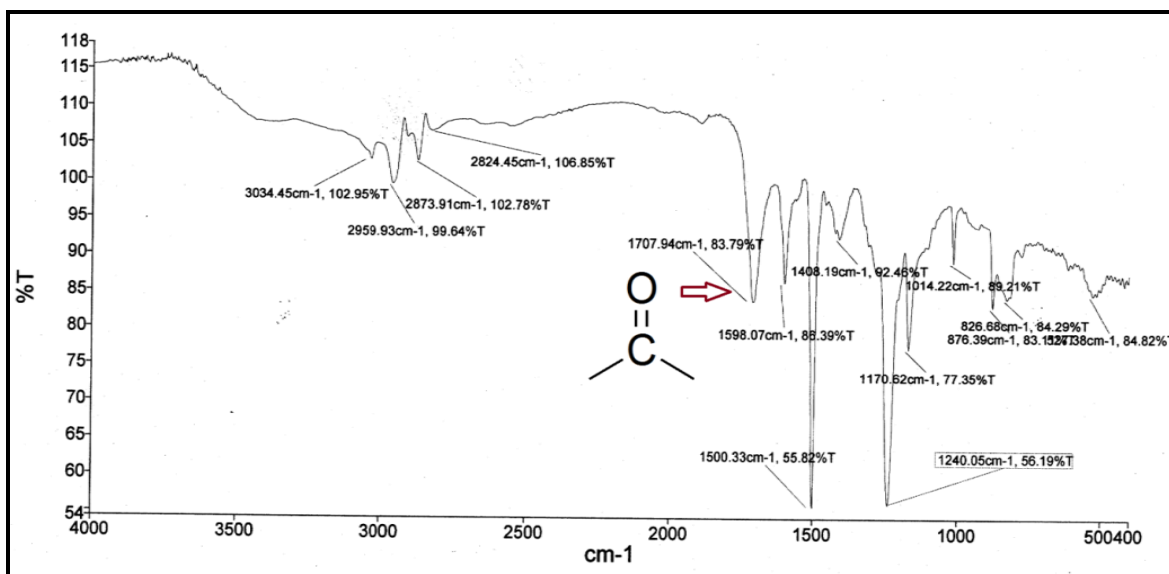


Fig. 3: FTIR of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV)

