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Synthesis and characterization of poly(amideimide)s from 4-(*p*-carboxyphenoxy)phthalic anhydride and 4-(*p*-carboxybenzoyl) phthalic anhydride

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ABSTRACT

A series of poly(amideimide)s were prepared by the reaction of two new anhydride acidchloride monomers with aromatic diamines. 4-(*p*-Carboxyphenoxy)phthalic anhydride was synthesized by nucleophilic displacement reaction of N-methyl-4-nitrophthalimide with *p*-hydroxybenzoic acid, followed by hydrolysis. The tricarboxylic acid was converted to the corresponding anhydride acidchloride. 4-(*p*-Carboxybenzoyl)phthalic anhydride was synthesized by Friedel–Craft's acylation of toluene with N-phenylphthalimide-4-carbonylchloride, which was then converted to anhydride acidchloride of 4-(*p*-carboxybenzoyl)phthalic acid. The monomers were characterized by IR and NMR. Several PAI were prepared by the reaction of these anhydride acidchloride monomers with aromatic diamines. The inherent viscosities of the polymers were in the range of 0.42–0.58 dL/g. All polymers were soluble in polar aprotic solvents. The polymers showed good thermal stability and T_g values were in the range of 226–269 °C. X-Ray diffractograms of polymers indicate amorphous nature of these polymers.

1. Introduction

Aromatic polyimides are important class of high performance polymeric materials that has outstanding thermal stability, excellent mechanical properties and good chemical resistance [1–4]. These polymers are widely used in aerospace, electronics and automobile industries [5,6]. However, aromatic polyimides have close packed polymer chains due to the strong intermolecular forces and these polymers have very high melting points and limited solubility in organic solvents [7–11]. In order to improve the processability of aromatic polyimides, polymers have been prepared from structurally modified dianhydrides and diamines [12]. The other structural modifications include incorporation of flexible groups such as aryl ether, thioether and carbonyl linkages into the polymer backbone [13,14], incorporation of groups such as amide, ester, etc. to obtain polyimide derivatives such as poly(amideimide)s, poly(esterimide)s, etc. and introducing substituents in the aromatic groups present in the polymer backbone [15–19].

Among modified polyimides, poly(amideimide)s are the most successful materials (e.g. Torlons®). The poly(amideimide)s are generally prepared by the polycondensation of trimellitic anhydride chloride or aromatic diacids containing preformed imide rings with aromatic diamines [20–23].

In the present work, two new monomers 4-(*p*-carboxyphenoxy) phthalic anhydride and 4-(*p*-carboxybenzoyl)phthalic anhydride were synthesized and polymers were prepared by the polycondensation of these anhydride acidchloride monomers with several aromatic diamines. These polymers showed good thermal stability comparable to aromatic polyimides. The improved processability of these polymers compared to polyimides results from the incorporation of amide groups into polymer backbone.

2. Materials and methods

2.1. Materials

N-Methyl-4-nitrophthalimide, 4-hydroxy benzoic acid and trimellitic anhydride were used as received. Aniline, toluene, thionyl chloride and pyridine were purified by distillation. The commercially available aromatic diamines such as *m*-phenylenediamine, oxydianiline, methylenedianiline and 4,4′-diaminodiphenyl sulfone were purified by recrystallization. Dimethylsulfoxide (DMSO),

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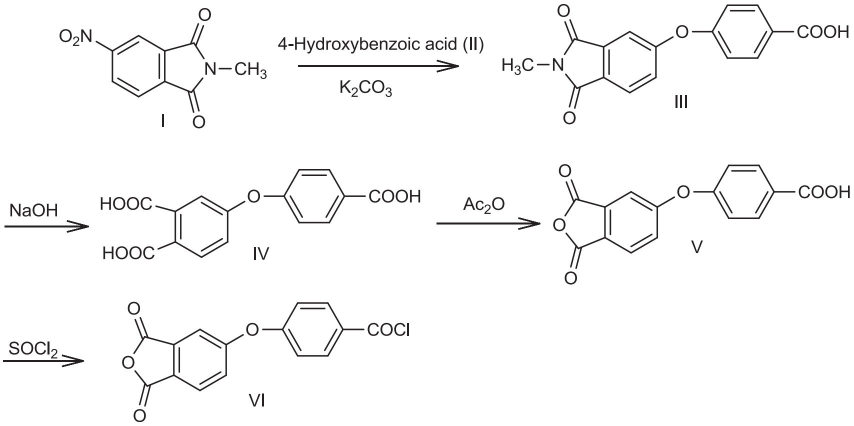


Scheme 1. Synthesis of 4-(*p*-chlorocarbonylphenoxy)phthalic anhydride.

dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure and stored over 4 Å molecular sieves.

