

Synthesis and Properties of New Poly(amide-imide)s Based on 1,3-Bis[4,4'-(trimellitimido) phenoxy] Propane and Aromatic Diamines

Hossein Nasr Isfahani,¹ Khalil Faghihi,² Nasim Valikhani²

¹Faculty of Chemistry, Shahrood University of Technology, Shahrood, Iran

²Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak 38156, Iran

Received 6 August 2008; accepted 5 April 2009

DOI 10.1002/app.30674

Published online 6 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Six new poly(amide-imide)s **8a–f** containing trimethylene moiety in the main chain were synthesized by the polycondensation reactions of 1,3-bis[4,4'-(trimellitimido) phenoxy] propane **6** with six different aromatic diamines **7a–f** in a medium constituting *N*-methyl-2-pyrrolidone, triphenylphosphite, CaCl₂, and pyridine as condensing agents. The polycondensation reaction produced a series of novel poly(amide-imide)s **8a–f** in high yields with inherent viscosities between 0.35 and 0.63 dL/g. The resulting poly(amide-imide)s were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility tests, and FTIR spectroscopy. 1,3-Bis[4,4'-(trimellitimido) phenoxy] propane **6** as a new monomer containing trimethylene

moiety was synthesized using a three-step reaction. At first 1,3-bis[4,4'-nitrophenoxy] propane **3** was prepared by the reaction of 4-nitrophenol **1** with 1,3-dibromo propane **2** in DMF solution. Then, dinitro **3** was reduced to 1,3-bis[4,4'-aminophenoxy] propane **4** by using a solution of sodium sulfite in ethanol. Finally, 1,3-bis[4,4'-(trimellitimido) phenoxy] propane **6** was prepared by the reaction of one equivalent diamine **4** with two equivalents of trimellitic anhydride **5** in a mixture of acetic acid-pyridine (3 : 2). © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3293–3299, 2010

Key words: Poly(amide-imide)s; direct polycondensation; aromatic diamines; trimethylene moiety