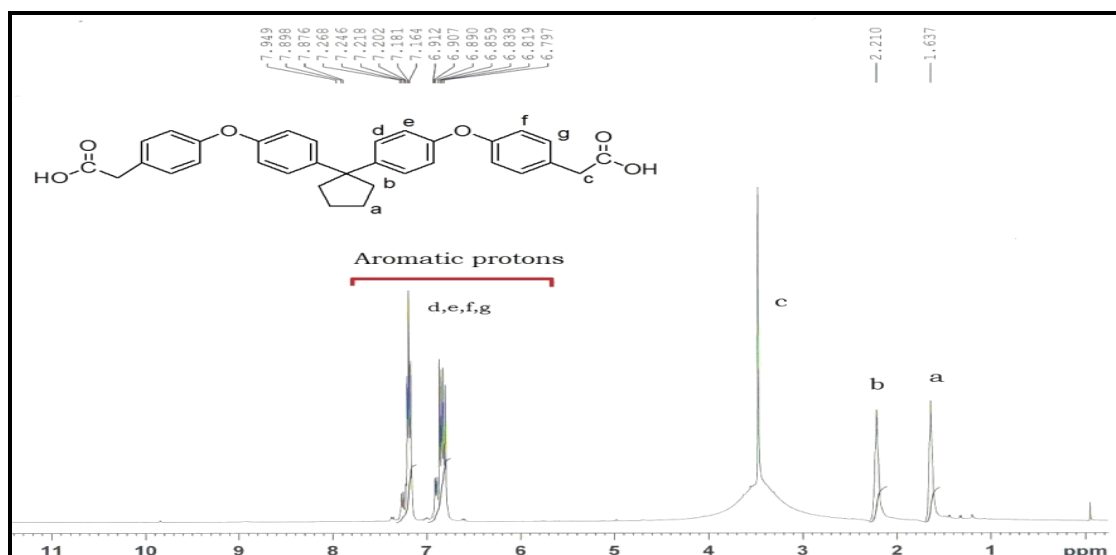


Fig. 4: ¹H NMR of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane

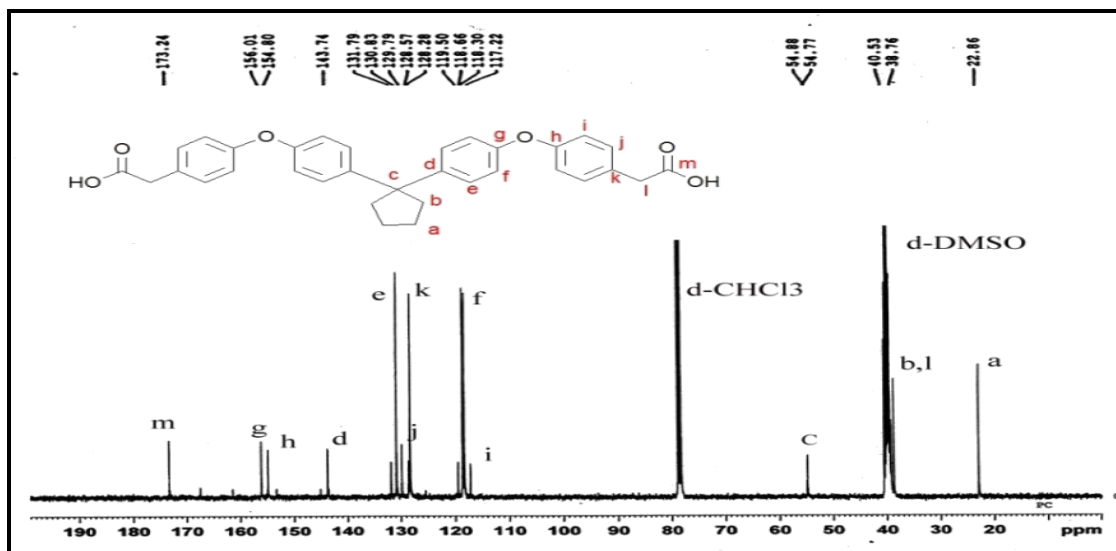


Fig. 5: ¹³C NMR of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane

The DEPT-135 spectrum (Fig. 6) of (IV) also confirms the diacid monomer wherein all the quaternary carbons are absent in the spectrum and the peaks of CH carbons are upper sides at 131.80, 128.58, 119.52, 118.65, 118.30 δ and CH₂ appeared at down side at

40.52, 38.74, 22.85 δ .

The mass spectrum of (Fig 7) (IV) showed molecular ion peak at m/e 521 corresponding to molecular weight of BAMPC.

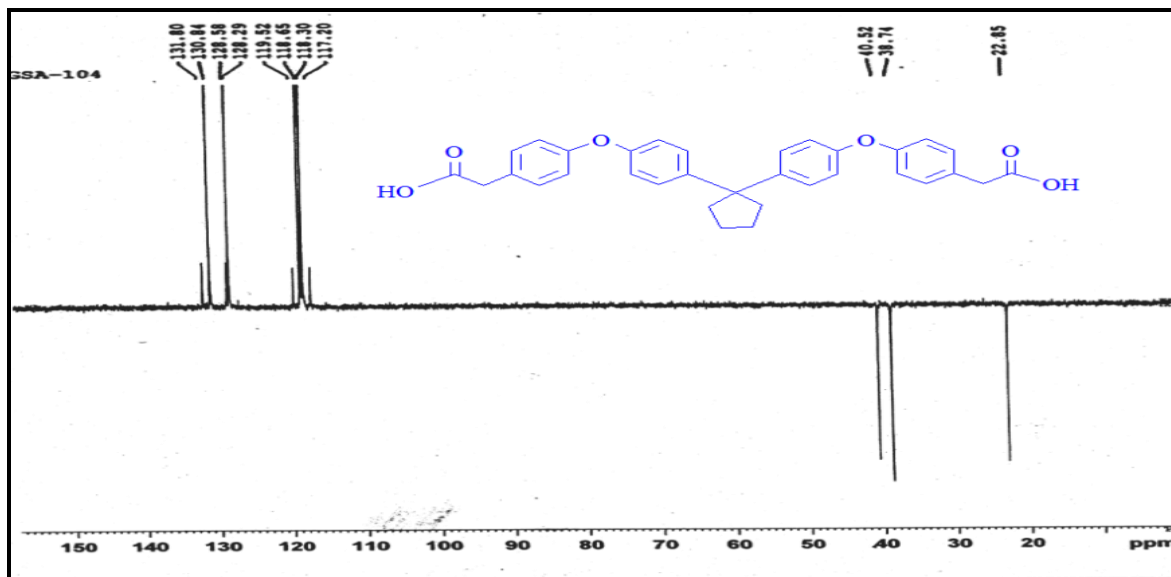


Fig. 6: DEPT-135 of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV)

