

Synthesis and Characterization of New Polyamides Containing *p*-Phenylenediacryloyl Moieties in the Main Chain

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ABSTRACT: Six new polyamides **8a–f** containing *p*-phenylenediacryloyl moieties in the main chain were prepared by the direct polycondensation reaction of bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid **6** with 1,4-diphenylene diamine **7a**, 1,3-diamino toluene **7b**, 1,5-diamino naphthalene **7c**, 4,4'-diamino diphenyl ether **7d**, 4,4'-diamino diphenyl sulfone **7e**, and 3,3'-diamino diphenylsulfone **7f** by using thionyl chloride, *N*-methyl-2-pyrrolidone, and pyridine as condensing agents. These new polymers **8a–f** were obtained in high yield and inherent viscosity between 0.35–0.65 dL/g. The resulting polyamides were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test, FTIR and UV-vis spectroscopy. Diacid acid **6** as a new monomer con-

taining *p*-phenylenediacryloyl moiety was synthesized by using a three-step reaction. First, *p*-phenylenediacrylic acid **3** was prepared by reaction of terephthal aldehyde **1** with malonic acid **2** in the presence of pyridine, then diacid **3** was converted to *p*-phenylenediacryloyl chloride **4** by reaction with thionyl chloride. Finally, bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid **6** was prepared by the condensation reaction of phenylenediacryloyl chloride **4** with *p*-aminobenzoic acid **5**. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1136–1141, 2008

Key words: polyamides; *p*-phenylenediacryloyl moieties; bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid; aromatic diamine

INTRODUCTION

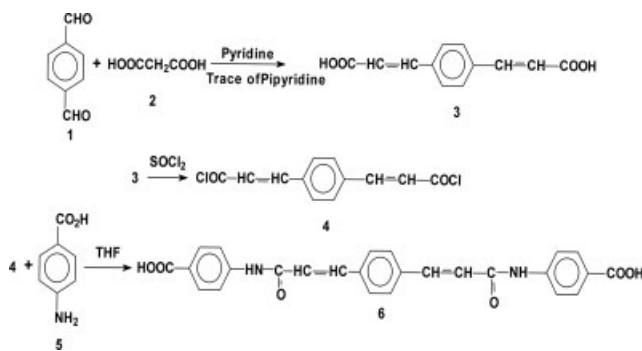
Thermally stable polymers have been received extensive interest in recent decades because of increasing demands for high-temperature polymers as a replacement for metals or ceramics in automotive, aerospace, and microelectronic industries.^{1–4} Aromatic polyamides are certainly one of the most successful classes of high-temperature polymers, and have found extensive use in the aviation, automotive, and electronic industries.^{5–7} However, these polymers encounter processing difficulties because of their infusibility and poor solubility in organic solvents.^{4,8} Therefore, much research has been focused on maintaining considerable thermal stability and improving their solubility. These studies include the following: (1) introducing rather soft segments on the main chain such as methylene and vinyl segments; (2) breaking its symmetry and regularity, thereby making crystallization impossible; (3) introducing the bulky side groups to be exempt from crystallization; and (4) destroying the hydrogen

bonding by *N*-substitution with certain groups such as methyl.^{9–18}

The conventional method for synthesis of polyamides begins with having diamine reaction with a diacid chloride monomer by low-temperature solution polycondensation. In another method, Yamazaki et al. reported a direct polycondensation reaction for synthesis of aromatic polyamides. According to their investigation, this procedure could obtain a high yield of polymers at a high-molecular weight.^{19,20}

In this article, we used Yamazaki method for synthesis of a series of novel polyamides containing *p*-phenylenediacryloyl moieties from the direct polycondensation reaction of bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid **6** with six different aromatic diamine **7a–f** by use of thionyl chloride, *N*-methyl-2-pyrrolidone, and pyridine as condensing agents. These polymers have a soft segment such as vinyl moiety in main chain for improving solubility in organic solvents in comparison with aromatic polyamides. On the other hand, there is a considerable attention for synthesizing polymers containing *p*-phenylenediacryloyl moiety in the main chain, so that they can be used for preparing photosensitive liquid crystalline polymers. There are some reported articles about synthesis of polyester, polyimides, polyamides and poly(amid-co-imide)s containing *p*-phenylenediacryloyl moiety in the main chain.^{21–24}

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Scheme 1 Synthesis route of diacid 6.

