

Research Article

Synthesis and Characterization of Novel Processable and Flexible Polyimides Containing 3,6-Di(4-carboxyphenyl)pyromellitic Dianhydride

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A series of six novel polyimides containing 3,6-di(4-carboxyphenyl)pyromellitic dianhydride were synthesized via two steps condensation method. Aromatic diamines monomers, 4-(4-aminophenoxy)-N-(4-(4-aminophenoxy)benzylidene)-3-chloroaniline (DA1), 4-(4-amino-3-methylphenoxy)-N-(4-(4-amino-3-methylphenoxy)benzylidene)-3-chloroaniline (DA2), 4-(4-amino-2-methylphenoxy)-N-(4-(4-amino-2-methylphenoxy)benzylidene)-3-chloroaniline (DA3), 4-(4-aminophenoxy)-N-(4-(4-aminophenoxy)benzylidene)-2-methylaniline (DA4), 4-(4-amino-3-methylphenoxy)-N-(4-(4-amino-3-methylphenoxy)benzylidene)-2-methylaniline (DA5), and 4-(4-amino-2-methylphenoxy)-N-(4-(4-amino-2-methylphenoxy)benzylidene)-2-methylaniline (DA6) were prepared and used to synthesize new polyimides by reaction with resynthesized 3,6-di(4-carboxyphenyl)pyromellitic dianhydride by using two-step condensation method. The inherent viscosities of polyimides range from 0.68–1.04 dL gm⁻¹ and were soluble in polar solvents. Polyimides have excellent thermal stability by showing 10% weight loss temperature was above 450°C. Their glass transition temperatures lie in the range of 250–335°C. Wide-angle X-ray diffractometer investigations revealed the amorphous nature of polyimides. Therefore, these polymers can be a potential candidate as processable high performance polymeric materials.

1. Introduction

Polyimides are very interesting group of amazingly strong and marvellously heat resistant polymers [1]. Aromatic polyimides have received much attention for half a century, due to their excellent combination of properties and potential applications in aerospace, microelectronics (flexible printed boards for electronic devices), photoelectronic industry (as photoresists), and separation industry [2–6]. Other applications include adhesives and matrix resins for composites. However some of their properties like limited solubility, rigid chain characteristics, strong chain-chain interaction, high glass transition, and melting temperatures create difficulties in their processing. That is why applications of these rigid polyimides are restricted in technological and

industrial applications. Extensive research has been carried out to improve their solubility by synthesizing soluble polyimides without disturbing their excellent properties [7–15]. In present days a number of ways exist to alter chemical structure of synthesizing polymeric materials while maintaining the excellent level of their thermal and mechanical properties. Several modifications have been made in their chemical structure by the introduction of bulky alkyl side substitution, noncoplanar, alicyclic structures, flexible aryl, or alkyl ether linkages and asymmetric biphenyl moieties in the back bone of rigid polyimides [16–20]. By the introduction of flexible linkages progress in solubility and significant processability have been achieved by altering crystallinity and intermolecular interactions. The incorporation of aliphatic segments