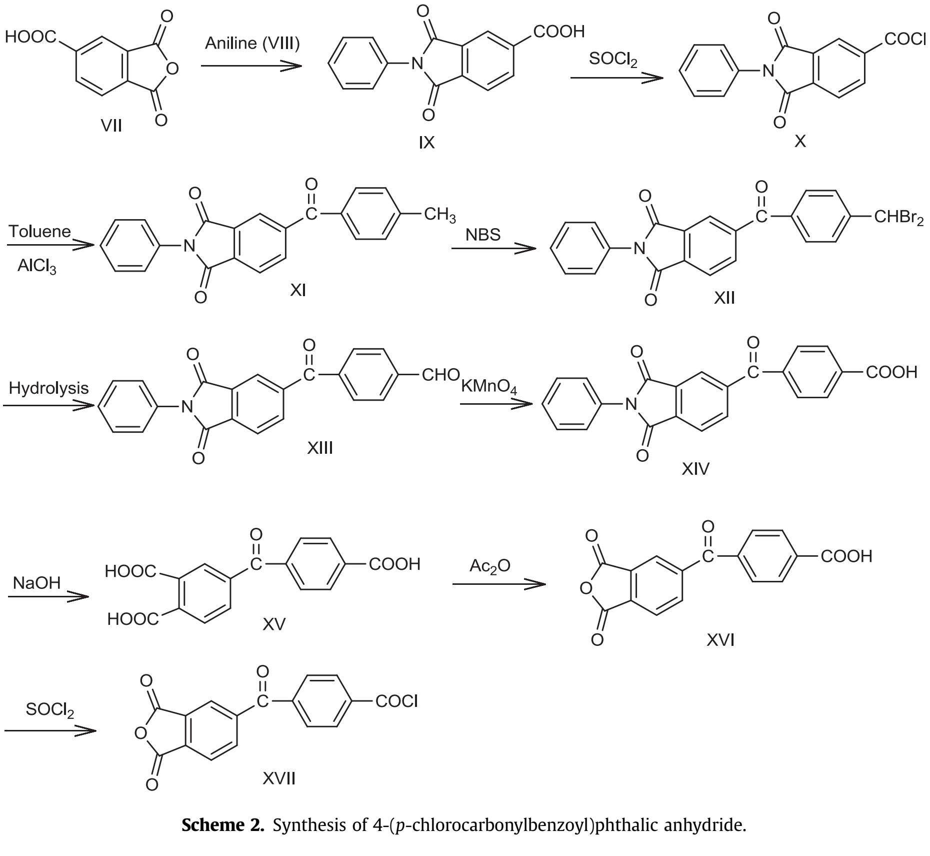
2.2. Measurements

Infrared spectra were recorded on PerkinElmer spectrum 100 FTIR. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance (300 MHz). The inherent viscosities of the polymers were measured with an Ostwald viscometer at 0.5 dL/g concentration. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TA Instruments SDT Q600 and DSC Q20. X-Ray diffraction measurements were recorded on a Bruker XRD D8 FOCUS using Cu Kα radiation.

2.3. Methods

2.3.1. Synthesis of 4-((N-methylphthalimide)-4-oxy) benzoic acid (III)

To 4-hydroxy benzoic acid (I) (1.38 g, 0.01 mol) and DMSO (15 mL) in a round-bottom flask was added potassium carbonate (3.04 g, 0.022 mol) and toluene (20 mL). The reaction mixture was heated to 140 °C and water was azeotropically removed from the reaction mixture. The temperature was raised to 160 °C and remaining toluene was removed. The reaction mixture was cooled to 40 °C, N-methyl-4-nitrophthalimide (II) (2.06 g, 0.01 mol) was added and reaction mixture was heated at 120 °C for 6 h. The reaction mixture was allowed to cool and hydrochloric acid was added. The precipitated pale yellow compound was isolated by



Scheme 2. Synthesis of 4-(*p*-chlorocarbonylbenzoyl)phthalic anhydride.

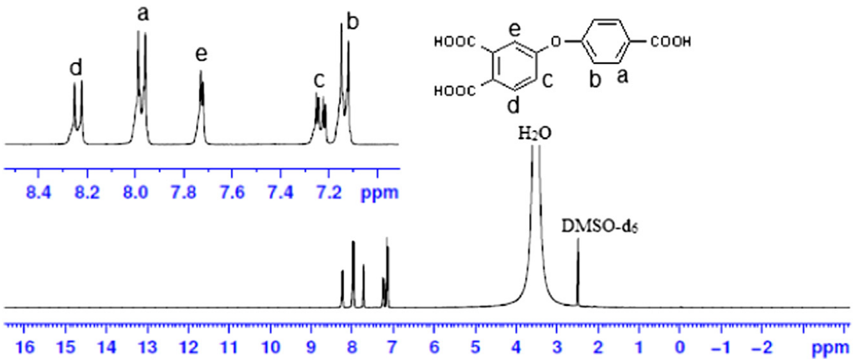


Fig. 1. ^{1}H NMR spectrum of 4-(*p*-carboxyphenoxy)phthalic acid (IV) in DMSO-d_6.

filtration, washed with water and dried. Yield: 2.62 g (88%); m.p: 217 °C; FTIR (KBr): 3570 cm^{-1} (O–H stretch, –COOH), 1680 cm^{-1} (C=O stretch, –COOH), 1780 cm^{-1} (C=O stretch, imide) and 1240 cm^{-1} (C–O stretch, Ar–O–Ar); ^{1}H NMR (DMSO-d_6): δ (ppm) 2.71 (s, 3H), 7.12 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 1H), 7.52 (s, 1H), 7.99 (d, $J = 8.7$ Hz, 2H), 8.27 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (DMSO-d_6): δ (ppm) 26.2, 119.5, 120.2, 120.8, 127.2, 129.8, 131.4, 135.6, 157.3, 158.6, 166.2, 168.2.

2.3.2. *Synthesis of 4-(p-carboxyphenoxy)phthalic acid (IV)*

The tricarboxylic acid IV was prepared by hydrolysis of compound III. The flask was charged with compound III (2.97 g, 0.01 mol) and NaOH solution (40 mL, 10% solution). The reaction mixture was refluxed for 24 h. The reaction mixture was added to dilute hydrochloric acid. The precipitated solid was isolated by filtration, washed with water and dried. Yield: 2.8 g (92%); m.p: >300 °C; FTIR (KBr): 3700–2500 cm^{-1} (O–H stretch, –COOH), 1690 cm^{-1} (C=O stretch, –COOH) and 1240 cm^{-1} (C–O stretch, Ar–O–Ar); ^{1}H NMR (DMSO-d_6): δ (ppm) 7.12 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz, 1H), 7.72 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 8.22 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (DMSO-d_6): δ (ppm) 167.2, 167.0, 166.7, 159.7, 157.3, 137.7, 135.4, 131.8, 130.3, 126.3, 121.9, 120.7, 118.6.