EXPERIMENTAL

Materials

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

Techniques

^1H NMR spectra were recorded on a Bruker 500 MHz instrument. UV-vis absorptions were recorded at 25°C in the 200–700 nm spectral region with a Perkin-Elmer Lambda 19 spectrophotometer on DMF solutions by using cell path lengths of 1 cm. Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed by using KBr pellets. Vibrational transition frequencies were reported in wave number (cm^{-1}). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a rate of 10°C/min. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran.

Monomer synthesis

Bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid 6

This compound was prepared according to a typical procedure that is shown in Scheme 1.

p-Phenylenediacrylic acid 3

Into a 100-mL round-bottomed flask, terephthalaldehyde 1 (3.48 g, 26 mmol) and malonic acid 2 (8.27 g, 94 mmol) were added to 30 mL of pyridine containing small amount of piperidine. The reaction mixture was stirred for 2 h at 45°C, 4 h at 80°C, and 3 h at 110°C, respectively. The solution was poured into large amount of distilled water and neutralized

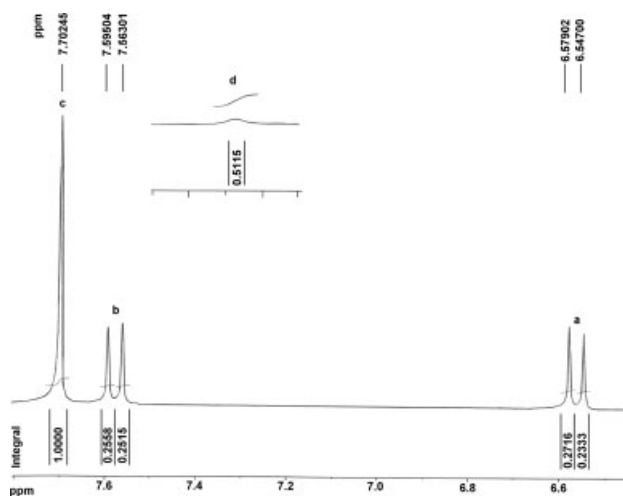
with 10% HCl to obtain white precipitate. The precipitate was filtered, washed with water, acetic acid and acetone, respectively, and dried in a vacuum oven at room temperature to give 5.16 g (91%) of white crystals compound 3: mp >300°C, FTIR (KBr): 3400–2500 (m, br), 1665 (s, br), 1610 (s), 1501 (w, sh), 1412 (m), 1287 (s), 1262 (s), 1209 (s), 1135 (m), 979 (m), 938 (m), 862 (w) cm^{-1} . ^1H NMR (DMSO- d_6 , TMS): δ 6.54–6.57 (d, 2H); 7.56–7.59 (d, 2H); 7.70 (s, 4H); 12.85 (b, 2H) ppm. Analysis: Calculated for $\text{C}_{12}\text{H}_{10}\text{O}_4$: C, 66.07; H, 4.58; found: C, 66.2; H, 4.4.