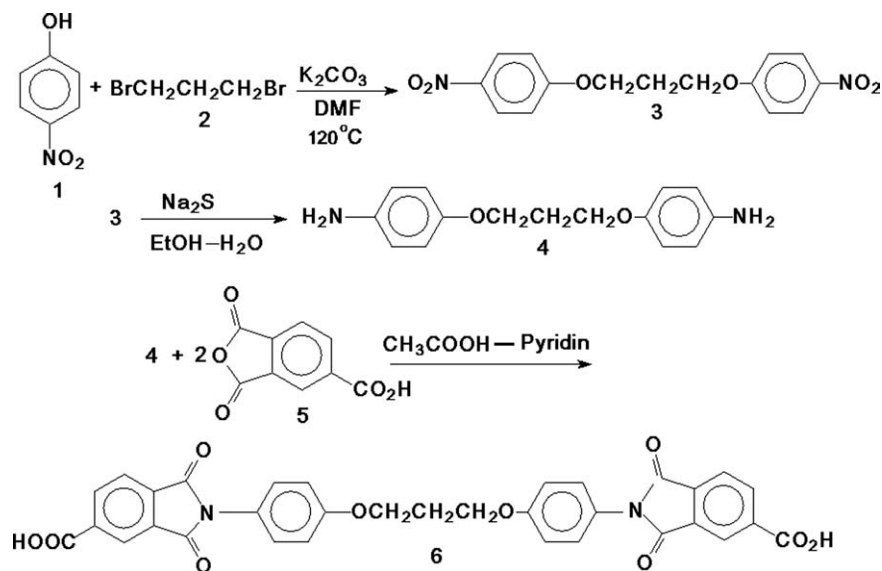
INTRODUCTION

Aromatic polyimides are one of the most important class of thermally stable polymers,^{1–3} which are well known for their high-performance properties but they have one major disadvantage of typically being insoluble and unprocessable after conversion from the poly(amic-acid) to the polyimide form. Replacement of polyimides by copolyimides, such as poly(amide-imide)s (PAIs), may be useful in modifying the intractable nature of polyimides. PAIs contain both amide and cyclic imide units along the polymer chain and hence constitute a polymer class with average properties between aromatic polyamides and polyimides. This class of polymers seems to provide a favorable balance between processability and performance.^{4–7} PAIs can be synthesized readily by general synthetic methods similar to those for both aromatic polyamides and polyimides. Various approaches have been carried out successfully in the synthesis of PAIs.⁸ One of the most convenient and efficient synthesis of high-molecular-weight PAIs is

the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines by Yamazaki-Higashi phosphorylation technique.⁹ The direct polycondensation route is a very useful laboratory method and avoids using moisture-sensitive acid chlorides or isocyanates.^{10–12} Also, the properties of PAIs can be readily modified by the incorporation of different segments such as flexible linkages [–O–, –SO₂–, –(CH₂)_{*n*}–, –C(CF₃–)₂], bulky pendent groups (such as *t*-butyl, adamantyle, and naphthyl), large pendent groups, or polar constituents such as heterocyclic segments into the polymer backbone due to the altering crystallinity and intermolecular interactions. If the flexible segments are carefully chosen, it is possible to promote solubility without affecting the thermal and mechanical properties to a great extent.^{13–21} In our previous articles, we described the synthesis of different polyamides and PAIs containing heterocyclic moieties in the main chain such as hydantoin derivatives and pyridyl moiety with improved solubility and thermal properties.^{22–28}

In this article, we describe the synthesis and characterization of a new series of PAIs **8a–f** containing trimethylene segments between imide rings in the main chain from the direct polycondensation reaction of 1,3-bis[4,4'-(trimellitimido) phenoxy] propane

Correspondence to: K. Faghihi (k-faghihi@araku.ac.ir).



Scheme 1 Synthetic route of 1,3-bis[4,4'-(trimellitimido) phenoxy] propane 6.

6 with six different aromatic diamines 7a–f in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), triphenyl phosphite, calcium chloride, and pyridine.

EXPERIMENTAL

Materials

All chemicals were purchased from Merck Chemical Company (Germany) and Alderich Chemical Company (USA).

Techniques

$^1\text{H-NMR}$ spectra were recorded on a Bruker 500-MHz instrument. Fourier transform infrared (FTIR) spectra were recorded on a Galaxy (England) FTIR 5000 spectrophotometer. Spectra of the solids were taken with KBr pellets. Vibrational transition frequencies were reported as wave numbers (cm^{-1}). The band intensities were designated as weak (w), medium (m), shoulder (sh), strong (s), or broad (br). The inherent viscosities were measured by a standard procedure with a Technico viscometer. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) data for polymers were taken on a Mettler TA4000 system under an N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Elemental analyses were performed by Arak Petrochemical (Arak, Iran).

Monomer synthesis

1,3-Bis[4,4'-(trimellitimido) phenoxy] propane 6

Diacid 6 was prepared according to a typical procedure that is shown in Scheme 1.

1,3-Bis[4-nitrophenoxy] propane 3

To a 100-mL round-bottomed flask, 4-nitrophenol 1 (6.00 g, 43.11 mmol) and dry K_2CO_3 (2.97 g, 21.55 mmol) in 30 mL dimethyl formamide (DMF) were added. Then, a solution of 1,3-dibromo propane 2 (4.17 g, 20.67 mmol) in 5 mL dry dimethyl formamide was added dropwise to the reaction mixture. The reaction mixture was heated for 6 h at 120°C , then cooled and poured onto crushed ice. The precipitated yellow product was collected by filtration, dissolved in CH_2Cl_2 , and washed successively with NaOH (2M), HCl (1M), and water. The CH_2Cl_2 solution was then dried over Na_2SO_4 and concentrated in vacuum and the product was recrystallized from ethanol, affording 2.33 g (35.5%) of yellow solid 3. mp: $134\text{--}135^\circ\text{C}$, FTIR (KBr, cm^{-1}): 3092 (w), 2962 (w), 2833 (w), 1604 (s,sh), 1504 (s, sh), 1469 (m), 1340 (s, sh), 1259 (s), 1172 (m), 1111 (s), 1053 (m), 966 (m), 841 (s), 752 (m), 688 (m), 650 (m), 534 (w), 499 (w). Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_6$: C, 56.6%; H, 4.4%; N, 8.8%. Found: C, 56.2%; H, 4.5%; N, 8.3%.