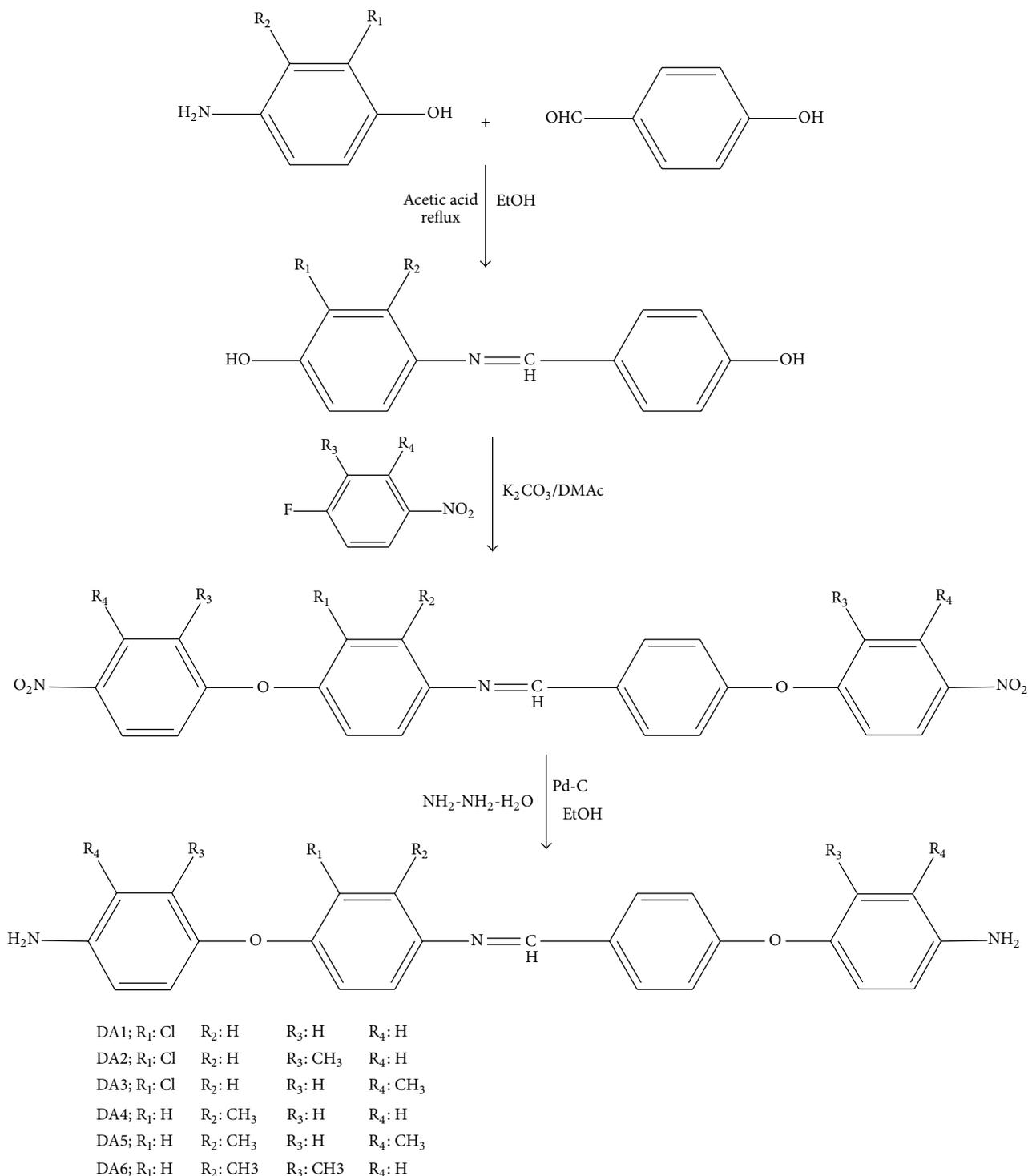
and noncoplanar structures helps to improve solubility of polyimides but is deleterious for thermal and mechanical properties. To achieve better quality polyimides there is need to design new monomers, that is, diamines and dianhydride with structural modifications [21–24]. Researchers are doing efforts to design and synthesize new diamines and dianhydride monomers, thus, producing a wide range of polyimides with promising processability and solubility for various technological and industrial applications. These efforts make it possible to synthesize many polyimides which are soluble and easily processable without disturbing their excellent properties. Among these polyimides fluorinated monomers have also gained attention. When bulky fluorinated groups are incorporated, soluble polyimides with excellent thermal properties can be achieved [25–28]. Asymmetric introduction of bulky substituent or linkages in the backbone of polyimides is another effective approach to improve the solubility of polyimides. Another approach is the introduction of ether linkages using a nucleophilic aromatic substitution reaction. Due to the presence of flexible moieties on the polyimide backbone; there will be a decrease in rigidity of polymer chain to improve the solubility of polyimides. To improve the solubility of polyimides carboxy groups were also introduced in the backbone of polyimides and were found very helpful in improving solubility of polyimides. The carboxy functionality is desirable in developing new applications such as fabrication of nanostructure by molecular self-assembly, ion exchange membranes polymer electrolytes, or ionomers. Thus, components into the polyimide main chain are one of the most successful approaches in attaining solubility without changing their excellent properties. These structural modifications for monomers have also led to new polyimides with several improved properties. Consequently, it was of interest to investigate the thermal stability of aromatic polyimides with various linking groups in their backbone. The azomethine linkage is of distinctive significance due to its remarkable properties such as liquid crystalline property, semiconductivity, ability to form metal chelates, fibre-forming ability, fine thermal stability, and nonlinear optical activity [26–29]. A variety of polymers with a Schiff-base structure have been synthesized, characterized, and investigated with respect to their properties [30]. Keeping in view the useful properties of polyimides, thus, a diamine monomer containing ether and azomethine linkage has been designed, synthesized, and exploited to prepare novel poly azomethine imides with good thermal stability and processability. The aromatic diamines containing azomethine moiety along with ether linkages were incorporated in polymer backbone to examine their structure-property relationship in terms of inherent viscosity, solubility in various solvents, thermal stability, glass transition temperature, and so forth. Introduction of azomethine moiety in the polymer backbone will incorporate features like semiconductivity [31], biomedical activity [32], as thermal stabilizers [33], and corrosion inhibition [34–36] in the newly synthesized polymers. The monomers and polyimides, PI (1–6), were characterized by means of elemental analyses, FTIR, $^1\text{H-NMR}$ spectroscopy.

2. Experimental

2.1. Materials. 4-amino-3-methylphenol, 4-amino-2-chlorophenol, 4-fluoronitrobenzene, 5-fluoro-2-nitrotoluene, 2-fluoro-5-nitrotoluene, 4-hydroxybenzaldehyde, potassium permanganate, tetrakis(triphenylphosphine) palladium, *p*-tolylboronic acid, sodium carbonate, dibromodurene, hydrazine monohydrate, and pyridine were purchased from E. Merck and Aldrich and used without further purification. All organic solvents dimethyl sulfoxide (DMSO), dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-dimethylpyrrolidone (NMP), *m*-cresol, methanol, ethanol, and toluene were purchased from E. Merck, Germany and were dried before used according to the standard methods [37].