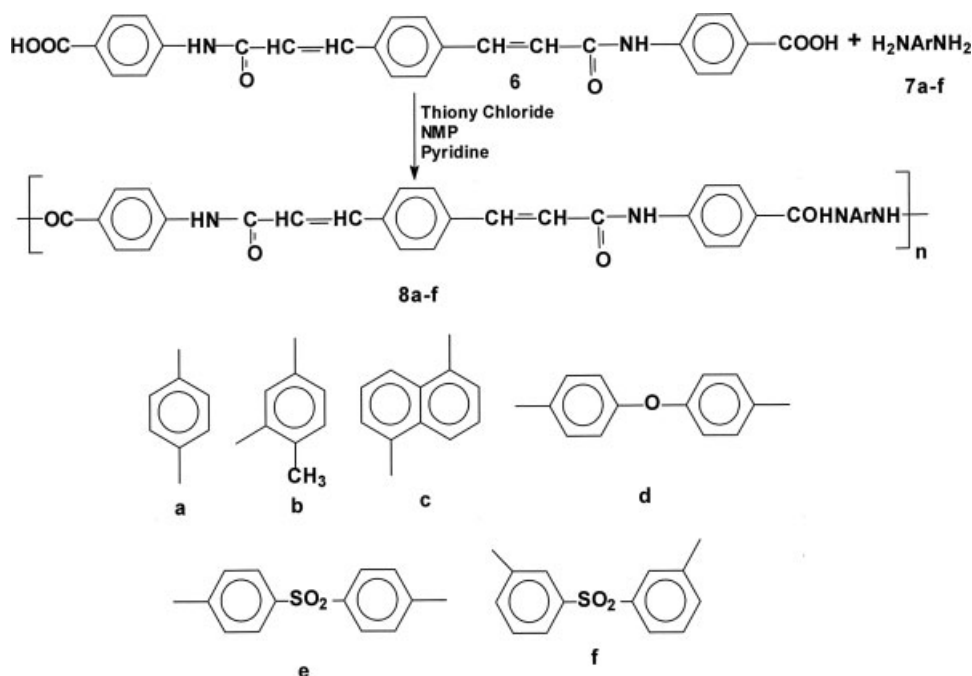
Synthesis of *p*-phenylene diacryloyl chloride 4

Into a 50-mL round-bottomed flask, *p*-phenylenediacrylic acid 3 (2.12 g, 10 mmol) and 15 mL of thionyl chloride and 0.1 mL DMF as a base were placed. The mixture was heated on an oil bath up to 60°C, until the suspension mixture was converted to a clear solution. Then, the solution was stirred for overnight at room temperature. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with dry *n*-hexane two times, to leave 2.27 g (89%) of yellow crystals of compound 4: mp 170–172°C, FTIR (KBr): 1738 (s, br), 1635 (w), 1597 (m), 1550 (w), 1460 (m), 1400 (m), 1304 (w), 1162 (m), 1091 (s), 1022 (w), 902 (w) cm^{-1} . Analysis: Calculated for $\text{C}_{12}\text{H}_8\text{O}_2\text{Cl}_2$: C, 56.49; H, 3.13; found: C, 56.6; H, 3.0.

Synthesis of bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid 6

Into a 100-mL round-bottomed flask, *p*-phenylene diacryloyl chloride 4 (2.55 g, 10 mmol) in 50-mL THF was added in an ice bath. Then a solution of *p*-aminobenzoic acid 5 (2.74 g, 20 mmol) in 40 mL THF was added to mixture in 20 min. The reaction mixture was stirred

Figure 1 ^1H NMR spectrum of diacid 3.



Scheme 2 Synthesis route of polyamide 8a-f.

for overnight at room temperature. A dark-yellow precipitate was formed. Then the reaction mixture was concentrated up to 10 mL, and the solid was filtered off and washed with methanol and dried under vacuum to give 4.33 g (95%) of yellow solid. mp >300°C, FTIR (KBr): 3400–2500 (m, br), 1692 (s, br), 1610 (s), 1595 (s, br), 1525 (s, br), 1408 (s), 1313 (m), 1248 (s), 1172 (s), 979 (m), 878 (w), 854 (w), 769 (m) cm⁻¹. ¹H NMR (DMSO-*d*₆, TMS): δ 6.62–6.65 (d, 2H); 6.92–6.95 (d, 2H); 7.73–8.00 (m, 8H); 10.61 (b, 2H), 12.80–13.20 (br, 2H) ppm. Analysis: Calculated for C₂₆H₂₀N₂O₆: C, 68.43; H, 4.38; N, 6.13. Found: C, 68.3; H, 4.4. N, 6.0.

Polymer synthesis

The polyamides 8a–f were prepared by using the following general procedure, taking polymer 8a as an example: the diacid 6 (0.45 g, 1 mmol) was dissolved in 10-mL *N*-methyl pyrrolidone in a dry three-necked

flask. The solution was cooled to –10°C, then thionyl chloride (0.29 g, 2.5 mmol) was added and stirred for 5 min. 1,4-Phenylene diamine 7a (0.10 g, 1 mmol) and pyridine (0.19 g, 2.5 mmol) were added to the mixture. It was stirred for 15 h at 0°C and then 2 h at room temperature. The viscous reaction mixture was added into 25 mL of methanol. The precipitated polymer 8a was collected by filtration and dried at 80°C for 8 h under vacuum to leave 0.48 g (91%) of solid.

