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Synthesis and characterization of some novel thermally stable poly(amide–imide)s

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Abstract Two new diamines with built-in amide linkage were synthesized from *p*-nitrobenzoyl chloride in two steps and characterized by their melting points, elemental analyses, FT-IR and ^{1}H–NMR spectral studies. One of the diamine precursors was also characterized by single crystal X-ray analysis indicating the *trans* orientation of amide bonds. The planes of the aromatic rings formed dihedral angles in the range of 11.7°–56.2° and the crystal packing was stabilized by N–H···O hydrogen bonds. The synthesized diamines were then polymerized with three commercially available dianhydrides either by one-step solution technique or by two-step procedure involving ring-opening poly-addition to give polyamic acid followed by cyclic dehydration. The resulting poly(amide–imide)s were characterized by their elemental analyses and FTIR spectroscopy. The polymers possessed excellent chemical resistance and were found insoluble in almost all the common solvents tested except conc. H_2SO_4, in which these showed inherent viscosities in the range 0.47–0.73 dL g^{-1} at 28 °C. The thermal behavior of the polymers, investigated by the DSC and TG analyses, revealed that the products were stable up to 300 °C in nitrogen. The activation energies of pyrolysis, entropy, and enthalpy values for each of the synthesized polymers were also estimated by Horowitz and Metzger method using thermal degradation data. These values were high exhibiting the remarkable thermal stability of the poly(amide–imide)s. Wide-angle X-ray studies of the polymers were also carried out which provided information about their morphology.

Introduction

Polyimides constantly attract much interest because of their unique property combination which renders them to be classified as high performance polymers that combine high thermal stability with chemical resistance and excellent electrical and mechanical properties [1, 2]. Therefore, these are widely used in the aerospace and microelectronic industry in the forms of films and moldings [3, 4]. Other uses for these polymers such as adhesives, gas separation membranes, composite matrices, coatings, and foams are also rapidly increasing [5–7]. To further enhance their applicability in different fields, it is desirable to synthesize polyimides that are soluble in spin coating and casting processes [8]. Several approaches such as the introduction of bulky substituents to the main chain to enhance the free volume [9–11], the incorporation of flexible linkages to reduce the packing force [12–14], the replacement of aromatic groups with alicyclic groups [15–18], and the introduction of twisted [19–21] or unsymmetrical structures [22–24] into the polymer chain have been extensively used to achieve the goal of processable polyimides. Addition of other rigid groups in the main chain, whose rigidity is not far lower or higher than that of the imide group, is another important approach for this purpose [25–28]. Amide group is one such group which is a bit less rigid than the imide group and its inclusion to the main polyimide chain not only improves the processability by distortion of the main chain regularity but also maintains the thermal stability by

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the retention of the main chain rigidity [29, 30]. Thus, the resulting poly(amide–imide)s are certainly the most important type of modified polyimides which combine and inherit the desirable characteristics from both polyamides and polyimides and are particularly useful in electrical wire enamel, adhesives, injection-molding, and extrusion products [31, 32].

Keeping in view, the favorable balance between processability and performance of the poly(amide–imide)s, it was planned to synthesize two sets of novel aromatic polyimides based on two new diamines containing amide linkage in the core structure. The diamines were synthesized from the reaction of *p*-nitrobenzoyl chloride with 1,4-phenylene diamine and 4,4′-diaminodiphenylether, respectively, and subsequently used for the synthesis of two sets of novel polyimides utilizing three commercially available dianhydrides. The poly(amide–imide)s so produced were characterized by their physical properties, spectral studies, and thermal analyses. Their structure–property relationship was also elucidated from these studies.

Experimental

Materials

All chemicals and reagents used were of highest purity or otherwise mentioned. 4-Nitrobenzoic acid, 1,4-phenylene diamine, 4,4′-diaminodiphenyl ether, triethyl amine, 5% palladium charcoal, and isoquinoline were purchased from Fluka (Switzerland); thionyl chloride and hydrazine monohydrate from Merck, Germany and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 3,4,9,10-perylene tetracarboxylic acid dianhydride (PRDA) were obtained from Aldrich (Germany) and used without further purification. *N,N*′-dimethylacetamide (DMAc) and *m*-cresol were purchased from Fluka (Switzerland) and distilled under reduced pressure over CaH_2 and P_2O_5, respectively, prior to use in polymerization reactions. All the manipulations were conducted under the atmosphere created by vacuum line and dry N_2 gas. The purity of the products was monitored by thin layer chromatography using pre-coated TLC plates.

Measurements

The elemental analysis was performed using CHNS-932 LECO instrument. Melting temperatures of the products were determined on melting point apparatus, Mel-Temp, Mitamura Riken Kogyo, Inc Tokyo, Japan. ^{1}H NMR spectral analysis was carried out on ultra-shield 300 MHz instrument in DMSO-d_6/$CDCl_3$ using teteramethyl silane as internal reference. The solid-state Fourier transform infrared spectra were recorded using KBr pellets on Biorad Excalibur FTIR, Model 3000 MX. The data for the crystal structure analysis were collected on a STOE IPDS-II diffractometer with monochromated Mo-K_α radiation at 173 K. Thermal characterizations were performed on Perkin-Elmer Pyris 1 at a rate of 10 °C/min in nitrogen atmosphere. Wide-angle XRD analysis of the polymers was carried out using 3040/60 X'Pert PRO diffractometer and inherent viscosities of the polyimides were determined by using Ostwald Viscometer.