2.2. Measurements. Melting points were determined by using capillary tube on an electrochemical melting point apparatus, model MP-D Mitamura Riken Kogyo, Japan and are uncorrected. Infrared absorption spectra were recorded as KBr disc on Bio-Rad Excalibur FT-IR Model FTS 3000 MX. Elemental analysis was performed using a Perkin Elmer 2400 CHN elemental analyzer. The ^1H spectra were recorded on a BRUKER Spectrometer operating at 300 MHz. Solvent used for analysis was deuterated dimethyl sulfoxide (DMSO- d_6). Thermal and DSC analysis were carried out using Perkin Elmer TGA-7 and DSC 404C Netzsch under nitrogen atmosphere. Wide-angle diffractograms were obtained using 3040/60 X'Pert PRO diffractometer. Viscosities were obtained by using Gilmount falling ball viscometer. Solubility was determined in different solvents. Moisture absorption values were determined by changes in weight of the dried film before and after immersion of water at 25°C.

2.3. Synthesis of Monomers. Six new diamine monomers, i.e., 4-(4-aminophenoxy)-*N*-(4-(4-aminophenoxy)benzylidene)-3-chloroaniline (DA1), 4-(4-amino-3-methylphenoxy)-*N*-(4-(4-amino-3-methylphenoxy)benzylidene)-3-chloroaniline (DA2), 4-(4-amino-2-methylphenoxy)-*N*-(4-(4-amino-2-methylphenoxy)benzylidene)-3-chloroaniline (DA3), 4-(4-aminophenoxy)-*N*-(4-(4-aminophenoxy)benzylidene)-2-methylaniline (DA4), 4-(4-amino-3-methylphenoxy)-*N*-(4-(4-amino-3-methylphenoxy)benzylidene)-2-methylaniline (DA5), and 4-(4-amino-2-methylphenoxy)-*N*-(4-(4-amino-2-methylphenoxy)benzylidene)-2-methylaniline (DA6), were synthesized in three steps as shown in the Scheme 1. In first step Schiff bases were prepared by condensation of 0.025 mol of substituted *p*-hydroxyamines and 0.025 mol of 4-hydroxyaldehyde in dry ethanol (15–20 mL) in the presence of acetic acid which act as catalyst. After stirring of about 1 h the reaction mixture was refluxed 4–5 h. Reaction was monitored by thin layer chromatography (TLC). The reaction mixture was filtered and precipitates were collected. The crude product was washed with ethanol and recrystallized with methanol. In the second step 1 g of dihydroxy Schiff base compound was treated with 0.01 mol of substituted 4-fluoronitrobenzene and 0.01 mol of potassium



SCHEME 1

carbonate in DMAc (60 mL) in two necks round bottom flask under inert conditions. The reaction mixture was heated at 100°C for 18–20 h. The reaction mixture was cooled to room temperature and poured into water. Solid obtained was washed thoroughly with water and filtered. Product obtained was recrystallized with ethanol. In third step for reduction of

nitro compounds, 1 g of above synthesized dinitro compound was suspended in 250 mL of two-necked flask with 10 mL of hydrazine monohydrate and 0.06 g of 5% palladium on carbon (Pd-C) and 60 mL of dry ethanol. The reaction mixture was heated at reflux for 16 h and then filtered to remove Pd-C. Solvent was evaporated through rotary

evaporator and the solid product obtained was recrystallized from ethanol [24].

Data of DA1. Molecular formula; $C_{25}H_{20}N_3O_2Cl$, melting point; 172 ± 1 , yield; 75, elemental analysis; calculated (found), %C; 69.77(69.75), %H; 4.65(4.63), %N; 9.76(9.7), IR(KBr)/ cm^{-1} 3400, 3325(-NH₂) 1624(-C=N) 1355 (-C-N), ¹H NMR (DMSO-d₆, δ , ppm), 5.11 (-NH₂); 6.68–7.80 (m, 15H, aromatic); 8.65 (s, 1H, azomethine).

Data of DA2. Molecular formula; $C_{27}H_{24}N_3O_2Cl$, melting point; 156 ± 1 , yield; 78, elemental analysis; calculated (found), %C; 70.74(70.73), %H; 4.94(4.92), %N; 8.65(8.5), IR(KBr)/ cm^{-1} 3415, 3330(-NH₂), 1650(-C=N), 1345 (-C-N), ¹H NMR (DMSO-d₆, δ , ppm) 2.20 (6H, CH₃); 5.45 (-NH₂); 6.48–7.68 (m, 13H, aromatic); 8.64(s, 1H, azomethine).