2.3.3. *Synthesis of 4-(p-carboxyphenoxy)phthalic anhydride (V)*

A mixture of 4-(*p*-carboxyphenoxy)phthalic acid (3 g, 0.01 mol) and acetic anhydride (10 mL) was refluxed for 5 h. The reaction mixture was cooled and precipitated acid anhydride was filtered, washed with hexane and dried under vacuum. Yield: 2.8 g (98%); m.p: 234 °C; FTIR (KBr): 3580 cm^{-1} (O–H stretch, –COOH), 1690 cm^{-1} (C=O stretch, –COOH), 1850 cm^{-1} (five-membered cyclic anhydride), 1285 cm^{-1} (C–O stretch, cyclic anhydride) and 1260 cm^{-1} (C–O stretch, Ar–O–Ar).

2.3.4. *Synthesis of 4-(p-chlorocarbonylphenoxy)phthalic anhydride (VI)*

A mixture of compound V (3 g, 0.0105 mol), thionyl chloride (20 mL) and pyridine (1 mL) was refluxed for 6 h. The excess thionyl chloride was removed under reduced pressure. The acidchloride (VI) was recrystallized from toluene. Yield: 3.1 g (100%); m.p: 116 °C; FTIR (KBr): 1770 cm^{-1} (C=O stretch, acidchloride), 1850 cm^{-1} (cyclic anhydride) and 1260 cm^{-1} (C–O stretch, Ar–O–Ar).

2.3.5. *Synthesis of N-phenyl phthalimide-4-carboxylic acid (IX)*

An RB flask was charged with trimellitic anhydride (VII) (1.92 g, 0.01 mol), aniline (VIII) (0.93 g 0.01 mol) and DMSO (20 mL). The reaction mixture was stirred for 4 h. Toluene (20 mL) was added and the reaction mixture was heated at 140 °C for 6 h while removing water as an azeotrope using Dean–Stark trap. Toluene was completely removed from the reaction mixture, cooled and the reaction mixture was poured into water. The precipitated yellow solid was isolated by filtration, washed with water and dried in vacuum. Yield: 2.6 g (97%); m.p: 248 °C; FTIR (KBr): 3700–2500 cm^{-1} (O–H stretch, –COOH), 1680 cm^{-1} (C=O stretch, –COOH), 1785 cm^{-1} (C=O stretch, imide); ^{1}H NMR (DMSO-d_6): δ (ppm) 7.11 (d, $J = 6.9$ Hz, 2H), 7.29–7.34 (m, 3H), 7.62 (d, $J = 7.8$ Hz,

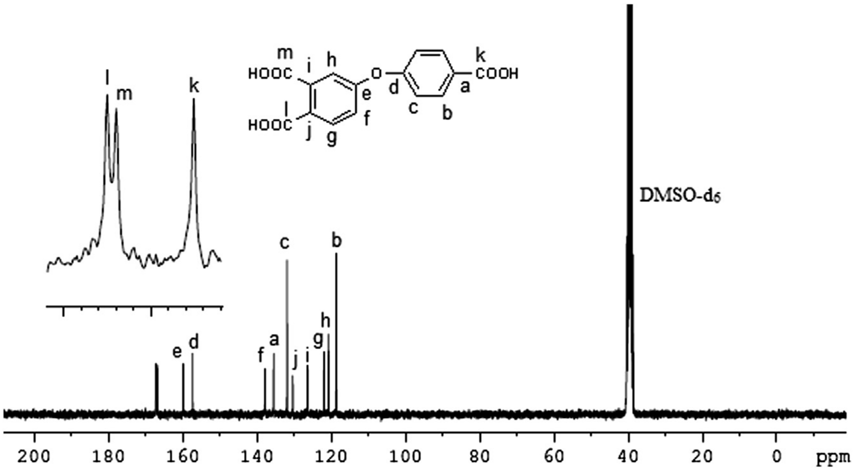


Fig. 2. ^{13}C NMR spectrum of 4-(*p*-carboxyphenoxy)phthalic acid (IV) in DMSO-d_6.

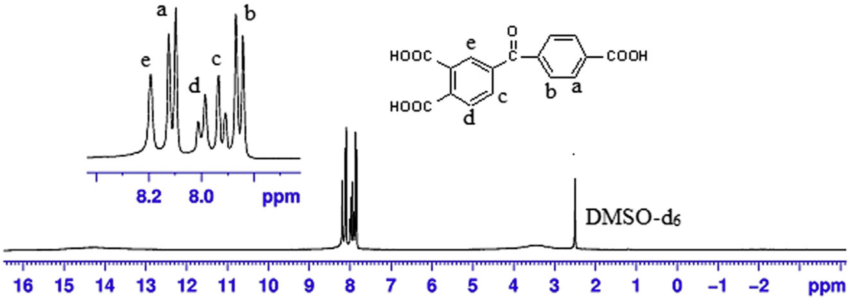


Fig. 3. ^{1}H NMR spectrum of 4-(p-carboxybenzoyl)phthalic acid (XV) in DMSO-d_6.