Monomer synthesis

Preparation of p-nitrobenzoyl chloride

A prebaked two-neck flask equipped with condenser and magnetic stirrer was charged with 5 g (30 mmol) of 4-nitrobenzoic acid in excess of thionyl chloride (12 mL) and refluxed for 4 h at 80 °C under N_2 till all the acid dissolved. The mixture was allowed to cool and excess thionyl chloride was evaporated under vacuum. The product obtained as yellow precipitates (Yield 94%, m.p. 66 °C) and stored in air tight bottle under inert conditions.

Synthesis of 1,4-bis[4-nitrobenzamide]phenylene (N_1)

A mixture of of *p*-nitrobenzoyl chloride (1.5 g; 8 mmol), 1,4-phenylenediamine (0.44 g; 4 mmol), and triethylamine (2 mL; 14.3 mmol) in 50 mL anhydrous toluene was refluxed in a pre-baked two-neck round bottom for 3 h under inert conditions and then allowed to stand for 16 h at room temperature. The solid obtained was filtered out and stirred with distilled water for 15 h, again filtered and recrystallized with chloroform (Yield 87%, m.p. 230 °C). Elemental analysis for $C_{20}N_4O_6H_{14}$ (MW = 406) in wt% calc. C = 59.11, H = 3.44, N = 13.79 and found C = 58.27, H = 3.38, N = 13.82. IR (KBr pellet) in cm^{-1}:1545, 1350 (NO_2), 3102 (aromatic C–H), 1404 (C–N), 3316 (amide N–H), 1644 (amide C=O). ^{1}H NMR ($CDCl_3$) in δ (ppm): 11.15 (s, 2H, amide N–H).

Synthesis of 1,4-bis[4-aminobenzamide]phenylene (DA_1)

A two-neck flask was charged with 1,4-bis[4-nitrobenzamide]phenylene (N_1) (1 g; (2.5 mmol), 8 mL of hydrazine monohydrate, 50 mL ethanol, and 0.06 g of 5% palladium on carbon (Pd–C) and the mixture was refluxed for 18 h and then filtered to remove the (Pd–C). The filtrate was concentrated on rotary evaporator and the resulting pale yellow precipitates were recrystallized from ethanol (Yield 76%, m.p. 238 °C). Elemental analysis for $C_{20}N_4O_2H_{18}$ (MW = 346) in wt% calc. C = 69.36, H = 5.20, N = 16.18 and found C = 68.81, H = 5.11, N = 15.85. IR (KBr pellet) in cm^{-1}: 3415, 3334 (N–H), 3102 (aromatic C–H), 1403 (C–N), 1630 (amide C=O). ^{1}H NMR (DMSO-d_6) in δ (ppm): 10.64 (s, 2H, amide N–H), 5.11 (s, 4H, aromatic NH$_2$).

Synthesis of 4,4′-bis[4-nitrobenzamide]1-phenoxybenzene (N_2)

The aforementioned procedure for 1,4-bis[4-nitrobenzamide]phenylene (N_1) was applied for the synthesis of dinitro specie, 4,4′-bis[4-nitrobenzamide]1-phenoxybenzene (N_2) except that 4,4′-diaminodiphenyl ether was used instead of 1,4-phenylene diamine (Yield 84%, m.p. 272 °C). Elemental analysis for $C_{26}N_4O_7H_{18}$ (MW = 498) in wt% calc. C = 62.65, H = 3.61, N = 11.24 and found C = 61.92, H = 3.45, N = 11.31. IR (KBr pellet) in cm^{-1}: 1538, 1349 (NO$_2$), 3108 (aromatic C–H), 1409 (C–N), 3358 (amide N–H), 1650 (amide C=O), 1222 (C–O–C). ^{1}H NMR (DMF-d_6) in δ (ppm): 10.73 (s, 2H, amide N–H).

Synthesis of 4,4′-di[4-aminobenzamide] 1-phenoxy benzene (DA_2)

The aforementioned procedure for 1,4-bis[4-aminobenzamide]phenylene (DA_1) was followed for the synthesis of diamine, 4,4′-di[4-aminobenzamide]1-phenoxy benzene (DA_2) except that 4,4′-bis[4-nitrobenzamide]1-phenoxybenzene (N_2) was used instead of 1,4-bis[4-nitrobenzamide]phenylene (N_1) (Yield 77%, m.p. 248 °C). Elemental analysis for $C_{26}N_4O_3H_{22}$ (MW = 438) in wt% calc. C = 71.23, H = 5.02, N = 12.78 and found C = 70.88, H = 4.86, N = 12.17. IR (KBr pellet) in cm^{-1}: 3407, 3320 (N–H), 3036 (aromatic C–H), 1405 (amide C–N), 1657 (amide C=O), 1223 (C-O-C). ^{1}H NMR (DMSO-d_6) in δ (ppm): 9.78 (s, 2H, amide N–H), 5.15 (s, 4H, aromatic NH$_2$).