Data of DA3. Molecular formula; $C_{27}H_{24}N_3O_2Cl$, melting point; 162 ± 1 , yield; 82, elemental analysis; calculated (found), %C; 70.74(70.73), %H; 4.94(4.96), %N; 8.65(8.62), IR(KBr)/ cm^{-1} 3405, 3340(-NH₂), 1618(-C=N), 1365 (C-N), ¹H NMR (DMSO-d₆, δ , ppm) 2.14 (s, 6H, CH₃); 6.01 (-NH₂); 6.61–7.60 (m, 13H, aromatic); 8.52 (s, 1H, azomethine).

Data of DA4. Molecular formula; $C_{26}H_{23}N_3O_2$, melting point; 185 ± 1 , yield; 85%, elemental analysis; calculated (found), %C; 76.28(76.19), %H; 5.62(5.60), %N; 10.27(10.22), IR(KBr)/ cm^{-1} 3443, 3365(-NH₂), 1698(-C=N)1350 (-C-N), ¹H NMR (DMSO-d₆, δ , ppm) 2.12 (s, 3H, CH₃); 5.74 (-NH₂); 6.45–7.88 (m, 15H, aromatic); 8.59 (s, 1H, azomethine).

Data of DA5. Molecular formula; $C_{28}H_{27}N_3O_2$, melting point; 160 ± 1 , yield; 80, elemental analysis; calculated (found), %C; 76.88(76.85), %H; 6.17(6.16), %N; 9.61 (9.60), IR(KBr)/ cm^{-1} 3405, 3355(-NH₂), 1645(-C=N), 1366(-C-N), ¹H NMR (DMSO-d₆, δ , ppm) 2.06 (s, 9H, CH₃); 6.12 (-NH₂); 6.75–7.82 (m, 13H, aromatic); 8.66 (s, 1H, azomethine).

Data of DA6. Molecular formula; $C_{28}H_{27}N_3O_2$, melting point; 160 ± 1 , yield; 80, elemental analysis; calculated(found), %C; 76.88(76.84), %H; 6.17(6.12), %N; 9.61 (9.59), IR(KBr)/ cm^{-1} 3412, 3362(-NH₂), 1645(-C=N), 1365(-C-N), ¹H NMR (DMSO-d₆, δ , ppm) 2.10 (s, 9H, CH₃); 5.52 (-NH₂); 6.65–7.96 (m, 13H, aromatic); 8.56 (s, 1H, azomethine).

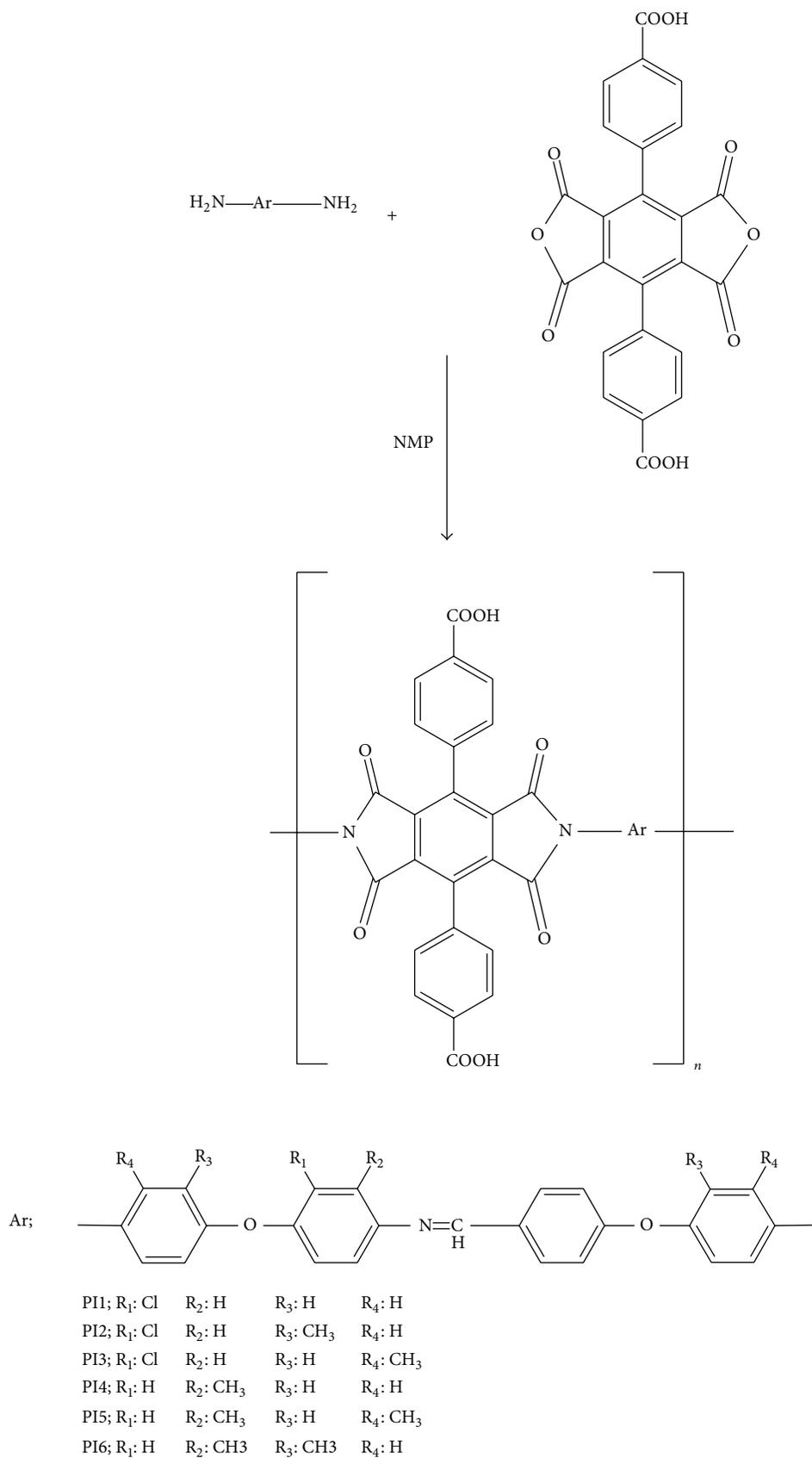
2.4. Synthesis of 4,2,3,5,6,4-Hexamethyl-*p*-terphenyl. Dianhydride used for the synthesis of polyimides was resynthesized by following the reported method [10]. A 250 mL flask was charged with 4.67 g (16 mmol) dibromodurene, 100 mL toluene, 1.1 g (0.96 mmol) Pd(PPh₃)₄, and 100 mL 2 M Na₂CO₃ solution. After addition of 4.7 g (35 mmol) *p*-tolylboronic acid in 30 mL ethanol, the mixture was refluxed for 24 hrs. After cooled to room temperature, 12.5 mL of H₂O₂ (30%) was added with great care under vigorous stirring and the mixture was again stirred for hour. After stirring, two layers were formed in the reaction mixture. Separate the organic layer and dried with MgSO₄. The solvent was evaporated to obtain crude product, which was washed by cold ethanol to remove byproducts and recrystallized from