1,3-Bis [4-aminophenoxy] propane 4

To a 100-mL round-bottomed flask, 1,3-bis[4-nitrophenoxy] propane 3 (1.00 g, 3.10 mmol) and 4.90 g of sodium sulfide in a mixture of 150 mL of ethanol and 30 mL of water were added. The reaction mixture was refluxed for 10 h. After the removal of the solvents by evaporation, the residue was washed with water and dried under vacuum until 0.32 g (39.5%) of yellow solid was obtained. mp: $109\text{--}112^\circ\text{C}$, FTIR (KBr, cm^{-1}): 3391 (m), 3304 (w), 2958 (w), 2885 (w), 1620 (w), 1512 (s), 1471 (m), 1381 (w), 1336 (w), 1296 (w), 1240 (s), 1170 (w), 1101 (w), 1062

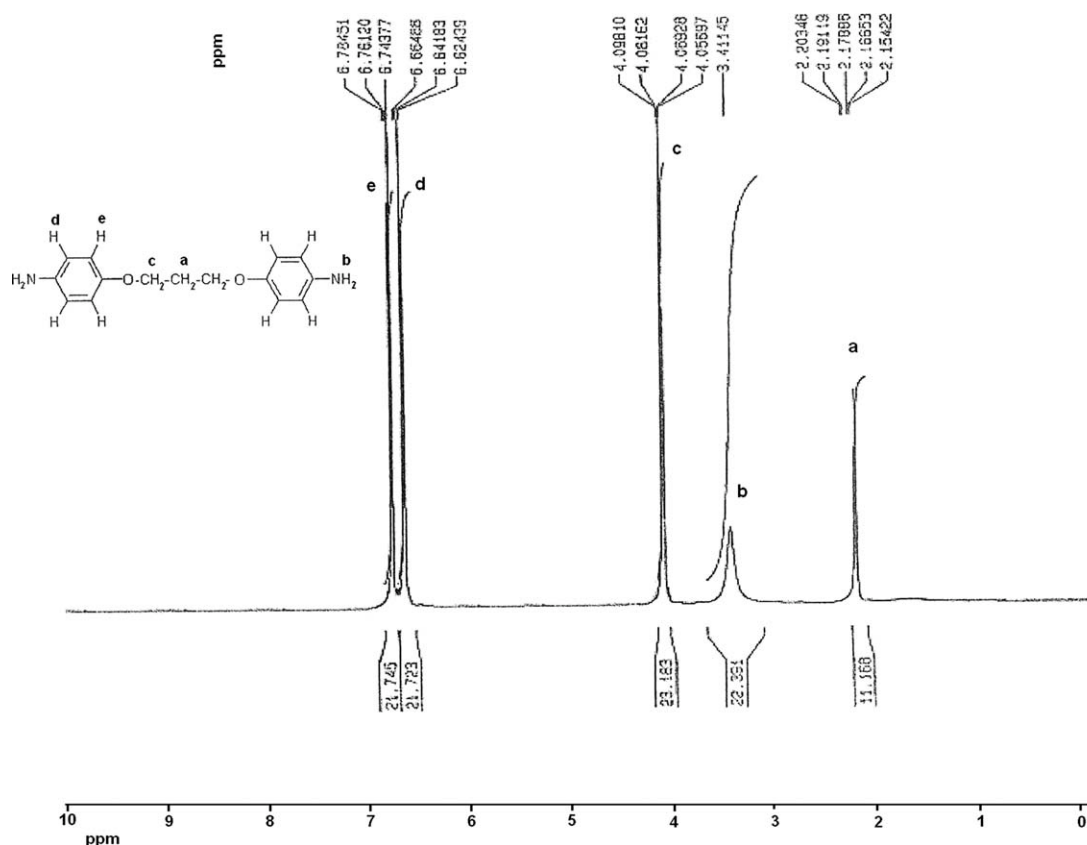


Figure 1 $^1\text{H-NMR}$ spectrum of diamine 4.

(m), 997 (m), 972 (m), 825 (s), 723 (m), 690 (w), 520 (w). $^1\text{H-NMR}$ [CDCl_3]: 2.15–2.20 (m, 2H), 3.41 (br, 2H), 4.05–4.09 (t, 4H), 6.62–6.66 (d, 4H), 6.74–6.78 (d, 4H) ppm. Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$: C, 69.7%; H, 6.9%; N, 10.8%. Found: C, 69.3%; H, 6.5%; N, 10.3%.

1,3-Bis [4,4'-(trimellitimido) phenoxy] propane 6

To a 100-mL round-bottomed flask, 1,3-bis[4-amino-phenoxy] propane 4 (0.30 g, 1.16 mmol) and trimellitic anhydride 5 (0.44 g, 2.32 mmol) in a 10 mL mixture of acetic acid and pyridine (3 : 2 V/V) were added. The reaction mixture was stirred overnight at room temperature and was refluxed for 4 h. Then, the residue was dissolved in 12 mL of cold water, and 0.50 mL of concentrated HCl was added. The green precipitate formed, then it was filtered off and dried to give 0.66 g (93.6%) of