Synthesis of polyimides

Two-step method

To a stirred solution of diamine DA$_1$ (0.43 g, 1.24 mmol) in 10 mL DMAc, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (0.40 g, 1.24 mmol) was gradually added and the mixture was stirred at room temperature for 24 h under inert atmosphere of nitrogen to yield the precursor, poly(amic acid). The film was casted onto a glass plate by heating this solution of poly(amic acid) for 18 h at 80 °C, 2 h at 150 °C, 2 h at 200 °C, 2 h at 250 °C and 2 h at 280 °C, which converted the poly(amic acid) into polyimide film. The same procedure was adapted for the polymerization of diamine DA$_1$ with Pyromellitic dianhydride (PMDA) and diamine DA$_2$ with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and Pyromellitic dianhydride (PMDA).

One-step method

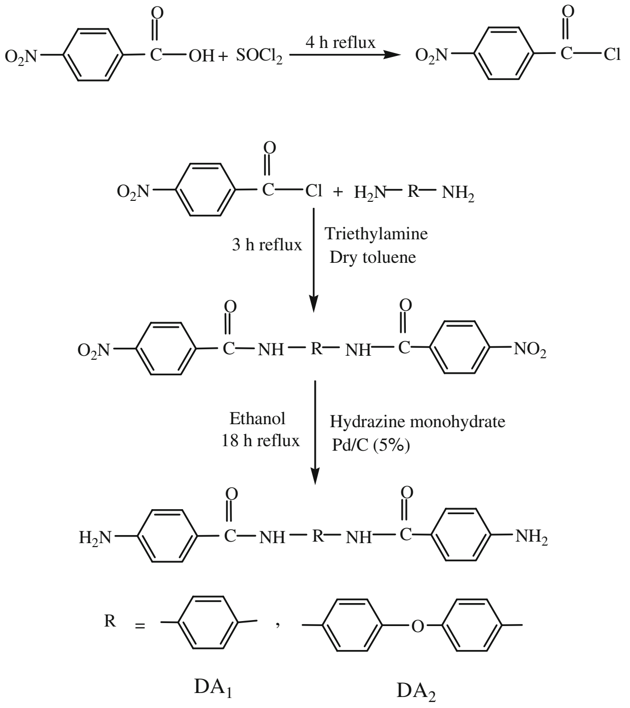
In a two-neck round bottom flask fitted with inlet and outlet of nitrogen gas, diamine DA$_1$ (0.43 g, 1.24 mmol), 3,4,9,10-Perylenetetracarboxylic acid dianhydride (PRDA) (0.48 g, 1.24 mmol), *m*-cresol (20 mL), and isoquinoline (1 mL) were added. The mixture was heated to 180–190 °C under nitrogen for 6 h and then cooled to room temperature. The resulting dark red solution was poured into 300 mL of acetone to obtain dark red solid, which was washed with sodium hydroxide (1 M) followed by water and dried in vacuum for 15 h. The polyimide from diamine DA$_2$ with 3,4,9,10-Perylenetetracarboxylic acid dianhydride (PRDA) was also prepared by the same procedure.

Three polyimides PAI$_1$, PAI$_2$, and PAI$_3$ were obtained from the synthesized diamine DA$_1$ and commercially available dianhydrides 3,3′,4,4-benzophenone tetracarboxylic dianhydride (BTDA), 1,2,4,5-benzene tetracarboxylic dianhydride (Pyromellitic dianhydride; PMDA), and 3,4,9,10-perylene tetracarboxylic dianhydride (PRDA), respectively, while the other three polyimides were prepared from the reactions of the dianhydrides with the synthesized diamine DA$_2$.

Results and discussion

Monomer synthesis and characterization

The diamine monomers were synthesized in two steps from *p*-nitrobenzoyl chloride and commercially available diamines; 1,4-phenylene diamine and 4,4′-diaminodiphenyl ether (Scheme 1). The dinitro species were formed in the first step by the nucleophilic substitution reaction under inert conditions. The observed values for carbon, hydrogen, and nitrogen of the dinitro compounds (N$_1$ and N$_2$) were found close to the calculated ones. Their structures were confirmed by their FTIR and ^{1}H NMR spectra. The FTIR spectra of N$_1$ and N$_2$ showed absorption bands of the asymmetric and symmetric nitro group stretching at 1545, 1350 cm^{-1} and 1538, 1349 cm^{-1}, respectively. These spectra also revealed the presence of amide linkage by corresponding peaks at 3316, 1644, and 1404 cm^{-1} in N$_1$ and at 3358 and 1650 and 1409 cm^{-1} in N$_2$ due to amide N–H, C=O, and C–N bonds, respectively. The difference in the spectra of the two dinitro species was the presence of a band due to ether linkage in the spectra of dinitro species N$_2$ at 1222 cm^{-1}. The ^{1}H NMR data of the synthesized dinitro compounds also verified their structures. The



Scheme 1 Synthesis of diamine monomers

presence of amide group was confirmed by the characteristic signals of amide N–H protons at 11.15 and 10.73 ppm (singlet) in N_1 and N_2, respectively. Moreover, the phenyl protons were indicated in both compounds by the appearance of their characteristic signals in the 7.0–9.0 ppm region.