1H), 7.77 (d, $J = 7.8$ Hz, 1H), 8.16 (s, 1H) and 10.58 (s, 1H); ^{13}C NMR (DMSO-d_6): δ (ppm) 123.6, 124.7, 127.9, 128.3, 129.2, 133.8, 134.3, 135.8, 136.5, 165.8 and 192.7.

2.3.6. Synthesis of 4-(N-phenyl phthalimide-4-carbonyl) toluene (XI)

An RB flask charged with N-phenyl phthalimide-4-carboxylic acid (IX) (2.67 g, 0.01 mol), thionyl chloride (20 mL) and pyridine (1 mL). The reaction mixture was refluxed for 12 h. The excess thionyl chloride was distilled under reduced pressure. N-Phenyl phthalimide-4-carbonyl chloride (X) was isolated and dried. Yield: 2.85 g (100%).

A mixture of compound X (2.85 g, 0.01 mol), toluene (30 mL) and aluminum chloride (3.33 g, 0.025 mol) was refluxed for 12 h. The excess toluene was removed and the reaction mixture was poured into dilute HCl (10%). The precipitated yellow solid was isolated by filtration, washed with NaOH solution and water and dried in vacuum. Yield: 2.66 g (78%); m.p: 196 °C; FTIR (KBr): 2925 (C–H stretch), 1720 cm^{-1} (C=O stretch, imide), 1660 cm^{-1} (C=O stretch, diaryl ketone); ^{1}H NMR ($CDCl_3$): δ (ppm) 2.46 (s, 3H), 7.32 (d, $J = 7.5$ Hz, 2H), 7.44 (d, $J = 6.9$ Hz, 2H), 7.46–7.52 (m, 3H), 7.73 (d, $J = 7.2$ Hz, 2H), 8.05 (d, $J = 7.5$ Hz, 1H), 8.18 (d, $J = 7.2$ Hz 1H), 8.26 (s, 1H); ^{13}C NMR (DMSO-d_6): δ (ppm) 21.8, 123.9, 124.8, 126.6, 128.4, 129.3, 129.5, 130.4, 131.5, 131.7, 133.6, 134.1, 135.7, 143.9, 144.7, 166.5 and 194.4.

2.3.7. Synthesis of 4-(N-phenyl phthalimide-4-carbonyl) benzaldehyde (XIII)

To a solution of XI (3.41 g, 0.01 mol) in CCl_4 (50 mL), N-bromosuccinimide (3.91 g, 0.022 mol) and benzoyl peroxide (100 mg) were added and the reaction mixture was refluxed for 12 h. The reaction mixture was cooled and filtered. The filtrate was concentrated and the compound XII was refluxed with NaOH solution (50 mL) for 10 h. The reaction mixture was cooled and the compound was extracted with diethyl ether. The organic layer was dried with anhydrous sodium sulfate and solvent was evaporated to give XII. Yield: 2.6 g (73%); m.p: 139 °C; FTIR (KBr): 2780 cm^{-1} (C–H stretch, aldehyde); ^{1}H NMR (DMSO-d_6): δ (ppm) 10.21 (s, 1H); ^{13}C NMR (DMSO-d_6): δ (ppm) 192.4 (aldehyde carbon).

2.3.8. Synthesis of 4-(N-phenyl phthalimide-4-carbonyl)benzoic acid (XIV)

An RB flask was equipped with reflux condenser and magnetic stirrer and charged with compound XIII (3.55 g, 0.01 mol), pyridine (1 mL) and water (50 mL). To the reaction mixture $KMnO_4$ solution (15.8 g, 0.1 mol) was added in small portions and refluxed for 6 h. After the reaction, MnO_2 was removed by filtration and filtrate was acidified with dilute hydrochloric acid. The pale yellow color compound was isolated by filtration, washed with water and dried. Yield: 2.67 g (72%); m.p: 224 °C; FTIR (KBr): 3700–2500 cm^{-1} (O–H stretch, –COOH), 1690 cm^{-1} (C=O stretch, –COOH), 1770 cm^{-1} (C=O stretch, imide), 1670 cm^{-1} (C=O stretch, diaryl ketone); ^{1}H NMR (DMSO-d_6): δ (ppm) 7.45 (d, $J = 6.9$ Hz, 2H), 7.52–7.57 (m, 3H), 7.86 (d, $J = 7.8$ Hz, 2H), 8.12–8.14 (m, 3H), 8.25 (d, $J = 7.8$ Hz 2H); ^{13}C NMR (DMSO-d_6): δ (ppm) 194.2, 166.3, 142.1, 139.3, 135.7, 134.5, 131.8, 131.7, 129.9, 129.6, 128.9, 128.3, 127.4, 123.8.

2.3.9. Synthesis of 4-(4-carboxybenzoyl)phthalic acid (XV)

The compound XIV (3.71 g, 0.01 mol) was refluxed with NaOH solution (40 mL, 10%). for 48 h. After the reaction, dilute

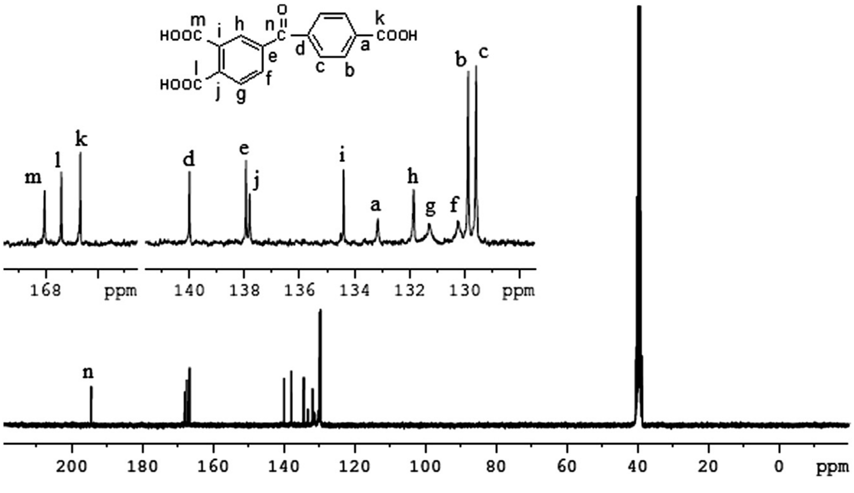


Fig. 4. ^{13}C NMR spectrum of 4-(p-carboxybenzoyl)phthalic acid (XV) in DMSO-d_6.