diacid 6. mp: 330–331°C, FTIR (KBr, cm^{-1}): 2540–3113 (m,br), 1782 (w), 1720 (s), 1610 (w), 1514 (s), 1419 (w), 1384 (m), 1300 (m), 1238 (m, sh), 1172 (m), 1122 (m), 1095 (m), 1053 (w), 935 (w), 864 (w), 835 (w), 794 (w), 729 (s), 607 (w), 526 (m). $^1\text{H-NMR}$ [DMSO-d_6]: 2.23 (m, 2H), 4.20–4.22 (t, 4H), 7.09–7.11 (d, 4H), 7.34–7.36 (d, 4H), 8.02–8.04 (d, 2H), 8.26 (s, 2H), 8.37–8.39 (d, 2H), 13.5 (s, 2H) ppm. Anal. Calcd. for $\text{C}_{33}\text{H}_{22}\text{N}_2\text{O}_{10}$: C, 65.3%; H, 3.6%; N, 4.6%. Found: C, 65.1%; H, 3.2%; N, 4.4%.

Polymer synthesis

The PAIs **8a–f** were prepared by the following general procedure (**7e** is used as an example). To a 50-mL round-bottomed flask, which was fitted with a stirring bar, bis(3-aminophenyl) sulfone **7e** (0.08 g, 0.32 mmol), diacid **6** (0.19 g, 0.32 mmol), calcium chloride (0.10 g, 0.90 mmol), triphenyl phosphite (TPP) (0.84 mL, 3.00 mmol), pyridine (0.20 mL), and NMP (1.0 mL) were placed. This mixture was heated under reflux on an oil bath at 60°C for 1 h, then at 90°C for 2 h and 130°C for 8 h. The reaction mixture was cooled at room temperature and then the reaction mixture was poured into 25 mL of methanol. The precipitated polymer **8e** was collected by filtration and washed thoroughly with methanol and dried at 80°C for 12 h under vacuum. 0.24 g (90.0 %) of solid polymer was produced.

RESULTS AND DISCUSSION

Monomer synthesis

1,3-Bis[4,4'-(trimellitimido) phenoxy] propane **6** was prepared in a three-step reaction sequence, as shown in Scheme 1.