The molecular structure of the dinitro compound (N_2) was also confirmed by X-ray crystal analysis (Fig. 1; Table 1). The analysis revealed that the asymmetric unit contained one molecule of dimethylacetamide having amide bonds in a *trans* orientation (torsion angles: C1–N1–C1–C34 179.38(13°) and C21–N2–C2–C44 −172.10(13°)) (Table 2). The planes of the aromatic rings formed dihedral angles in the range of 11.7–56.2°. The crystal packing showed that the molecules form centrosymmetric dimers connected by N–H···O hydrogen bonds (N2···O51 2.9255 (17) Å, N2–H2···O51 168.5(17°); N1···O2^{i} 2.8975(17) Å, N1–H1···O2^{i} 156.0(17°), symmetry operator (i) $2-x$, $2-y$, $2-z$).

The synthesized dinitro species were then reduced in the second step to diamine monomers using hydrazine monohydrate and 5% Pd–C in refluxing ethanol solvent. Their found values for carbon, hydrogen, and oxygen were in good agreement with the calculated ones and all the key structural features were identified by their FTIR and ^{1}H NMR spectra. The FTIR spectra of diamines DA_1 and DA_2 exhibited the characteristic peaks due to N–H, amide C=O, and C–N bonds at 3334, 1630, and 1403 cm^{-1} and 3320, 1657, and 1405 cm^{-1}, respectively. The absence of bands due to nitro group stretching (symmetric and asymmetric) confirmed the reduction of dinitro species. The presence of diaryl ether moiety in diamine DA_2 was verified by a band at 1223 cm^{-1}.

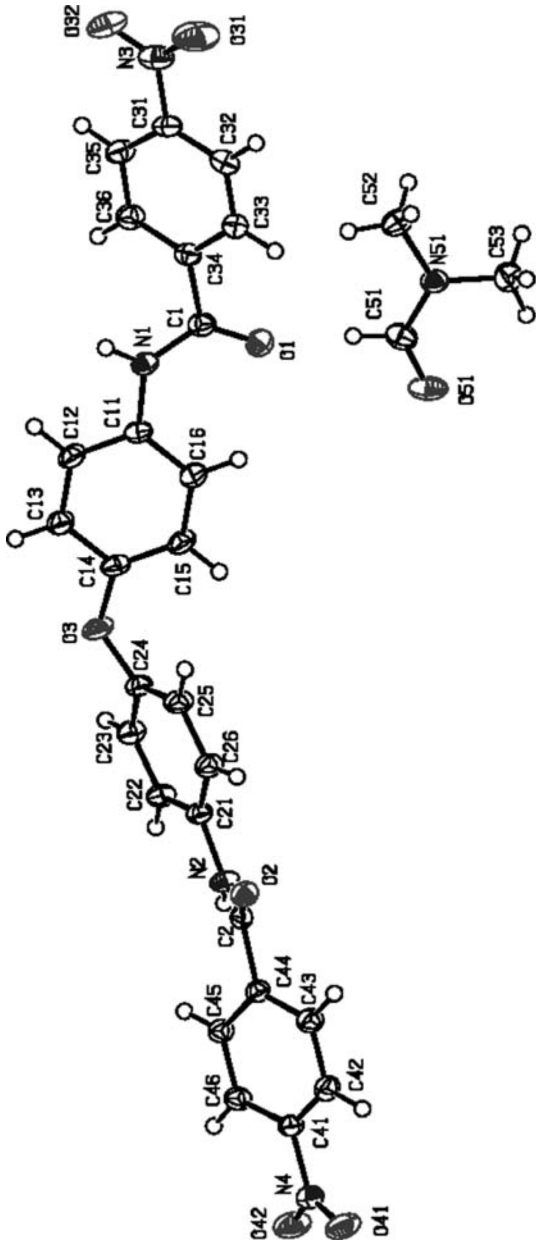


Fig. 1 An ORTEP drawing of N_2

The ^{1}H–NMR spectra confirmed the conversion of dinitro species to diamines DA_1 and DA_2 by the appearance of characteristic signals of aromatic NH_2 protons at 5.11 and 5.15 ppm, respectively. The presence of amide group was also indicated by signals of amide N–H protons at 10.64 and 9.78 ppm (singlet) in DA_1 and DA_2, respectively.

Table 1 Crystal data and structure refinement for N_2

Identification code	N_2
Empirical formula	$C_{29}H_{25}N_5O_8$
Formula weight	571.54
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions	$a = 10.0217(12)$ Å $\alpha = 103.659(9)°$ $b = 11.9476(14)$ Å $\beta = 107.952(9)°$ $c = 12.0195(13)$ Å $\gamma = 93.653(10)°$
Volume	1315.8(3) Å^3
Z	2
Density (calculated)	1.443 Mg/m^3
Absorption coefficient	0.107 mm^{-1}
$F(000)$	596
Crystal size	0.31 × 0.29 × 0.24 mm^3
Theta range for data collection	3.53°–25.72°
Index ranges	$-10 \le h \le 12, -14 \le k \le 14, -14 \le l \le 14$
Reflections collected	10140
Independent reflections	4899 [R(int) = 0.0265]
Completeness to theta = 25.00°	99.5%
Absorption correction	None
Max. and min. transmission	0.9747 and 0.9674
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4899/0/390
Goodness-of-fit on F^2	1.011
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0367$, w$R2 = 0.0919$
R indices (all data)	$R1 = 0.0502$, w$R2 = 0.0973$
Extinction coefficient	0.0093(14)
Largest diff. peak and hole	0.229 and −0.213 e Å^{-3}