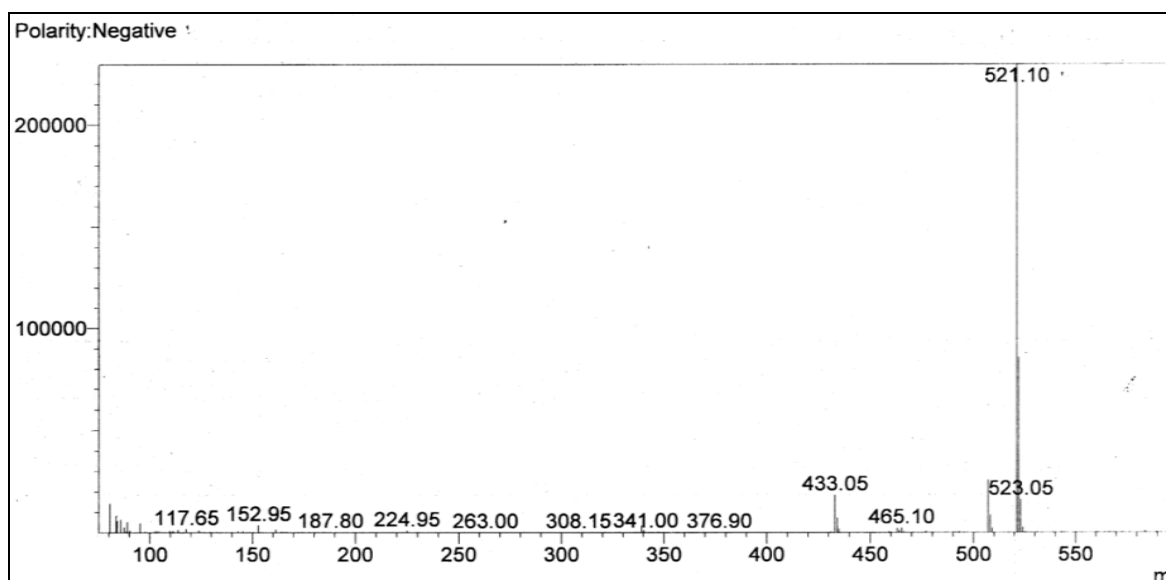


Fig. 7: Mass Spectrum of 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (BCMPP) (IV)

4.2. Polymerization

The poly(ether-amide)s were synthesized by Yamazaki's phosphorylation method.

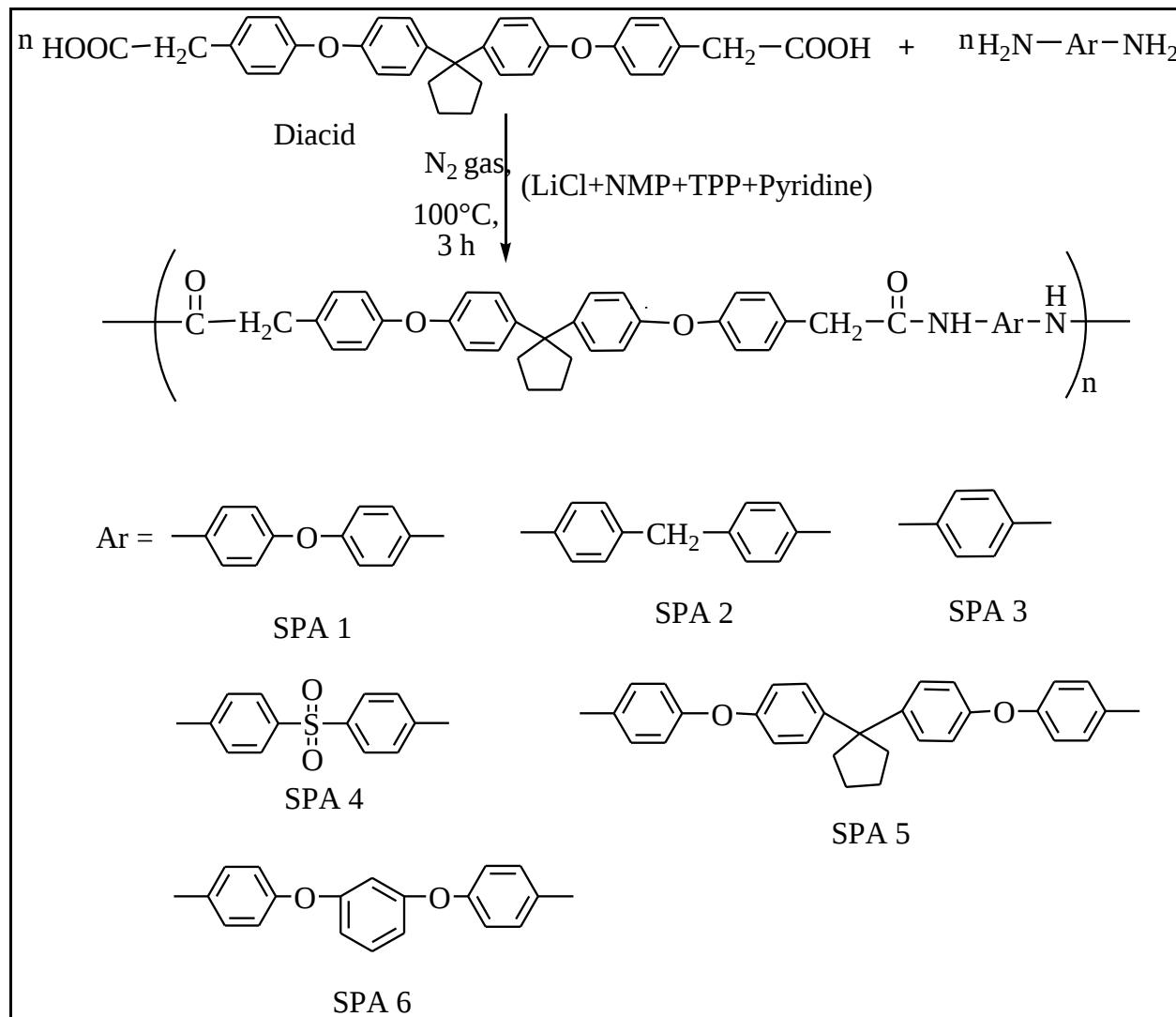
A series of poly(ether-amide)s were synthesized from the stoichiometric quantities of 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) and various aromatic diamines by direct polycondensation