Compound **6** was synthesized by the condensation reaction of 1 equivalent of diamine **4** with 2

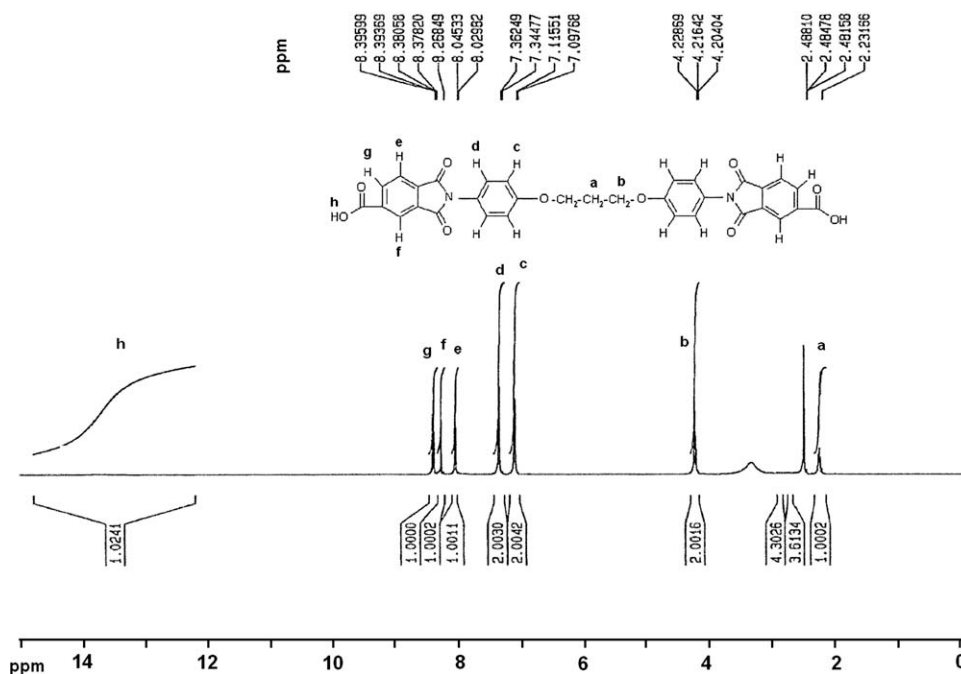
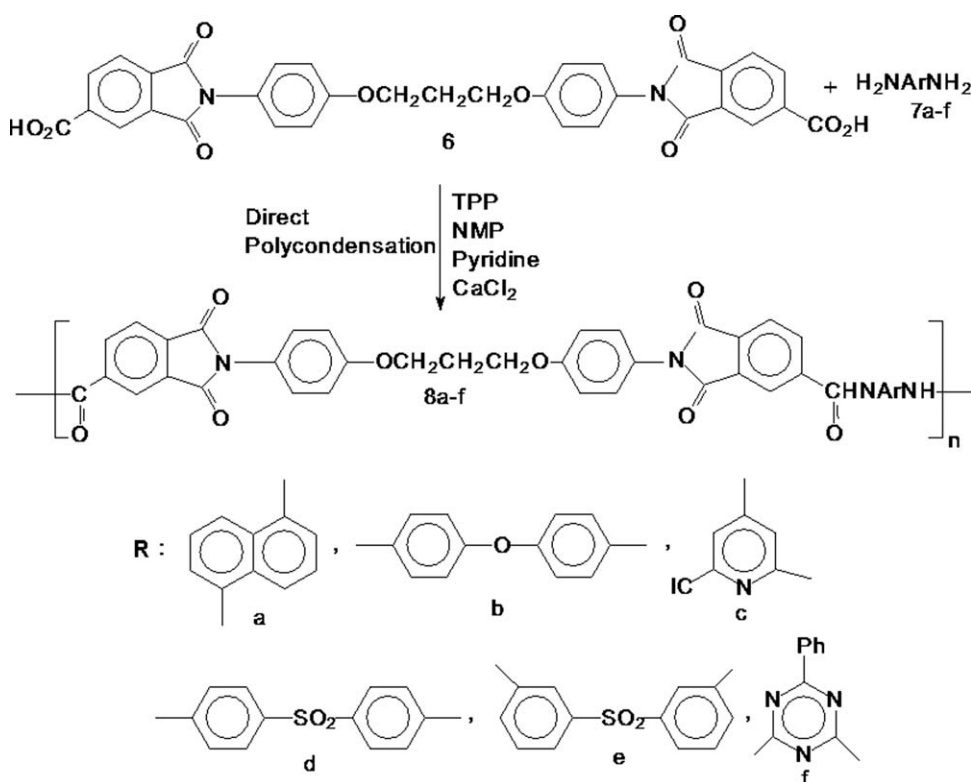