Synthesis and characterization of the polyimides

Six different polyimides were synthesized from the reaction of amide linkage containing diamine monomers DA_1 and DA_2 with three different aromatic dianhydrides namely 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 1,2,4,5-benzene tetracarboxylic dianhydride (Pyromellitic dianhydride; PMDA), and 3,4,9,10-perylene tetracarboxylic dianhydride (PRDA). The polyimides from BTDA and PMDA were prepared by conventional two-step polymerization method which involves the ring-opening polyaddition resulting in the formation of polyamic acid, which is subsequently converted into polyimide by thermal cyclodehydration (Scheme 2a). On the other hand, the polyimides from perylene dianhydride (PRDA) were prepared by one-step method in a high boiling solvent (*m*-cresol) at 180–190 °C in the presence of a basic catalyst (isoquinoline) (Scheme 2b).

Table 2 Bond lengths (Å) and angles (°) for N_2

N(1)–C(1)	1.3599(19)
N(1)–C(11)	1.4218(18)
C(1)–O(1)	1.2276(19)
N(2)–C(2)–C(44)	115.83(12)
C(14)–O(3)–C(24)	123.46(12)
O(31)–N(3)–O(32)	123.74(14)
O(31)–N(3)–C(31)	118.30(15)
C(12)–C(11)–N(1)	116.25(13)
C(15)–C(14)–O(3)	125.09(14)
C(15)–C(14)–C(13)	120.46(13)
C(16)–C(15)–H(15)	120.0
C(22)–C(23)–C(24)	119.91(14)
C(22)–C(23)–H(23)	120.0
C(24)–C(23)–H(23)	120.0
C(25)–C(24)–C(23)	120.37(14)
C(25)–C(24)–O(3)	124.83(13)
C(23)–C(24)–O(3)	114.38(13)
C(35)–C(34)–C(33)	119.66(14)
C(35)–C(34)–C(1)	122.29(13)

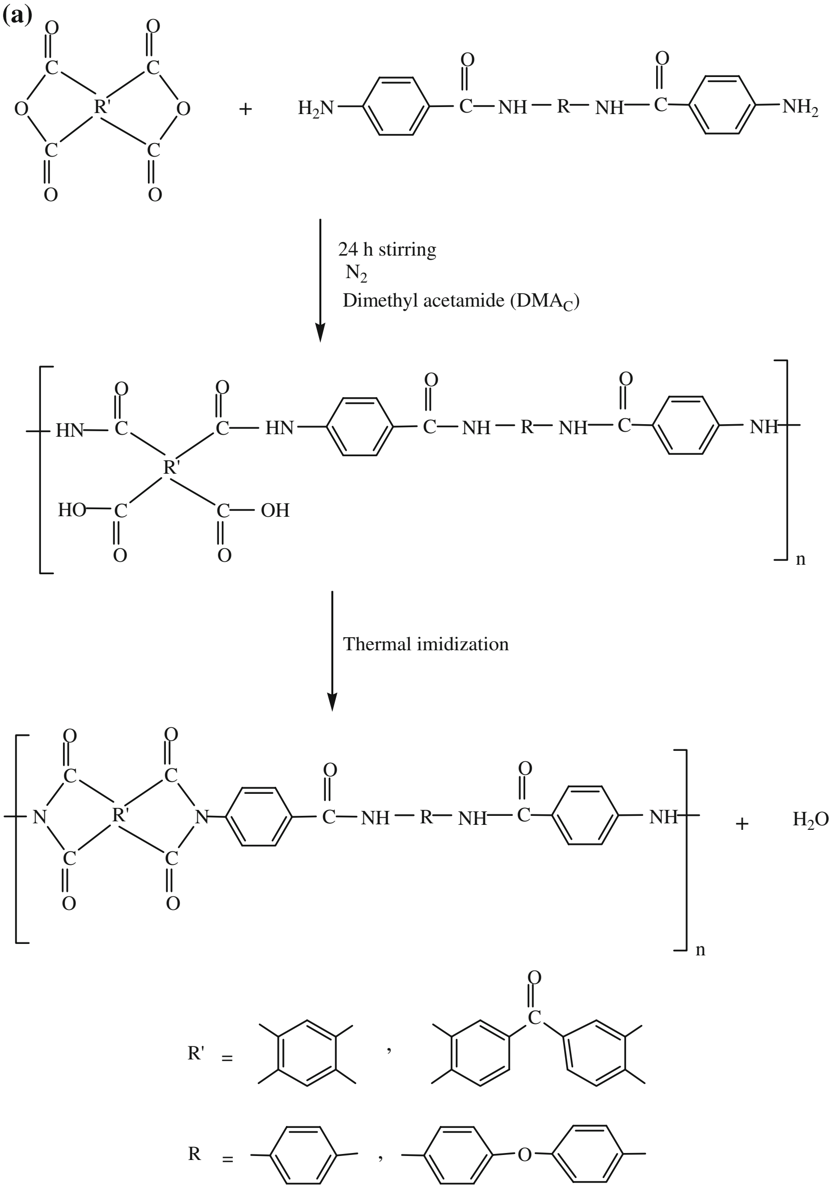
The elemental analyses data for the synthesized polyimides is given in Table 3. These results are in good agreement with the calculations based on the number of atoms in the polyimide repeat unit.