method (Scheme 2), triphenyl phosphite was used as the condensing agent, where in the mixture of NMP and pyridine (4:1 by volume) containing 8 wt. % anhydrous lithium chloride was employed as solvent. The polymerization was carried out at 100°C for 3 h. The different aromatic diamines used are shown below. The polymerization proceeded smoothly giving highly viscous

solution. The resulting polymers were precipitated by pouring the viscous solutions in methanol.

The results of yield and viscosity of polyamides synthesized from 1, 1-bis [4- (4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) are tabulated in **Table1**. All the polymers were obtained in the good

yields (96 to 100 %) as pale yellow to white fibrous materials. The inherent viscosities of these polymers were in the range of 0.20 to 0.40 dL/g; this is indicated the formation of moderate to high molecular weight of polymers. Polymerization was carried out with 1 mmol of diamine and 1 mmol of diacid (IV).



Scheme 2: Synthesis of Poly(ether-amide)s

Table 1: Yield and Viscosity of Poly(ether-amide)s SPA-1 to SPA-6

Polymer	Monomers		Yield %	Inherent Viscosity dL/g ^a
	New Diacid	Diamine		
SPA-1	BCMPP	ODA	100	0.20
SPA-2	BCMPP	MDA	99	0.28
-SPA-3	BCMPP	p-PDA	100	0.40
SPA-4	BCMPP	SDA	97	0.35
SPA-5	BCMPP	BAPC	96	0.24
SPA-6	BCMPP	BAPB	96	0.21

The structures of polymers were characterized by infrared spectroscopy. Polyamide SPA-1 showed an absorption band at 3269 cm^{-1} ($-\text{NH}$ stretching), a sharp band at 1598 cm^{-1} (characteristic for $-\text{NH}$ bending) and absorption band at 1658 cm^{-1} (due to $\text{C}=\text{O}$ in amide group). The absorption band at 3035 cm^{-1} characteristic

for aromatic $-\text{CH}$ stretching; and absorption band at 2954 cm^{-1} corresponding for aliphatic ($-\text{CH}$ stretch) methylene linkage were observed. (Fig. 8 & 9) Disappearance of absorption bands at 3500 and 3340 cm^{-1} indicated that all the acid and amine groups reacted completely to yield polyamide.