Figure 2 ¹H-NMR spectrum of diacid 6.

equivalents of trimellitic anhydride 5 in a mixture of acetic acid and pyridine (3 : 2). Dissolving the residue in cold water produced a gummy solid, which provided a green solid with the addition of concentrated HCl. The chemical structure and purity of dia-

mine 4 and diacid 6 were proved by elemental analysis, FTIR, and ¹H-NMR spectroscopy techniques. The FTIR spectrum of compound 4 showed two peaks at 3304–3391 cm⁻¹, which were assigned to the NH₂ groups. Also, the absorptions found at



Scheme 2 Synthetic route of poly(amide-imide)s 8a-f.

1062–1296 cm^{-1} were assigned to the vibration of the C–O band. The $^1\text{H-NMR}$ spectrum of compound **4** showed a multiple peak between 2.15 and 2.20 ppm, which was assigned to the H_a protons of the methylene group. A broad peak at 3.41 ppm was assigned to H_b protons of the NH_2 groups. The triplet peak between 4.05 and 4.09 ppm was assigned to H_c protons of the two similar methylene groups ($\text{CH}_2\text{—O}$). Finally, two doublet peaks between 6.62 and 6.66 and 6.74 and 6.78 ppm were assigned to the H_d and H_e protons of the phenyl rings, respectively (Fig. 1).

The FTIR spectrum of compound **6** showed a broad peak between 2540 and 3113 cm^{-1} , which was assigned to the COOH groups. Also, the absorptions found at 1720 and 1782 cm^{-1} were assigned to carbonyl function of imide rings (symmetric and asymmetric stretching) and carboxy groups. The $^1\text{H-NMR}$ spectrum of compound **4** also showed one multiple peak at 2.33 ppm, which was assigned to the H_a protons of the methylene group. The triplet peak between 4.20 and 4.22 ppm was assigned to H_b protons of the two similar methylene groups (OCH_2). Also two doublet peaks between 7.09 and 7.11 and 7.34 and 7.36 ppm were assigned to the H_c and H_d protons of the phenyl rings, respectively. Peaks between 8.02 and 8.04 and 8.37 and 8.39 ppm (two doublets) were assigned to the H_e and H_f protons of the imide rings, respectively. The singlet peak at 8.26 ppm was assigned to H_g protons of the imide rings. Finally, a broad peak at 13.5 ppm was assigned to H_h protons of the COOH groups (Fig. 2).

Polymer synthesis

PAIs **8a–f** were synthesized by the direct polycondensation reactions of an equimolar mixture of **6** with six different aromatic diamines **7a–f** with NMP, TPP, and pyridine as condensing agents (Scheme 2). The syntheses and some physical properties of these PAIs **8a–f** are given in Table I.