The FTIR spectra of polyamic acid precursors (obtained from two-step procedure) and synthesized polyimides provided evidence for the presence of all expected functional groups as listed in Table 4. The FTIR spectra of polyamic acids showed characteristic absorptions of carboxyl and amide group in the regions 1634–1630 and 3500–3000 cm^{-1}, respectively, while those of poly(amide–imide)s exhibited the characteristic peaks around 1785 and 1720 cm^{-1} (imide carbonyl asymmetric and symmetric stretch), 1380 cm^{-1} (C–N stretch), and 1100 and 730 cm^{-1}(imide ring deformation) along with the absorptions of amide carbonyl (around 1630 cm^{-1}).

Solubility and viscosity analysis of the polyimides

The solubilities of the synthesized polymers were tested by taking a little solid (0.1 g) per deciliter of solvent in a test tube and then subsequent heating. All these polyimides were found insoluble or partially soluble in the common solvents tested as shown in Table 5. The reason might be the compact aggregation of the polymer chains which occurred because the imidization was carried out at higher temperatures [33, 34]. Four of these polymers (PAI_1, PAI_2, PAI_4, and PAI_5) were soluble in H_2SO_4, which is a

Scheme 2 Synthesis of polyimides: **a** PAI_1, PAI_2, PAI_4, and PAI_5; **b** PAI_3 and PAI_6



commonly used solvent for most of the polyimides [35]. It is believed that the intermolecular hydrogen bonding in the polyimides is mainly responsible for their limited solubility [35] and the solubility is improved in the aggressive H_2SO_4 solvent because of its ability to overcome the hydrogen bonding. The polyimides PAI_3 and PAI_6 derived from perylene dianhydride (PRDA) were found insoluble even in H_2SO_4. The one-step procedure followed for the synthesis of these polyimides and/or the compact structure of PRDA having rigid phenyl rings may be responsible for this insolubility. Moreover, this inability to of the aggressive H_2SO_4 solvent to solubilize polymers PAI_3 and PAI_6 may also be attributed to their crystalline nature (Fig. 3), in agreement with the general rule that the solubility decreases with increasing crystallinity [36]. It is also reported that the presence of flexible units like –O– in the backbone helps to enhance the solubility of polymers [35] but the polymers PAI_4, PAI_5, and PAI_6 having ether linkage in the main chain did not show any improvement in their solubility. This may be due to the rigid phenyl groups around the ether moiety in the polyimide backbone.

Inherent viscosities of the soluble polyimides were measured in H_2SO_4 (0.1 g/dL) at 28 °C using Ostwald's Viscometer and the viscometric data were tabulated in Table 5. The viscosity of the synthesized polymers, which is a good criterion for estimation of molecular weight, was in the range 0.47–0.73 g/dL, reflecting moderate molecular weights of the polymers [37–39].