ethyl acetate. Yield: 68%; m.p.: 282–285°C; IR (KBr, cm^{-1}); 528 (para-subst. oop), 1524(-C=C), 1565, 1645, 1789, 1900 (para-subst.), 2915–3045(-CH); ¹H NMR (DMSO-d₆, ppm): 1.85(s, 6H, CH₃), 2.48(s, 12H, CH₃), 7.15–7.30(m, 8H, Ar).

2.5. Synthesis of 3,6-Di(4-carboxyphenyl)pyromellitic Acid. A 250 mL three-necked flask equipped with magnetic stirrer and condenser was charged with 3.14 g (0.01 mol) of 1,4-ditolylidurene, 120 mL of pyridine, and 10 mL of water. The mixture was heated up to 120°C then added 28.4 g (0.18 mol) of KMnO₄ portion wise. After complete addition of KMnO₄ the reaction mixture was further refluxed 12 h. This hot reaction mixture was vacuum filtered over a glass funnel to remove MnO₂. After evaporating the filtrate, a solid residue was left behind. That solid was put into a 250 mL three-necked flask with stirrer and condenser. It was treated with 100 mL of 4% aqueous NaOH solution under agitation. After that flask contents were heated to 100°C, 9.48 g (0.06 mol) of KMnO₄ was added and refluxed it for 12 hrs. Excess KMnO₄ was removed using ethanol until the KMnO₄ colour disappeared. Then filtered the reaction mixture to remove MnO₂ and the filtrate was acidified with HCl to get product, which was further purified by recrystallization in water. Yield: 79%; IR (KBr, cm^{-1}); 1610(C=C, Ar), 1678(-C=O), 3550–2565(-OH, acid); ¹H NMR (DMSO-d₆, ppm) 7.24–7.82(m, 8H) 13.1(s, 6H, COOH) [10].

2.6. Synthesis of 3,6-Di(4-carboxyphenyl)pyromellitic Dianhydride. A 100 mL two-necked flask was charged with white crystal of 3,6-di(4-carboxy)phenylpyromellitic acid (4.58 g, 10 mmol) and 50 mL of acetic anhydride in inert conditions. After the reflux of 5 h, acetic anhydride was evaporated out to get yellow solids which were further recrystallized from dried DMAc. Yield: 87%; elemental analysis ($C_{24}H_{10}O_{10}$), (458.33) calculated (found) %C 62.83(62.90), %H 2.18(2.23), O 34.90; 34.67 IR (KBr, cm^{-1}); 1675(C=O, acid), 1868 and 1775(C=O, anhydride), 3545–2550(O-H, acid); ¹H NMR (DMSO-d₆, ppm): 7.65–8.26(m, 8H, Ar), 13.01(s, 2H, acid) [10].