Polymer characterization

The synthesis and some physical properties of PAIs **8a–f** are summarized in Table I. All the poly-

TABLE I
Synthesis and Some Physical Properties of polyamides **8a–f**

Diamines	Polymer	Yield (%)	$\eta_{\text{inh}}(\text{dL/g})^a$
7a	8a	82	0.45
7b	8b	72	0.42
7c	8c	75	0.40
7d	8d	90	0.45
7e	8e	90	0.63
7f	8f	89	0.30

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

TABLE II
Elemental Analysis of PAIs **8a–f**

Polymer	Formula		C%	H%	N%
8a	$\text{C}_{43}\text{H}_{28}\text{N}_4\text{O}_8$	Calc.	70.8	3.8	7.6
	$(728.55)_n$	Found	70.0	3.1	7.0
8b	$\text{C}_{45}\text{H}_{30}\text{N}_4\text{O}_9$	Calc.	70.1	3.8	7.2
	$(770.59)_n$	Found	69.7	3.0	7.0
8c	$\text{C}_{37}\text{H}_{23}\text{N}_6\text{O}_{10}\text{Cl}$	Calc.	62.1	3.2	11.7
	$(714.88)_n$	Found	61.5	3.0	10.9
8d	$\text{C}_{45}\text{H}_{30}\text{N}_4\text{SO}_{10}$	Calc.	66.0	3.6	6.8
	$(818.66)_n$	Found	65.0	3.2	5.9
8e	$\text{C}_{45}\text{H}_{30}\text{N}_4\text{SO}_{10}$	Calc.	66.0	3.6	6.8
	$(818.66)_n$	Found	65.2	3.1	6.0
8f	$\text{C}_{42}\text{H}_{27}\text{N}_7\text{O}_8$	Calc.	66.5	3.5	12.9
	$(757.56)_n$	Found	65.9	3.1	12.0

condensations proceeded in a homogeneous, transparent, and viscous solution throughout the reaction, and the resulting PAIs were isolated as fibers or powders with almost quantitative yield (70–90%). These polymers have inherent viscosities between 0.35 and 0.63 dL/g and were white to cream crystal. Inherent viscosities were measured in DMF at a concentration of 0.5 g/dL at 25°C.

The resulting polymers were confirmed to be PAIs with FTIR spectroscopy and elemental analyses (Table II). The FTIR spectrum of these polymers had absorption bands between 1780 and 1709 cm^{-1} due to imide and amide carbonyl groups. Also a medium peak at 3308 cm^{-1} was assigned to the –NH groups (Appendix).

The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table II).

The solubilities of the poly (amide-imide)s **8a–f** were investigated with 0.01 g polymeric samples in 2 mL of a solvent. All of the polymers are soluble in organic solvents such as DMF, DMAc, DMSO, and NMP at room temperature and are insoluble in solvents such as methanol, ethanol, chloroform, THF, and water.

TABLE III
Thermal Behavior of PAIs **8a–f**

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield ^c (%)
8a	290–295	305–310	25
8b	260–265	370–375	47
8c	260–265	345–350	55
8d	385–390	390–395	52
8e	375–380	390–395	38
8f	290–295	330–335	56

^{a,b} Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N_2 , respectively.

^c Percentage weight of material left undecomposed after TGA analysis 600°C.