Scheme 2 continued

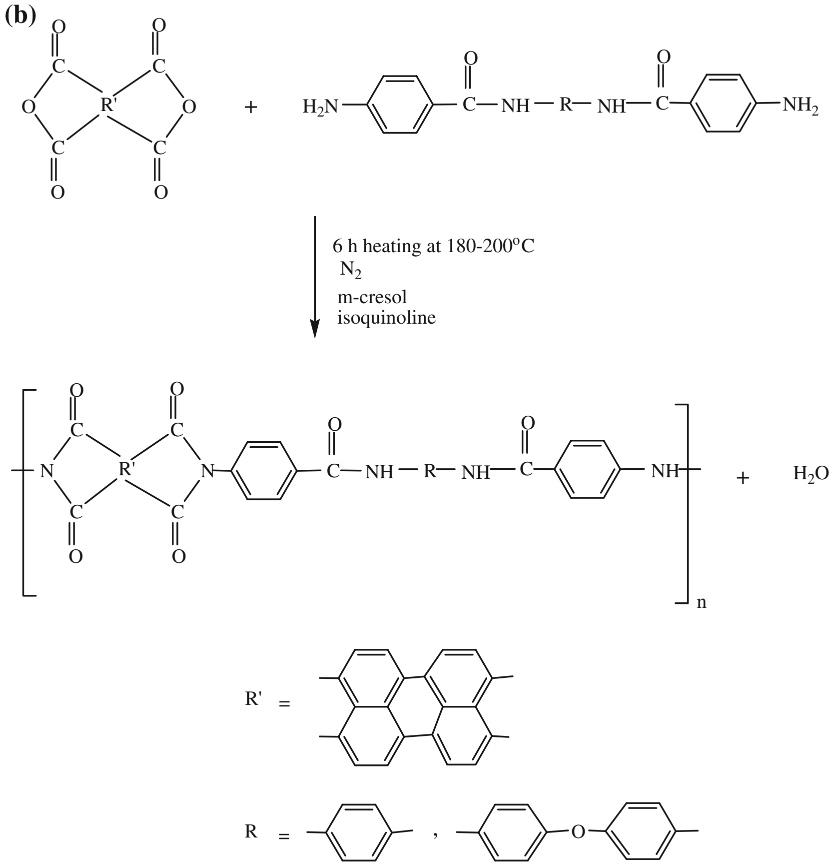


Table 3 Elemental analysis of the synthesized polyimides

Polyimide	Repeat unit (formula wt)	C		H		N	
		Calculated %	Found %	Calculated %	Found %	Calculated %	Found %
PAI_1	$C_{30}H_{16}N_4O_6$ (528)	68.18	68.27	3.03	3.22	10.60	10.55
PAI_2	$C_{37}H_{20}N_4O_7$ (632)	70.25	69.82	3.16	3.05	8.86	8.77
PAI_3	$C_{44}H_{22}N_4O_6$ (702)	75. 21	75.38	3.13	3.15	7.97	7.58
PAI_4	$C_{36}H_{20}N_4O_7$ (620)	69.67	68.91	3.22	3.27	9.03	9.15
PAI_5	$C_{43}H_{24}N_4O_8$ (724)	71.27	71.11	3.31	3.34	7.73	7.49
PAI_6	$C_{50}H_{26}N_4O_7$ (794)	75.56	74.90	3.27	3.18	7.05	7.20

All values are calculated on the basis of structure of repeat units

Table 4 FTIR (KBr pellets, cm^{-1}) analysis of the synthesized polyimides

Band assign	PAc_1	PAc_2	PAc_4	PAc_5	PAI_1	PAI_2	PAI_3	PAI_4	PAI_5	PAI_6
Ar. amide C=O	1632	1630	1633	1634	1640	1644	1638	1643	1637	1636
Ar. imideb C=O asym.	–	–	–	–	1779	1780	1781	1774	1779	1781
Ar. imide C=O sym.	–	–	–	–	1722	1726	1724	1726	1721	1719
C=O bend.	739	739	740	739	715	723	724	721	712	721
C–N str.	1379	1396	1398	1381	1376	1393	1399	1358	1375	1398
N–H str.	3014	3015	3014	3014	3050	3049	3130	3123	3203	3223
O–H str.	3464	3449	3456	3444	–	–	–	–	–	–
C–O–C str.	–	–	1240	1231	–	–	–	1234	1250	1234

Ar. aromatic, *asym* asymmetric stretching, *sym* symmetric stretching, *bend.* bending, *str.* stretching

Table 5 Solubility data and inherent viscosities of the synthesized polyimides

Polyimide	DCM	THF	Ethanol	Toluene	DMSO	DMF	DMAc	NMP	*m*-Cresol	H_2SO_4	$\eta_{inh\ (dL/g)}$[a]
PAI_1	−	−	−	−	+ −	+ −	−	+ −	−	++	0.73
PAI_2	−	−	−	−	+ −	−	−	+ −	−	++	0.47
PAI_3	−	−	−	−	+ −	−	−	+ −	−	+ −	−
PAI_4	−	−	−	−	+ −	+ −	+ −	+ −	−	++	0.56
PAI_5	−	−	−	−	+ −	−	−	+ −	−	++	0.49
PAI_6	−	−	−	−	+ −	−	−	+ −	−	+ −	−

++ (soluble at room temperature); + − (slightly soluble on heating); − (insoluble)

[a] Measured at a concentration of 0.1 g/dL in H_2SO_4 at 28 °C

Thermal analysis of polyimides

The thermal stability of the polymers was estimated from the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. The TGA thermograms of the synthesized polyimides are presented in Fig. 2 and thermal behaviour data are listed in Table 6.