2.7. Synthesis of Polyimide (PI). The synthesized monomers were subjected to polyimide synthesis. polyimides were synthesized by polycondensation of diamine monomers DA1, DA2, DA3, DA4, DA5, and DA6 with resynthesized dianhydride monomer 3,6-di(4-carboxyphenyl)pyromellitic dianhydride [10]. Three-necked flask equipped with nitrogen inlet and mechanical stirrer was charged with 1.2 mol of diamine in 5–10 mL of NMP. Then 1.2 mol of 3,6-di(4-carboxyphenyl)pyromellitic dianhydride was added slowly in the dissolved diamine in NMP. The reaction mixture was stirred for 24 h at room temperature to produce polyamic acid in inert conditions. The resulting polyamic acid solution was converted into polyimides through chemical imidization and thermal method. For chemical imidization, in polyamic acid solution equimolar pyridine and acetic anhydride was added. The reaction mixture was stirred at room temperature for one hour and then heated at 100°C for 3 h. The resulting solution was poured into methanol and fibrous precipitates of polyimides were collected and dried as shown in Scheme 2.



SCHEME 2

TABLE 1: FTIR, ^1H NMR of polyimides (PI-1–PI-6).

Compound	IR (KBr)/ cm^{-1}	^1H NMR (DMSO- d_6 , δ , ppm) (s; singlet, m; multiplet)
PI-1	1725, (CO) $_{\text{sym}}$, 1788 (CO) $_{\text{asym}}$ 1665 (C=N)	13.01 (s, 2H, COOH) 6.78–7.90 (m, aromatic protons); 8.65 (s, 1H, azomethine)
PI-2	1718, (CO) $_{\text{sym}}$, 1772 (CO) $_{\text{asym}}$ 1650 (C=N)	13.21 (s, 2H, COOH); 6.65–7.89 (m, aromatic protons); 8.15 (s, 1H, azomethine)
PI-3	1725, (CO) $_{\text{sym}}$, 1778 (CO) $_{\text{asym}}$ 1664 (C=N)	13.12 (s, 2H, COOH) 6.41–7.90 (m, aromatic protons); 8.52 (s, 1H, azomethine)
PI-4	1715 (CO) $_{\text{sym}}$, 1782 (CO) $_{\text{asym}}$ 1657 (C=N)	12.98 (s, 2H, COOH) 6.75–7.97 (m, aromatic protons); 8.15 (s, 1H, azomethine)
PI-5	1725 (CO) $_{\text{sym}}$, 1775 (CO) $_{\text{asym}}$ 1665 (C=N)	12.99 (s, 2H, COOH) 6.45–7.78 (m, aromatic protons); 8.62 (s, 1H, azomethine);
PI-6	1717 (CO) $_{\text{sym}}$, 1780 (CO) $_{\text{asym}}$ 1638 (C=N)	13.08 (s, 2H, COOH) 6.35–7.88 (m, aromatic protons); 8.25 (s, 1H, azomethine)

In DMSO- d_6 at 295 K.

For thermal treatment polyamic acid solution was poured in glass petri dishes and placed in oven at 90°C overnight for film preparation. Further the film was treated by heating at 150°C for 30 min, 200°C for 30 min, and 280°C for 1 h [37].

3. Results and Discussion

Six new different polyimides were synthesized by polycondensation method. All the synthesized diamines were characterized by IR, NMR, and elemental analysis. FT-IR and NMR spectroscopic techniques confirmed the structures of diamines monomers and polyimides.

3.1. IR Spectroscopy. FT-IR analysis and spectral data confirmed the chemical structure of monomers diamines (DA1–DA6) and their respective polyimides. The data is presented in Table 1. The presence of imide ring was confirmed by the characteristic bands at $1788\text{--}1715\text{ cm}^{-1}$ for (CO) $_{\text{asym}}$ and (CO) $_{\text{sym}}$ stretching, respectively. The dehydration cyclization of polyamic acid (PAA) to form an imide ring was confirmed by the disappearance of the band at 1690 cm^{-1} (related to C=O of amic acid). Further the formation of polyimides was confirmed by the absence of N–H vibration at 3500 and 3200 cm^{-1} . Characteristic band at $1627\text{--}1664\text{ cm}^{-1}$ corresponding to the azomethine group ($-\text{CH}=\text{N}-$) indicated the presence of azomethine moiety in polyimides as shown in Figure 1. The disappearance of the amide and carbonyl bands indicated virtually a complete conversion of the imide ring in the resulting polyimide [38].