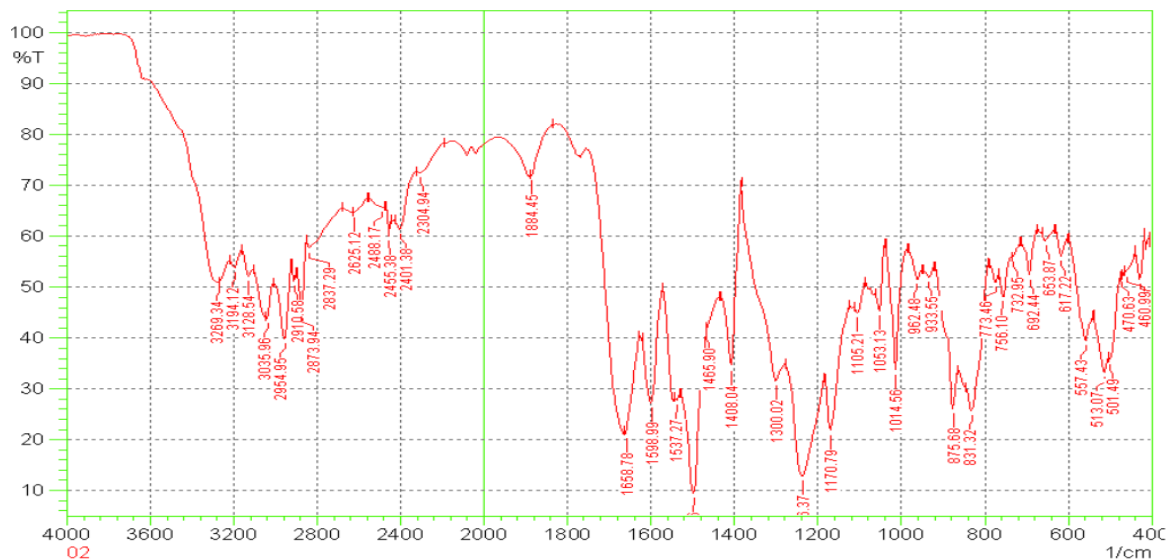


Fig. 8:FTIR spectrum of SPA-1

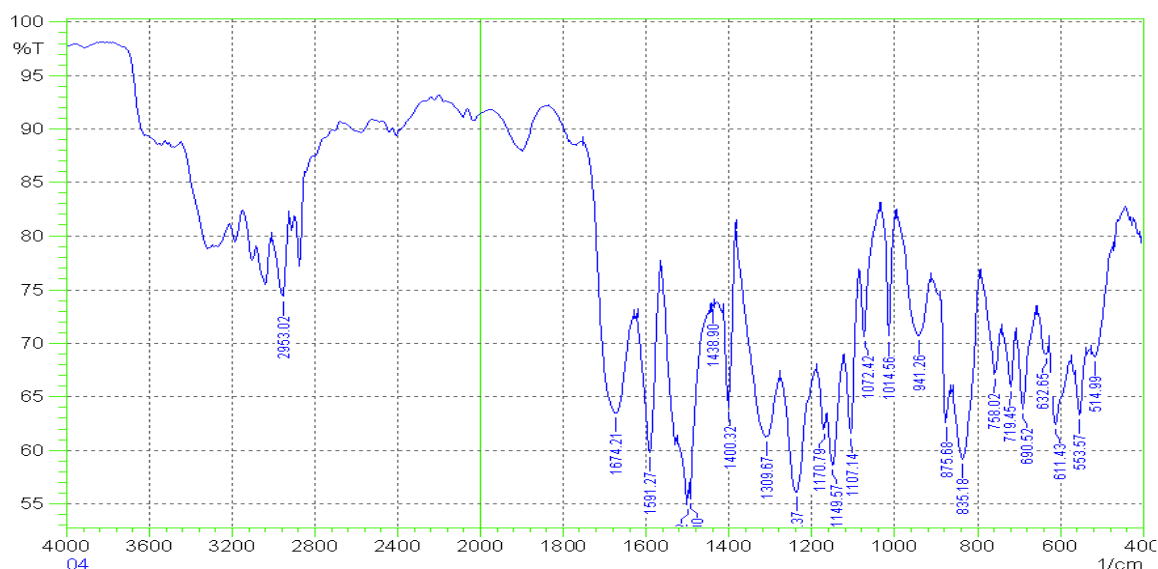


Fig. 9:FTIR spectrum of SPA- 4

Solubility characteristics of polyamides are tabulated in **Table 2**. The solubility of polymers was determined in different common organic solvents. It was observed that polyamides synthesized from 1, 1-bis[4-(4-carboxy methylene phenoxy) phenyl] cyclopentane (IV) exhibited better solubility in various polar aprotic solvents such as N-methylpyrrolidone (NMP), N, N-dimethyl sulphoxide (DMSO), N, N-dimethylacetamide (DMAc), N, N-dimethyl formamide (DMF). All these poly (ether -

amide)s also dissolved in pyridine, and Conc. H_2SO_4 . All these polyamides (SPA-1 to SPA-6) are insoluble in common solvents like THF, DCM and chloroform as well as are partly soluble in DMSO. Whereas reference polyamides derived from rigid diacids like biphenyl-4, 4'-dicarboxylic acid or terephthalic acid with 1, 3-phenylene diamine were reported to be insoluble in many solvents [33-35].