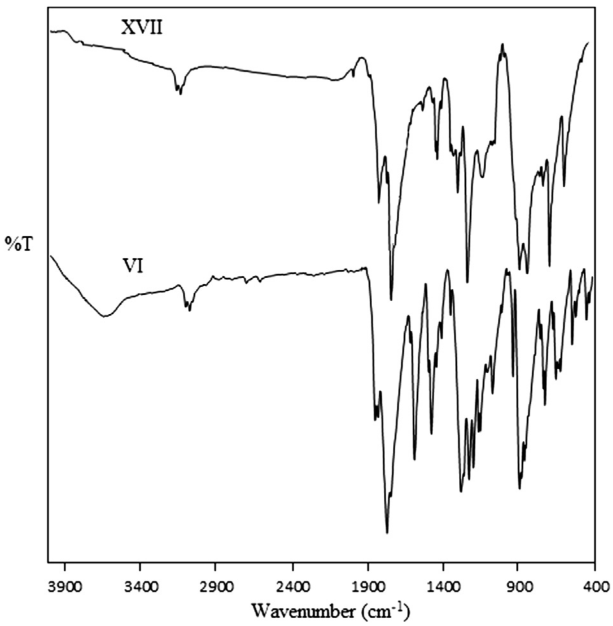


Fig. 5. FTIR spectra of 4-(*p*-chlorocarbonylphenoxy)phthalic anhydride (VI) and 4-(*p*-chlorocarbonylbenzoyl)phthalic anhydride (XVII).

hydrochloric acid (1.2 N) was added and precipitated white solid was isolated by filtration, washed with water and dried. Yield: 2.9 g (93%); m.p: >300 °C; FTIR (KBr): 3595 cm^{-1} (O–H stretch, –COOH), 1685 cm^{-1} (C=O stretch, –COOH), 1665 cm^{-1} (C=O stretch, diaryl ketone); ^1H NMR (DMSO-d_6): δ (ppm) 7.84 (d, $J = 8.1$ Hz, 2H), 7.9 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 8.09 (d, $J = 8.1$ Hz, 2H), 8.19 (s, 1H); ^{13}C NMR (DMSO-d_6): δ (ppm) 194.5, 168, 167.4, 166.6, 139.9, 137.9, 137.8, 134.3, 133.1, 131.8, 131.3, 130.2, 129.8, 129.5.

Table 1
Preparation of poly(amideimide)s.

Sl. No	Monomer	Diamine	Polymer	Inherent viscosity (η)	Yield (%)
1	VI	I	PAI-1	0.58	95
2	VI	II	PAI-2	0.47	97
3	VI	III	PAI-3	0.53	94
4	VI	IV	PAI-4	0.58	96
5	XVII	I	PAI-5	0.49	93
6	XVII	II	PAI-6	0.42	95
7	XVII	III	PAI-7	0.54	98
8	XVII	IV	PAI-8	0.57	96

2.3.10. Synthesis of 4-(4-carboxybenzoyl)phthalic anhydride (XVI)

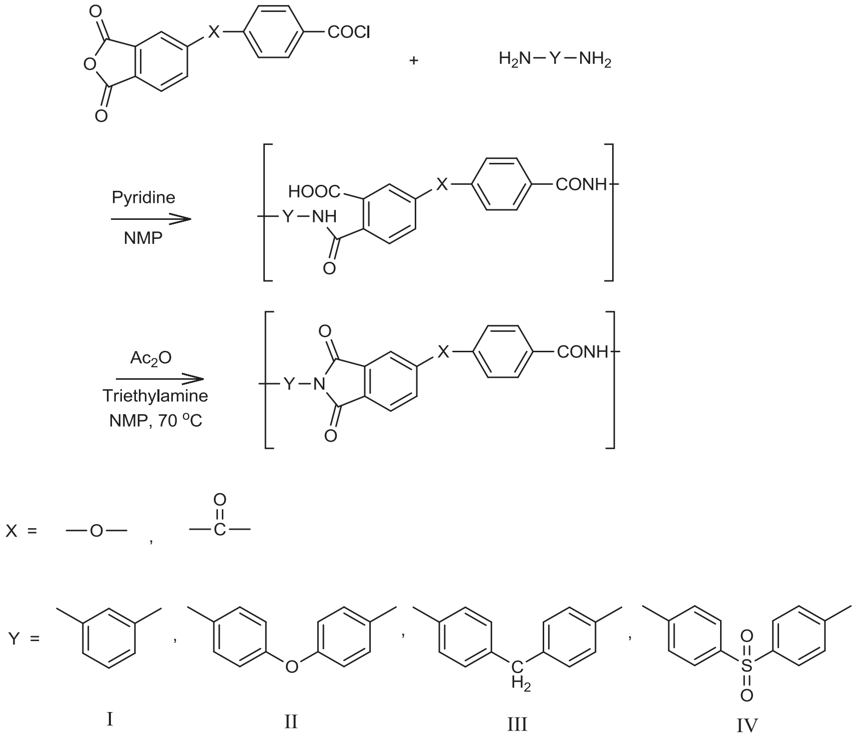
A mixture of compound XV (3 g, 0.01 mol) and acetic anhydride (10 mL) was refluxed for 5 h. The reaction mixture was cooled and the precipitated acid anhydride was isolated by filtration and dried under vacuum. Yield: 2.8 g (98%); m.p: 242 °C; FTIR (KBr): 3580 cm^{-1} (O–H stretch, –COOH), 1680 cm^{-1} (C=O stretch, –COOH), 1855 cm^{-1} (cyclic anhydride) and 1665 cm^{-1} (C=O stretch, diaryl ketone).