3.2. ^1H NMR Spectroscopy. Formation of diamines and their respective polyimides were confirmed by ^1H NMR. ^1H NMR confirmed the reduction of nitro compounds into

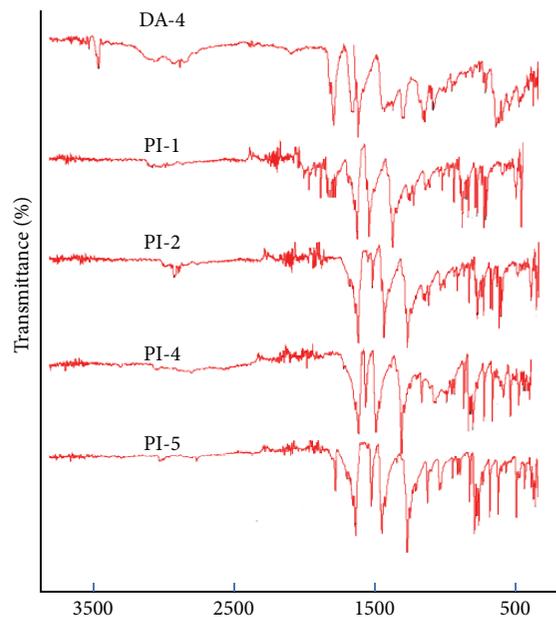


FIGURE 1: Spectra of DA-4, PI-1, PI-2, PI-4, and PI-5.

amines by high field shift of aromatic protons. Signals due to NH_2 protons were found near 5.11–6.12. Characteristic signals of C=N– at 8.15–8.66 in spectra of diamines and polymer confirmed the presence of azomethine moiety. The peaks between 2.06 and 2.20 ppm confirmed the presence of aliphatic proton structure in the polymer, that is, methyl. The aromatic proton peaks can be observed between 6.30 and 8.00 ppm regions. The characteristic signal of amino group disappears in the ^1H NMR of polyimides confirm the synthesis of polyimides and complete imidization [39].

TABLE 2: Solubility and inherent viscosity of polyimides (PI-1-PI-6).

Polyimide	DMSO	DMAc	DMF	THF	<i>m</i> -cresol	H ₂ SO ₄	η_{inn} (dL/g)
PI-1	++	+	+	–	+	+++	0.68
PI-2	++	+	–	–	++	+++	0.98
PI-3	+++	–	++	+	++	+++	1.01
PI-4	++	+	+	–	++	+++	0.72
PI-5	++	+	+	+	++	+++	0.94
PI-6	+++	+	–	+	++	+++	1.04

+++ = soluble at room temperature, ++ = soluble on heating, + = slightly soluble on heating, – = insoluble.

TABLE 3: Thermal stability of the polyimides (PI-1-PI-6).

Polymer code	T_g (°C)	Thermal stability			Char yield (%) ^d
		T_5 (°C) ^a	T_{10} (°C) ^b	T_{max} (°C) ^c	
PI-1	250	455	480	500	58
PI-2	325	470	498	498	60
PI-3	270	498	525	495	65
PI-4	280	460	485	525	59
PI-5	335	490	515	520	63
PI-6	310	498	520	496	64

^a T_5 %, ^b T_{10} %: temperatures at 5, 10% weight loss, respectively.

^cTemperature of maximum decomposition rate.

^dResidual weight when heated to 600°C in nitrogen.

3.3. Viscosity Measurement. Viscosities of all the synthesised polyimides were obtained by using Gilmount falling ball viscometer in H₂SO₄ at 30°C. The inherent viscosities of the synthesised polyimides were calculated between the ranges of 0.68 and 1.04 dL/g indicated that polymers have moderate to higher molecular weights. Most of the polyimides showed higher value of inherent viscosity than other reported polyimides having azomethine linkages [40, 41].

3.4. Organosolubility of Polymers. Solubility of the synthesized polyimides was investigated in different solvents like DMSO, DMac, DMF, *m*-cresol, and THF and summarized in Table 2. Polyimides were found to be soluble in most of the polar protic solvents. The improvement in solubility is attributed to flexibility induced by incorporated moieties along with carboxyl group in polyimide structure which is related with intermolecular interaction and packing of polyimide films. Some polyimides were soluble at room temperature and some were soluble on heating. The ether linkages along with other aliphatic substitutions like methyl and chloro also helpful in increasing solubility of polyimides [10, 24].

3.5. Moisture Absorption. The polyimides were also subjected to analyse the moisture absorption capacity through change in weight of dried polyimide before and after immersion in distilled water at 25°C for 24 hrs. The moisture absorption of the polyimides was in the range from 1.02 to 1.28%. That increase in water uptake of the polymers is might be due to the incorporation of carboxyl group [10].

3.6. Thermal Behavior. The thermal properties of the synthesized polyimides were evaluated by TGA and DSC at heating rate of 10°C min⁻¹. The obtained data is summarized in Table 3. Thermal properties of the compounds are strongly depended on their chemical structure. Polyimides showed excellent thermal properties (Figure 2). They were found thermally stable up to 480–525°C from the 10% weight loss, T_{max} of ca. 495–525°C and char yields of 58–65 at 600°C. The loss of weight in the first degradation step may be due to the –COOH group. So it may be predicted that first step was decarboxylation step and showed the decomposition of polyimide backbone. Dehydration behaviour of polymers was also observed by loss of 2-3% of weight. This might be due to water uptake ability of polyimides. Taking into account the results from TGA analysis, it was found that the presented polyimides possess good thermal stability without significant weight losses up to 380°C. This implies that no thermal decomposition occurs below this temperature and that the onset decomposition temperature was as high as 400°C for the all polyimides. The glass transition temperature (T_g) of the PIs samples, which is one of the key parameters of polymers when considering the high-temperature devices fabrication and the long-term heat releasing environment was taken as the midpoint of the change in slope of the baseline in DSC curves. The glass transition temperature T_g as a second order endothermic transition could be considered as the temperature at which a polymer undergoes extensive cooperative segmental motion along the backbone. The flexible linkages decreased the energy of internal rotation and lowered the T_g [42, 43]. Different intra- and intermolecular interactions including hydrogen bonding, electrostatic and ionic forces,