RESULTS AND DISCUSSION

Monomer synthesis

Bis(*p*-amidobenzoic acid)-*p*-phenylene diacrylic acid 6 as a new monomer containing *p*-phenylenediacryloyl moiety was synthesized by using a three-step reaction as shown in Scheme 1. At first *p*-phenylene-

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

Aromatic diamine	Polymer	Yield (%)	η _{inh} (dL/g) ^a
7a	8a	91	0.45
7b	8b	89	0.35
7c	8c	90	0.57
7d	8d	87	0.46
7e	8e	92	0.65
7f	8f	90	0.60

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

TABLE II
Elemental Analysis of Polyamides 8a–f

Polymer	Formula		C%	H%	N%
8a	C ₃₂ H ₂₄ N ₄ O ₄ (528.32) _n	Calcd.	72.74	4.54	10.60
		Found	71.9	4.7	9.7
8b	C ₃₃ H ₂₆ N ₄ O ₄ (542.33) _n	Calcd.	73.07	4.79	10.32
		Found	72.0	4.1	10.0
8c	C ₃₆ H ₂₆ N ₄ O ₄ (578.36) _n	Calcd.	74.75	4.49	9.68
		Found	73.8	4.3	8.6
8d	C ₃₈ H ₂₈ N ₄ O ₅ (620.38) _n	Calcd.	73.56	4.51	9.02
		Found	72.6	4.2	8.1
8e	C ₃₈ H ₂₈ N ₄ O ₆ S (668.38) _n	Calcd.	68.28	4.19	8.37
		Found	67.8	4.6	8.0
8f	C ₃₈ H ₂₈ N ₄ O ₆ S (668.38) _n	Calcd.	68.28	4.19	8.37
		Found	67.5	4.3	7.8

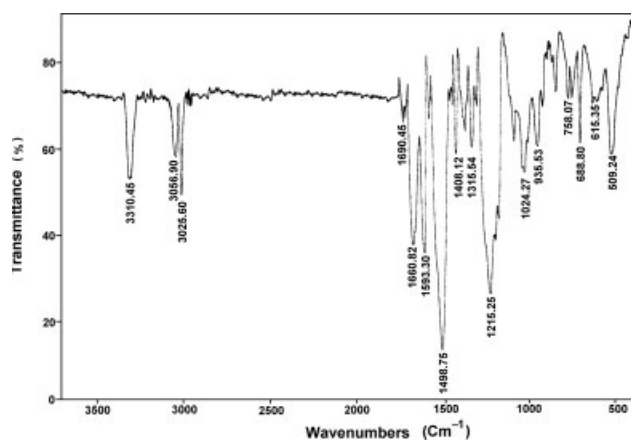


Figure 2 FTIR spectrum of polyamide 8a.

diacrylic acid **3** was prepared by reaction of terephthal aldehyde **1** with malonic acid **2** in the presence of pyridine, then diacid **3** was converted to *p*-phenylenediacryloyl chloride **4** by reaction with thionyl chloride. Finally, diacid **6** was prepared by condensation reaction of phenylenediacryloyl chloride **4** with *p*-aminobenzoic acid **5** as a yellow solid with high yield.

The chemical structure and purity of compounds **3** and **6** were proved by using elemental analysis, FTIR and ^1H NMR spectroscopic techniques. The ^1H NMR spectrum of diacid **3** showed two doublet peaks at 6.54–6.57 and 7.56–7.59 ppm, which were assigned, to the H_a and H_b protons of vinyl group. Peak at 7.70 ppm was assigned to the H_c protons of aromatic ring. Finally, the broad peak between 12.80 and 13.00 ppm was assigned to H_d protons of COOH groups (Fig. 1). The FTIR spectrum of compound **3** showed a broad peak between 2800 and 3500 cm^{-1} which was assigned to the COOH group. Also several absorption bands at 1692, 1595, 1525 cm^{-1} were observed which were characteristic peaks for carbonyl bond, vinyl segment, and aromatic ring.