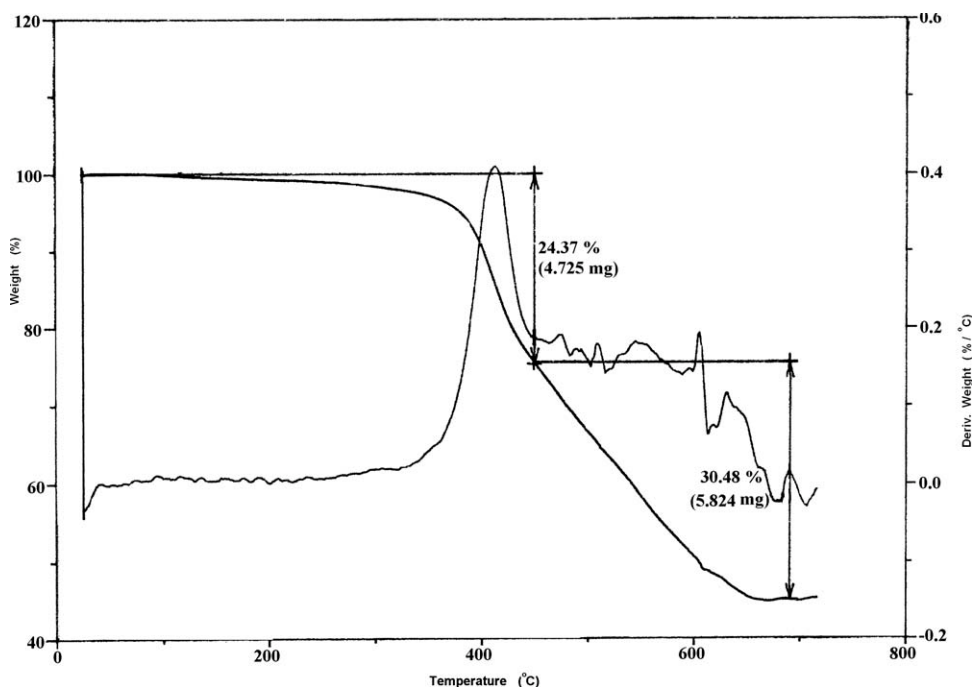


Figure 3 TGA and DTG thermogram of PAIs 8d.

Thermal properties

The thermal properties of PAIs 8a–f were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}/\text{min}^{-1}$, and the thermal data are summarized in Table III (Fig. 3). The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600°C for them are summarized in Table III. These polymers exhibited good resistance to thermal decomposition, up to 260 – 385°C in nitrogen, and began to decompose gradually above that temperature. T_5 for them ranged from 260 to 385°C and T_{10} ranged from 305 to 390°C , and the residual weight for these polymers at 600°C ranged from 25 to 56% in nitrogen. Results show that PAIs 8d and 8f containing sulfone moiety have higher thermal stability when compared with other polymers because they have a rigid structure such as sulfone moiety in the main chain.

CONCLUSIONS

This work involved the syntheses of several new PAIs 8a–f by direct polycondensation reactions of diacid 6 with six different aromatic diamines 7a–f by using NMP, TPP, and pyridine as condensing agents. These PAIs were soluble in various organic solvents and had good thermal stability. These properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics.

APPENDIX 1

The polyamides 8a–f analyses using FTIR

Polymer 8a, FTIR (KBr):

3211 (m), 2879 (w), 1934 (m), 1712 (s), 1651 (m), 1512 (s), 1381 (m), 1246 (m), 1170 (m), 1093 (m), 725 (m).

Polymer 8b, FTIR (KBr):

3308 (m), 3115 (w), 3013 (w), 2957 (w), 1709 (s, sh), 1656 (s), 1604 (m), 1512 (s, sh), 1402 (s), 1234 (s), 1101 (m), 827 (m), 727 (m).

Polymer 8c, FTIR (KBr):

3396 (m), 3067 (w), 2966 (w), 2883 (w), 1722 (s), 1610 (w), 1512 (s), 1384 (s), 1246 (s), 1097 (s), 937 (m), 727 (m).

Polymer 8d, FTIR (KBr):

3352 (m), 3111 (w), 2947 (w), 2872 (w), 1714 (s), 1591 (m), 1512 (s), 1384 (m), 1315 (m), 1248 (s), 1107 (m), 827 (m), 725 (m), 569 (m).

Polymer 8e, FTIR (KBr):

3329 (m), 3113 (w), 2955 (w), 2872 (w), 1720 (s, sh), 1656 (s), 1512 (s), 1384 (s), 1315 (m), 1244 (s), 1120 (s), 821 (m).

Polymer 8f, FTIR (KBr):

3400 (m), 3068 (w), 2947 (w), 2330 (w), 1722 (s, sh), 1591 (m), 1489 (s), 1384 (s), 1215 (s, br), 1097 (s), 935 (m), 727 (m).

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