2.3.11. Synthesis of 4-(4-(chlorocarbonyl)benzoyl)phthalic anhydride (XVII)

A mixture of compound XVI (3 g, 0.0101 mol), thionyl chloride (20 mL) and pyridine (1 mL) was refluxed for 6 h. The excess thionyl chloride was removed under reduced pressure. The compound XVII was recrystallized from toluene. Yield: 3.17 g (100%); m.p: 127 °C; FTIR (KBr): 1805 cm^{-1} (C=O stretch, acidchloride), 1855 cm^{-1} (cyclic anhydride) and 1660 cm^{-1} (C=O stretch, diaryl ketone).

2.3.12. Synthesis of poly(amideimide)s

A typical procedure followed for the preparation of poly(amideimide)s is as follows. Diamine (1.0 mmol) was dissolved in NMP (10 mL). To this solution anhydride acidchloride (VI or XVII)



Scheme 3. Synthesis of poly(amide–imide)s.

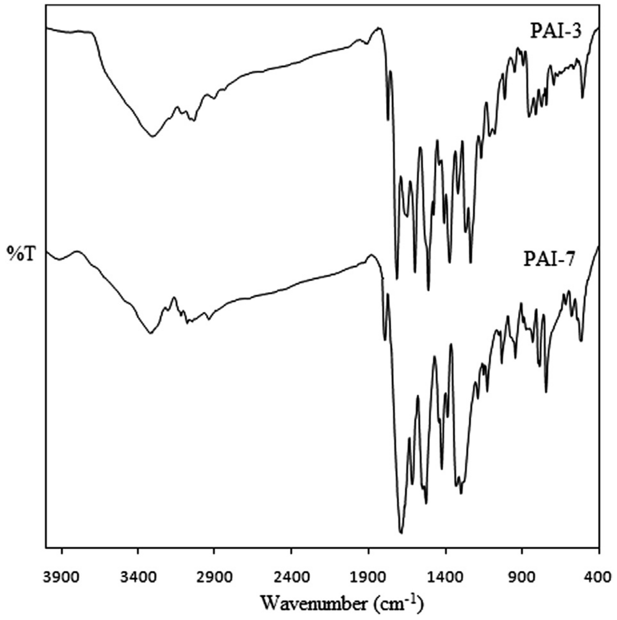


Fig. 6. FTIR spectra of poly(amideimide)s.

(1.0 mmol) and pyridine (0.5 mL) were added. The reaction mixture was stirred at room temperature for 6 h to yield poly(amide amic-acid) solution. Chemical imidization was achieved by using a mixture of acetic anhydride and triethylamine. The polymer solution was poured into methanol and the precipitated polymer was collected by filtration, washed with methanol and dried.

3. Results and discussion

3.1. Synthesis of monomers

The scheme used for the preparation of monomers 4-(*p*-carboxyphenoxy)phthalic anhydride) and 4-(*p*-carboxybenzoyl) phthalic anhydride is given in Schemes 1 and 2. The compound III was synthesized by nucleophilic substitution reaction of N-methyl-4-nitrophthalimide with *p*-hydroxybenzoic acid. The compound III (imide) was hydrolyzed to the corresponding dicarboxylic acid (IV) and the structure of 4-(*p*-carboxyphenoxy)phthalic acid (IV) was confirmed by FTIR and NMR. FTIR spectrum showed absorption bands at 2500–3500 cm^{-1} (O–H stretch, –COOH), 1715 cm^{-1} (C=O stretch, –COOH) and 1240 cm^{-1} (Ar–O–Ar, C–O stretching). The ^{1}H NMR and ^{13}C NMR spectra of the compound IV were shown in Figs. 1 and 2. The carbon atoms of three carboxylic acid groups showed absorption at 167.2–166.7 δ. ^{1}H NMR spectra showed peaks at 7.1–8.2 δ due to aromatic protons.

The monomer 4-(*p*-carboxybenzoyl)phthalic anhydride (XVI) was synthesized as shown in Scheme 2. Compound XI was prepared by Friedel–Craft's acylation reaction of N-phenyl phthalimide-4-carbonyl chloride with toluene. The structure of the compound XI was confirmed by ^{1}H NMR and ^{13}C NMR. The peaks at 2.5 δ and 7.3–8.2 δ are due to methyl and aromatic protons respectively. The signals due to methyl, imide and carbonyl carbon (ketone) were observed at 21.8 δ, 166.5 δ and 194.4 δ respectively. Compound XI was brominated with N-bromosuccinimide and the product XII was hydrolyzed using dilute sodium hydroxide solution to give the corresponding aldehyde XIII. The aldehyde XIII was oxidized to corresponding carboxylic acid XIV using $KMnO_4$. The hydrolysis of imide group was achieved using 10% NaOH solution to yield the corresponding tricarboxylic acid. A broad peak at 2400–3500 cm^{-1} was observed in IR spectrum of XV, confirming the presence of –COOH group. ^{1}H NMR spectrum of compound XV (Fig. 3) showed peaks at 7.8–8.1 δ due to aromatic protons. The ^{13}C NMR spectrum showed peaks at 166.6 δ, 167.4 δ, 168.0 δ and 194.5 δ due to carboxylic acid and ketone group (Fig. 4). The spectral data is in agreement with the proposed structure of the compound XV.