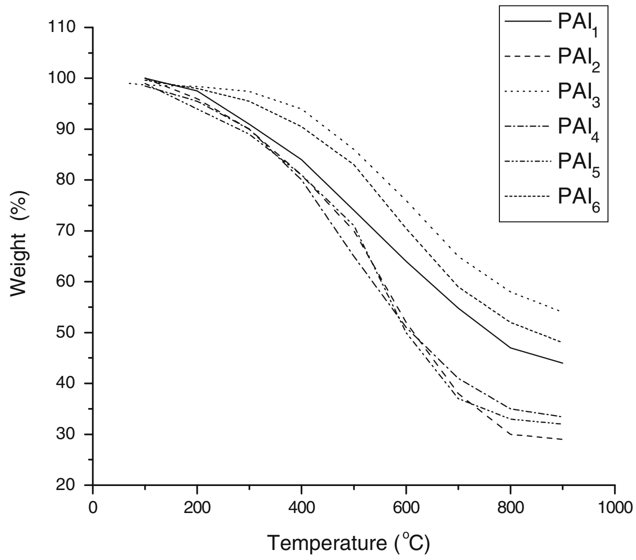


Fig. 2 TG thermograms of synthesized polyimides

Thermogravimetric analysis results showed no significant weight loss below 300 °C in nitrogen. The temperature at which maximum weight loss (T_{max}) occurs was observed at ~500 °C. The temperature at 10% weight loss (T_{10}) and maximum weight loss (T_{max}) of polyimides PAI_3 and PAI_6 derived from perylene tetracarboxylicacid dianhydride (PRDA) were higher as compared to others. This increase in thermal stability is attributed to the rigid and bulky nature of perylene unit which inhibits the rotation of the bonds resulting in an increase in chain stiffness [40–43]. All these polyimides showed no discernible Tgs on their DSC curves probably due to their rigid backbone with high aromaticity [44]. Residual weight at 600 °C was measured and found fairly high (range of 40–67.5%). The thermal degradation kinetic data for the synthesized polyimides was calculated from the TG curves and from those data activation energies of pyrolysis, entropy, and enthalpy values of the polymers were estimated by using Horowitz and Metzger method [45] as given in Table 6. All these values are high, exhibiting the excellent thermal stability of the polymers and could be attributed to the incorporation of imide units, performed amide groups,

Table 6 Thermal and kinetic studies of the polyimides

Polyimide	T_{10} (°C)	T_{max} (°C)	Activation energy of pyrolysis[a] (kJ mol^{-1})	Entropy[a] (kJ mol^{-1})	Enthalpy[a] (kJ mol^{-1})	R_{800} (%)
PAI_1	320	545	58.56	0.31	56.75	47.15
PAI_2	300	540	57.53	0.31	55.70	31.00
PAI_3	480	630	62.07	0.35	60.25	57.30
PAI_4	300	500	56.30	0.27	54.48	36.15
PAI_5	290	530	53.93	0.25	52.10	33.25
PAI_6	440	580	60.33	0.33	58.50	52.50

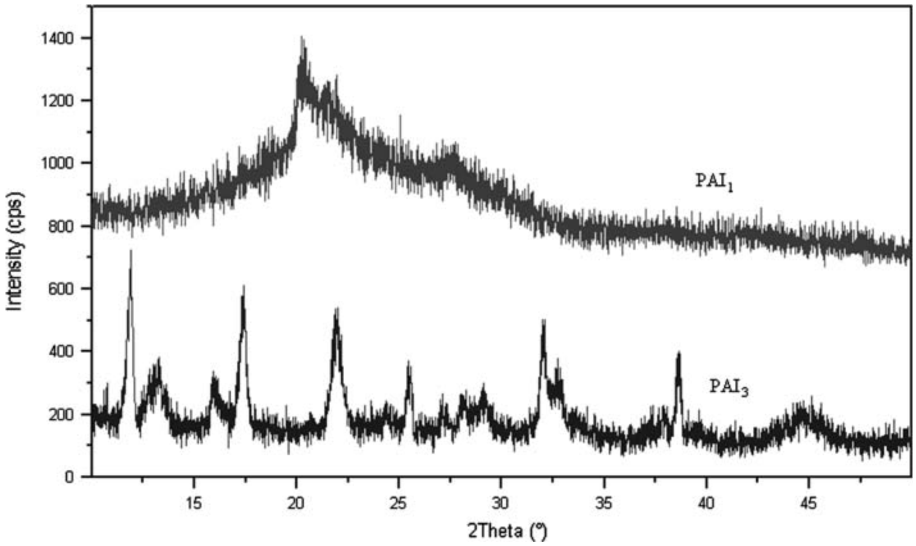
T_{10} = Temperature at 10% weight loss

T_{max} = Temperature at maximum weight loss

R_{800} = Residual weight at 800 °C

[a] Calculated by Horowitz and Metzger method using the data obtained from TG curves

Fig. 3 Wide-angle X-ray diffractograms of PAI_1 and PAI_3



phenylation of the backbone and avoid of any weak linkages [46, 47].

XRD analysis of the polyimides

Morphological information of the poly(amide–imide)s was obtained from their wide-angle X-ray diffraction pattern in the region of $2\theta = 0$–50° at room temperature. The representative X-ray diffractograms of polyimides are shown in Fig. 3. The sharp peak patterns of diffractograms of PAI_3 and PAI_6 exhibited that these are of considerable crystallinity. The rest of the polymers were amorphous as revealed by the diffused pattern in their diffractograms. This is probably due to the fact that polymers PAI_3 and PAI_6 were formed by the one-step chemical imidization method. This is in consistent with the reported fact that the degree of crystallinity of polyimides depends on the imidization methods and the imidization of the polyamic acid in solution form allows it to obtain a more favorable conformation for packing [44].

Conclusion

Two novel diamines containing amide group were successfully prepared in good yield and high purity, and polymerized with three different commercially available dianhydrides via conventional two-step thermal procedure or one-step chemical method. The diamine monomers and dinitro species were characterized by their physical properties, elemental analysis, FT-IR, and ^{1}H–NMR spectral analysis, while the poly(amide–imide)s were characterized by FT-IR, XRD, viscosity, and thermal analyses. The synthesized polymers had very limited solubility in the tested solvents and some of these were crystalline in nature. The thermal analyses (TG and DSC) of the polymers were performed and the thermal degradation kinetic studies were carried out on the basis of these analyses using Horowitz and Metzger method. The insolubility of the synthesized polyimides in the common solvents and their excellent thermal stability suggested that these polymers can be utilized in applications where severe conditions, like elevated temperatures and solvent resistance, are required.

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