Thus better solubility of these polyamides; as expected can also be attributed to the combined effect of introduction of aliphatic methylene linkage and ether linkage in the polymer backbone and cardo cyclopentylidene moiety.

Thus better solubility of these polyamides; as expected can also be attributed to the combined effect of introduction of aliphatic methylene linkage and ether linkage in the polymer backbone and cardo cyclopentylidene moiety.

Table 2: Solubility behavior of Poly(ether-amide)s SPA-1 to SPA-6

Polymer	Solubility					
	DMF	DMAc	DMSO	NMP	Pyridine	C.H ₂ SO ₄
SPA-1	+	+	+	+	+	+
SPA-2	+	+	±	+	+	+
SPA-3	+	+	+	+	+	+
SPA-4	+	+	+	+	+	+
SPA-5	+	+	+	+	+	+
SPA-6	+	+	±	+	+	+

+:Soluble; ± : Partly soluble; - : Insoluble

Table 3: Physical properties of Poly(ether-amide)s SPA-1 to SPA-6

Polymer	Thermal Behaviour ^b			
	T _i °C in N ₂	T _d °C in N ₂	T _g °C	ResidualWt % at 900°C
SPA-1	305	475	208	48
SPA-2	295	455	200	47
SPA-3	325	495	220	53
SPA-4	295	475	186	44
SPA-5	285	425	181	38
SPA-6	295	475	177	46

^bTemperature at which onset of decomposition was recorded by TG at a heating 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, T_i– Initial decomposition temperature.

Thermal behaviour of polymers was evaluated by means of thermogravimetry and differential scanning calorimetry. In Table-3, the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), 10 % Wt. loss temperature (T_d) and residual weight at 900°C were incorporated.

The thermal stability of the polyamides was studied by thermogravimetric analysis (**Fig. 10**) at a heating rate of 10°C/min in nitrogen atmosphere. The initial decomposition temperature (T_i), temperature at which 10 % weight loss (T_d), and char yields at 900°C were determined from the original thermograms. T_i and T_d values range between 285 to 325°C and 425 to 495°C respectively. Residual wt. % loss at 900°C was in the range of 38 % to 53 %.

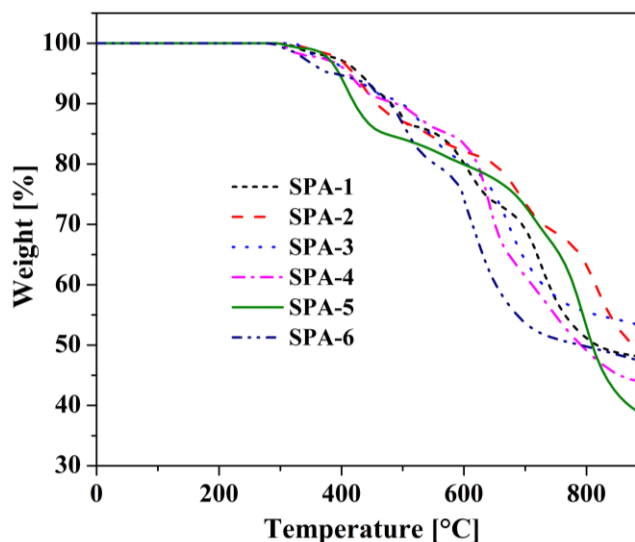


Fig. 10: TGA of Poly(ether-amide)s SPA-1 to SPA-6

The DSC curves shown in **Fig. 11** represent the T_g of polyamides synthesized from novel diacid (IV). The glass transition temperature (T_g) of various polyamides are in the range between 177 to 220°C which is shown in Table-3. The glass transition temperatures of the polymers SPA-1, SPA-2 and SPA-3 higher T_g value but SPA-4, SPA-5 and SPA-6 polymer indicated slightly lower T_g values. This can be explained on the basis of novel diacid and commercial diamine in corresponding polymers. A comparison of these values with glass transition temperature of some reported [36-40] polyamides based on diacids indicated that there is appreciable decrease in T_g of polyamides due to incorporation of flexible methylene linkage, ether linkages and cardo cyclopentane moiety.