The conversion of carboxylic acid (IV and XV) to anhydride acidchloride (VI and XVII) was achieved by reaction with acetic anhydride, followed by reaction with thionyl chloride. The two anhydride acidchloride monomers were characterized by FTIR (Fig. 5). IR spectra of monomers showed absorptions at 1850 cm^{-1} (VI) and 1845 cm^{-1} (XVII) due to cyclic anhydride group, 1170 cm^{-1} (VI) and 1180 cm^{-1} (XVII) due to C–O stretch and 1770 cm^{-1} (VI) and 1775 cm^{-1} (XVII) due to acidchloride group. These results confirm the structure of anhydride–acidchloride monomers.

3.2. Synthesis of poly(amideimide)s

A series of poly(amideimide)s (PAI-1 to PAI-8) were prepared from the two anhydride acidchloride monomers (Scheme 3). Poly(amic-acid)s were prepared by the reaction of anhydride acidchloride monomers with several aromatic diamines in NMP. All the polymerizations proceeded homogeneously. The chemical imidization of poly(amic-acid) was achieved using acetic anhydride and triethylamine. The poly(amideimide)s were obtained in quantitative yield (>93%) and had inherent viscosity in the range 0.42–0.58 dL/g (Table 1).

The structure of these polymers was confirmed by FTIR and ^{1}H NMR. FTIR spectra of PAI-3 and PAI-7 (Fig. 6) showed characteristic

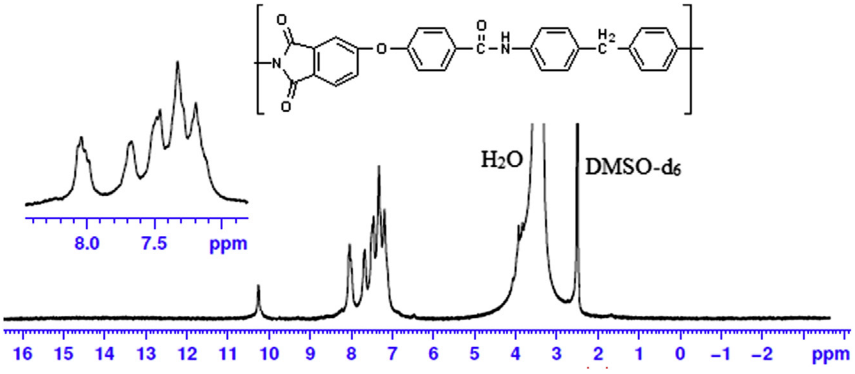


Fig. 7. ^{1}H NMR spectrum of PAI-3 in DMSO-d_6.

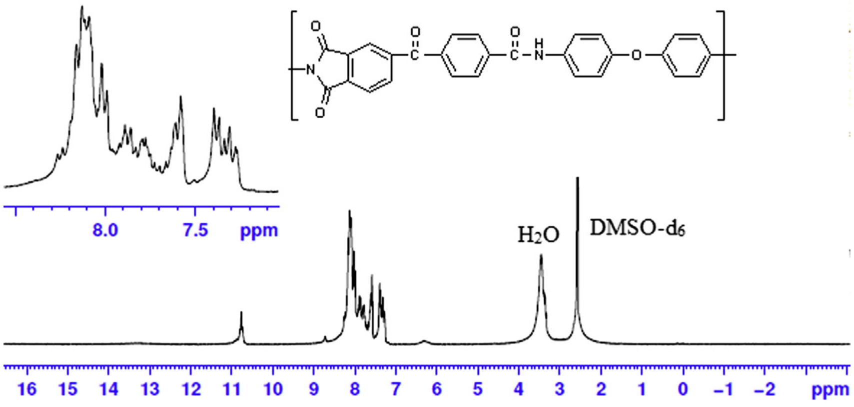


Fig. 8. ^{1}H NMR spectrum of PAI-6 in DMSO-d_6.

absorptions at 1775, 1770, 1715 and 1720 cm^{-1} (asymmetric and symmetric stretching, imide group), 3480 and 3490 cm^{-1} (N–H stretching) and 1649, 1657 cm^{-1} (amide group). ^{1}H NMR spectra of PAIs (Figs. 7 and 8) showed absorptions at 7.1–8.0 δ due to aromatic protons. The signals observed at 10.2 δ and 10.7 δ are due to amide protons.

3.3. Solubility characteristics

The solubility characteristics of these polymers were studied in various organic solvents (Table 2). All PAIs showed good solubility in polar aprotic solvents such as DMSO, DMF, DMAc and NMP at room temperature. PAI-4 and PAI-8 were highly soluble in pyridine and moderately soluble in THF due to the presence of sulfone group in the polymer backbone.

3.4. Thermal properties

The thermal properties of the poly(amideimide)s were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). A representative DSC curve is shown in Fig. 10. The glass transition temperature of these poly(amideimide)s was in the range 226–269 °C (Table 3). The 10% weight loss temperature as well as char yield at 800 °C were determined by TGA (Table 3). The 10% weight loss temperature of these poly(amideimide)s was in the range of 425–461 °C. The char yield of these polymers at 800 °C was in the range 40–61% (Fig. 9). The polymer backbone essentially contains aromatic rings, imide groups and amide groups, which is the reason for high thermal stability of these polymers.