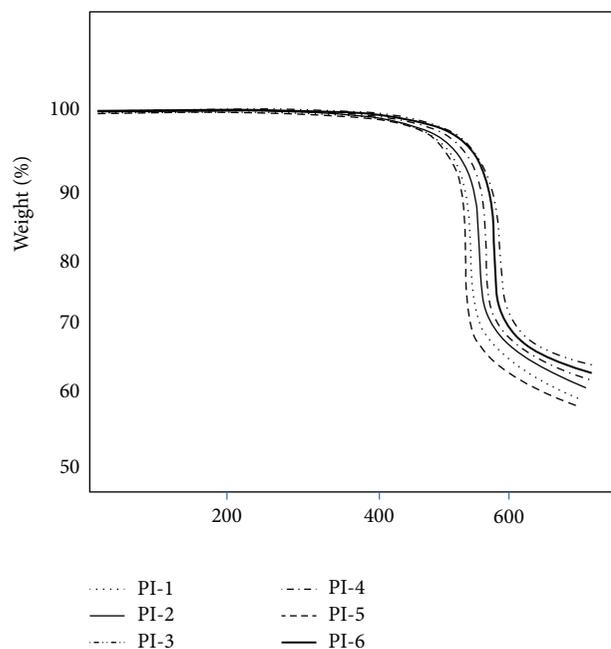


FIGURE 2: TGA curves of polyimides (PI-1 to PI-6).

chain packing efficiency, and chain stiffness also affected the T_g . The T_g of the polyimides (PI-1–PI-6) were observed in the range of 250–335°C, depending upon the structure of diamine component along with dianhydride and decreased with the decreasing of rigidity of the polymer backbone. (PI-5) exhibited the highest T_g (335°C) owing to the highly rigid pyromellitimide unit along with azomethine backbone with methyl substituents.

3.7. X-Ray Diffraction. X-ray diffraction analysis was also carried out for the characterization of polyimides (Figure 3). All the polyimides showed broad peaks in wide-angle X-ray diffraction pattern indicated the amorphous nature of polyimides. It might be due to strong chain interaction between the acid groups, which could not help in building regular structure and disturb chain packing of the polyimides. The strong interaction among carboxyl group hindered the chain mobility. The bulky phenyl groups inside the polymer chain with ether linkages might have introduced the amorphous characteristic in these polyimides. The amorphous nature of polyimides is responsible for the improvement in solubility of polyimides [10, 24].

4. Conclusion

A new series of polyimides were synthesized by condensation method of newly synthesized diamines having ether and azomethine linkages with resynthesized dianhydride. All the polyimides were found soluble in most of the polar aprotic solvents and have inherent viscosities in the range of 0.68–1.04 dL/g indicated the moderate to higher molecular weights of polyimides. All the polyimides were found thermally stable upto 498–523°C. All the polyimides have amorphous nature

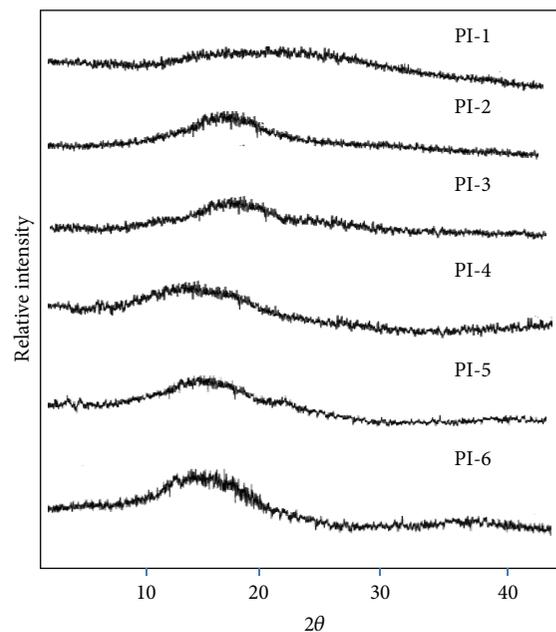


FIGURE 3: X-ray diffraction pattern of polyimides (PI-1 to PI-6).

indicated by the wide-angle X-ray diffraction analysis. On the basis of such results it is concluded that these polyimides could be considered for new processable high performance polymeric materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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