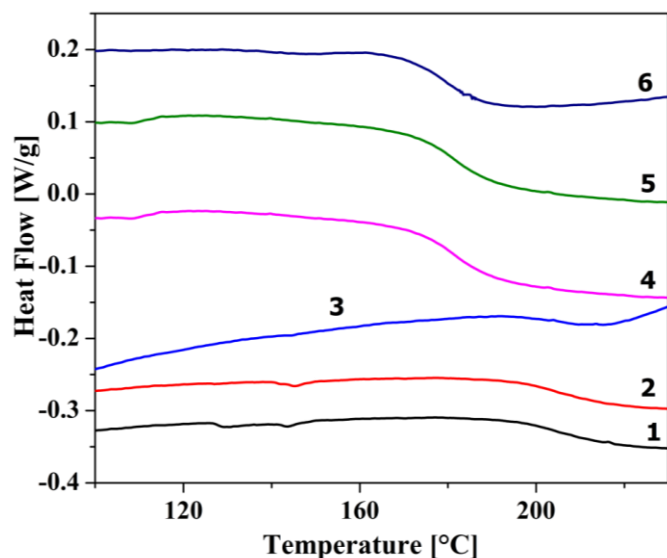


Fig. 11: DSC curve of Poly(ether-amide)s SPA-1 to SPA-6

The wide angle X-ray diffraction pattern of all polyamides is shown in **Fig. 12**. It is observed that all the polymers exhibit amorphous nature except SPA-3 which shows semicrystalline nature due to p-phenylene diamine which can be attributed to the close packing of the chains. Introduction of cyclopentylidene moiety and aliphatic methylene linkage may have disrupted the chain regularity and packing leading to amorphous polyamides. Similarly introduction of diether-diamine containing cyclopentylidene moiety in SPA-5 and phenylated moiety in SPA-6; disturbs symmetry to large extent and polymers become more amorphous. Polymers from diamine like ODA, SDA and p-PDA; are less amorphous which can be attributed to the close packing of the chains. Thus amorphous nature of the polymers was

depending on the structures of diacid and diamines chosen for synthesis of polymers.

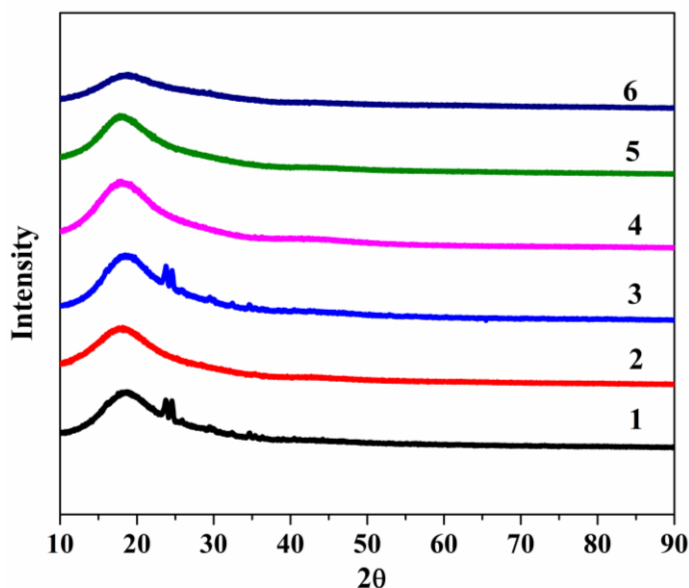


Fig. 12: XRD curve of Poly (ether-amide)s SPA-1 to SPA-6

5. CONCLUSIONS

Several novel aromatic poly(ether-amide)s containing cyclopentylidene cardo units in the polymer backbone were synthesized with the aim of improving the solubility and processability of polymers. The inherent viscosities of these polymers range from 0.20 to 0.40 dL/g. Most of these polymers are amorphous and soluble in a number of organic solvents, such as DMF, NMP, DMAc, and DMSO. The T_g 's in nitrogen and T_d 's for 10% weight loss in air range from 177 to 220°C and 425 to 495°C, respectively, depending on the exact polymer structure. This discussion is concluded that these polymers have comparatively very good solubility and low T_g , hence it can be easily processable for range of applications. Furthermore these polymers can be used to make composites with natural fillers and plant fibres as well as with nanoparticles to improve properties for automotive, packaging, construction, etc. applications

6. REFERENCES

1. Cassidy PE, Thermally Stable Polymers, Marcel Dekker, New York; 1980.
2. Park KP, Kakimoto MA, Imai Y, J Polym Sci Part A: Polym Chem, 1995; **33**:1031-1035.
3. Yang CP, Hsiao SH, Yang CC, J Polym Sci Part A: Polym Chem, 1997; **35**: 2147-2156.
4. Yang CP, Hsiao SH, Chung CL, Polym Int, 2005; **54**: 716-724.