Table 2
Solubility of the poly(amideimide)s in different organic solvents.

Polymer	DMSO	NMP	DMF	DMAc	Pyridine	THF	H_2SO_4
PAI-1	++	++	++	++	+−	−−	++
PAI-2	++	++	++	++	+−	−−	++
PAI-3	++	++	++	++	+−	−−	++
PAI-4	++	++	++	++	+	+−	++
PAI-5	++	++	++	++	−−	−−	++
PAI-6	++	++	++	++	+−	−−	++
PAI-7	++	++	++	++	+−	−−	++
PAI-8	++	++	++	++	+−	−−	++

++ soluble on RT, + soluble on heating, +− partially soluble on heating, −− insoluble even on heating.

3.5. X-Ray diffraction

The crystallinity of poly(amideimide)s was studied by powder X-ray diffraction and the representative diffractograms (PAI-4 and PAI-8) are shown in Fig. 11. The X-ray diffractograms of these polymers showed diffused pattern which indicate amorphous nature of these poly(amideimide)s. Aromatic poly(amideimide)s generally exhibit highly crystallinity. The decrease in crystallinity of

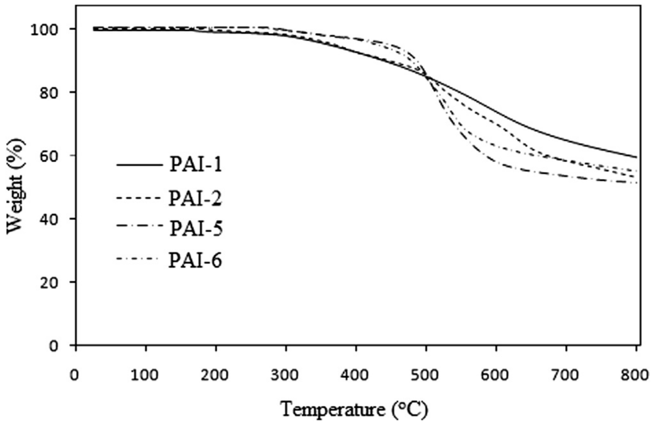


Fig. 9. TGA curves of poly(amideimide)s.

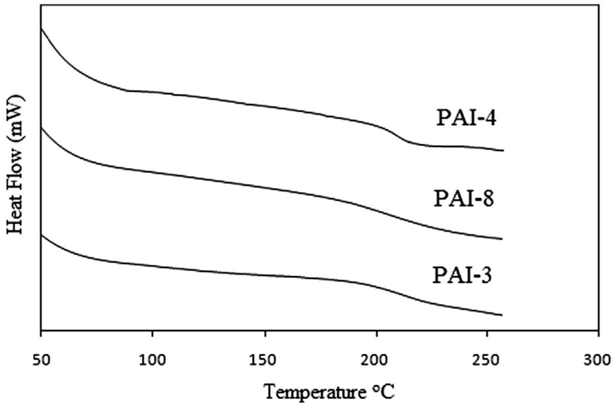


Fig. 10. DSC curves of poly(amideimide)s.

Table 3
Thermal properties of poly(amideimide)s.

Polymer	DSC[a]	Decomposition temperature[b] (°C)			Char yield[c] (%)
	T_g (°C)	Td_{10}	Td_{15}	Td_{20}	
PAI-1	–	438	473	525	57
PAI-2	247	442	484	516	50
PAI-3	228	451	493	527	61
PAI-4	229	448	485	518	40
PAI-5	266	454	494	527	49
PAI-6	248	461	490	508	52
PAI-7	269	429	469	523	43
PAI-8	226	425	475	505	57

[a] DSC measurements conducted at a heating rate 20 °C min^{-1}.

[b] Decomposition temperature was determined by TGA analysis at a heating rate 10 °C min^{-1}.

[c] Char yield at 800 °C in nitrogen.

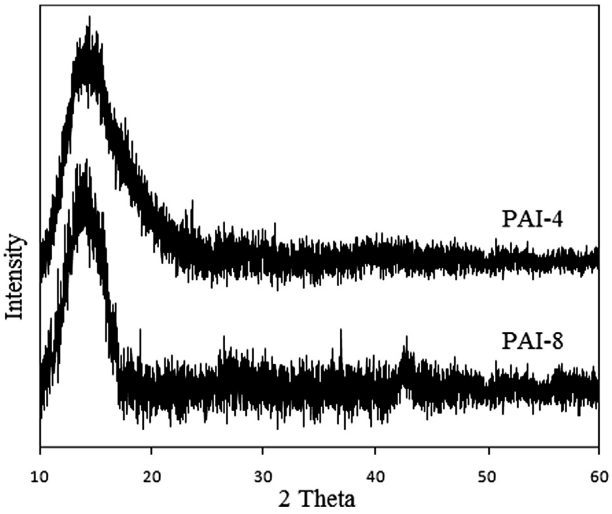


Fig. 11. X-Ray diffractograms of poly(amideimide)s.

these polymers is attributed to the presence of aryl ether and carbonyl groups in the polymer backbone, which restricts the ordered packing of polymer chains.

4. Conclusion

A series of poly(amideimide)s were prepared by the polycondensation of two anhydride acidchloride monomers with several aromatic diamines. All the polymers showed good solubility in polar aprotic solvents. These polymers had high glass transition temperature and showed excellent thermal stability comparable to aromatic polyimides. X-Ray diffractograms of poly(amideimide)s show diffused pattern which indicate amorphous nature of these polymers.

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