5. Thurber EL, Rasmussen PG, J Polym Sci-A, 1993; **31**: 351-364.
6. Ghaemy M, Amini-Nasab SM, Alizadeh R, J Appl Polym Sci 2010; **116**: 3725-3731.
7. Mehdipour-Ataei S, Gharehkhani E, High Perform Polym, 2013; **25**: 778-789.
8. Faghihi K, Mozaffari Z, JAppl Polym Sci, 2008; **108**: 1152-1157.
9. Li N, Cui Z, Zhang S, Xing W, Polym, 2007; **48**: 7255-7263.
10. Hamciuc E, Hamciuc C, Cazacu M, Eur Polym J, 2007; **43**: 4739-4749.
11. Ankushrao SS, Ghanwat AA, Kadam VN, Patil YS, et.al., J. Macro. Sci. A: Pur. & Appli. Chem, 2017; **54**: 124-132.
12. Zhao X, Li YF, Zhang SJ, Shao Y, et al., Polym, 2007; **48**: 5241-5249.
13. Ankushrao SS, Ghanwat AA, Gugwad VM, Ubale VP, et.al., Poly Sci Ser-B, 2018; **60**: 263-272.
14. Mehdipour Ataei S, Bahri Laleh N, Amirshaghghi A, Polym Degrad & Stab 2006; **91**: 2622-2631.
15. Salunkhe PS, Ghanwat AA, Kadam VN, Patil YS, et.al., Poly Plast techno and Mater, 2020; **59**: 95-105.
16. Ankushrao SS, Ghanwat AA, Kadam VN, Patil YS, et.al., J. Macro. Sci. A: Pur. & Appli. Chem, 2017; **54**: 411-417.
17. Mahindrakar JN, Ghanwat AA, Salunkhe PS, Patil YS, et.al., J. Macro. Sci. A: Pur. & Appli. Chem, 2018; **55**: 658-667.
18. Patil YS, Ghanwat AA, Salunkhe PS, Mahindrakar JN, et.al., J. Therm Anal and Calori, 2019; **135**: 3057-3068.
19. Yang CP, Chen YP, Woon EM, J Polym Sci Part A: Polym Chem, 2004; **42**: 3116-3129.
20. Maldar NN, Kakimoto MA, Imai Y, J Polym Sci Part A: Polym Chem, 1985; **23**: 1797-1803.
21. Maldar NN, Kakimoto MA, Imai Y, J Polym Sci Part A: Polym Chem, 1984; **22**: 2189-2196.
22. Pal RR, Patil PS, Dere RT, Salunkhe MM, et.al., Polym Int, 2005; **54**: 569.
23. Pal RR, Patil PS, Dere RT, Salunkhe MM, et. al., J Appl Polym Sci, 2005; **97**: 1377-1384.
24. Calderon V, Garcia FC, De La Pena JL, Maya CM, et.al., J Polym Sci Part A: Polym Chem, 2006; **44**: 2270-2281.
25. San JN, Gornez VA, Garcia FC, Serna F, et. al., J Polym Sci Part A: Polym Chem, 2007; **45**: 4026-4036.
26. Liou JS, Yen HJ, Su YT, Lin HY, J Polym Sci Part A: Polym Chem, 2000; **45**: 4352-4360.
27. Ataei MS, Heidari HJ, J Appl Polym Sci, 2004; **91**: 22-26.
28. Ghaemy M, Barghamadi M, JAppl Polym Sci, 2008; **110**: 1730-1738.
29. Basutkar PH, Joshi MD, Lonikar SV, Maldar NN, J Appl Polym Sci, 1990; **68**: 1523-1530.
30. Xuemei WF, Liu JL, Zhiqiang F, Xiaozeng Y, J Fluor Chem, 2014; **14**: 118.
31. Goikhmana M, Yevlampievab NP, Kamaninac NV, Podeshvoal V, et.al., Polymer Science Ser-A, 2011; **53**: 457-468.
32. Mel'nika OA, Dyachenko VI, Nikitina LN, Blagodatskikh IV, et.al., Polymer Science Ser-A, 2013; **55**: 625-630.
33. Hsiao SH, Chen CW, Liou GS, J Polym Sci Part A: Polym Chem, 2004; **42**: 3302-3313.
34. Lin J, Sherrington D, Adv Polym Sci, 1994; **111**: 180.
35. Hsiao SH, Yu CH, J Polym Res, 1966; **3**: 239-245.
36. Guo DD, Sheng SR, Sang XY, Huang ZZ, et.al., J Macromol Sci Part-A, 2015; **52**: 950-959.
37. Liou GS, Huang NK, Yang Y, J Polym Sci A: Polym Chem, 2006; **42**: 2283-2291.
38. Wu SC, Shu CF, J Polym Sci A: Polym Chem, 2003; **41**: 1160-1166.
39. Espeso JF, Ferrero E, de la Campa JG, Lozano AE, et. al., J Polym Sci A: Polym Chem, 2001; **39**: 475-485.
40. Hsiao SH, Chang YM, J Polym Sci A: Polym Chem, 2004; **42**: 4056-4062.