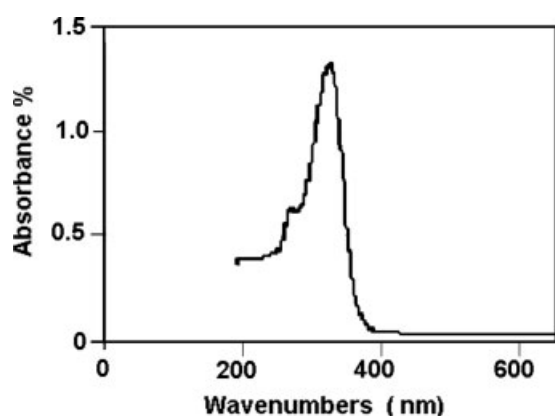


Figure 3 UV spectrum of diacid 6.

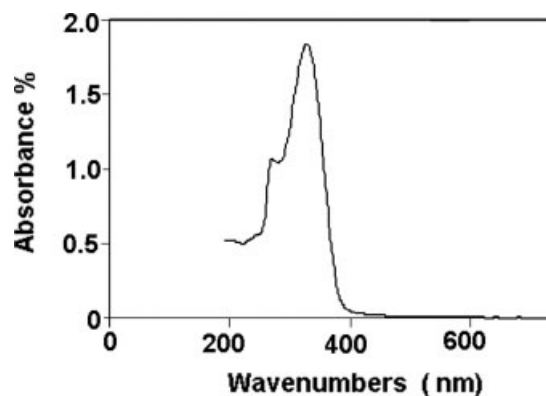


Figure 4 UV spectrum of polyamide 8e.

The structure of diacid **6** was also confirmed by its NMR spectrum. In the ^1H NMR spectrum, the protons H_a and H_b of vinyl bond appeared at 6.62–6.65 and 6.92–6.95 as a doublet of doublet peak. On the other hand aromatic ring protons (H_c , H_d , and H_e) appeared between 7.73 and 8.00 ppm as a multiple peak. A broad peak at 10.61 ppm showed protons of N—H group (H_f). Finally, the broad peak between 12.80 and 13.20 ppm was assigned to H_g protons of COOH groups. The measured results in elemental analyses of compounds **3**, **4**, and **6** closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

Also in the FTIR spectrum of diacid **6** a broad peak at 2700–3200 cm^{-1} was assigned to the COOH groups.

Polymer synthesis

The polyamides **8a–f** were synthesized by the direct solution, polycondensation reaction of an equimolar diacid **6** with six derivatives of aromatic diamine **7a–f** by using thionyl chloride, *N*-methyl-2-pyrrolidone, and pyridine as condensing agents (Scheme 2). The entire polycondensation readily proceeded in a ho-

TABLE III
Solubility of Polyamides 8a–f

Solvents	8a	8b	8c	8d	8e	8f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
CHCl_3	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–
H_2O	–	–	–	–	–	–

+, Soluble at room temperature; –, insoluble at room temperature.

TABLE IV
Thermal Behavior of Polyamides 8a–f

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char yield (%) ^c
8a	345–350	385–390	62
8b	315–320	355–360	56
8c	350–355	360–365	35
8d	340–345	355–360	38
8e	405–410	455–460	44
8f	370–375	395–400	61

^{a,b}Temperature at which 5 and 10% weight loss was recorded by TGA at heating rate of 10°C/min in N₂ respectively.

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

mogeneous solution. Tough and stringy precipitates formed when the viscous polymers solutions were trickled into stirred methanol. All the polymers were obtained in quantitative yields with inherent viscosities between 0.35 and 0.65 dL/g.

Polymer characterization

Synthesis and some physical properties of polyamides 8a–f are summarized in Table I. These polymers have inherent viscosities in a range between 0.35 and 0.65 dL/g. The structures of these polymers were confirmed as a polyamide by means of FTIR spectroscopy and elemental analyses (Table II). The FTIR spectrum of polyamide 8a shows absorption bands at 1690, 1660 cm⁻¹ due to carbonyl of amide and acid groups, respectively. Also absorption bands around 1450–1600 cm⁻¹ show the presence of the aromatic ring and vinyl moiety in this polymer (Fig. 2). The other spectra show a similar pattern (See Appendix).

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

The UV–vis absorption spectra of diacid 6 and polyamide 8e in *N,N*-dimethyl formamide are shown

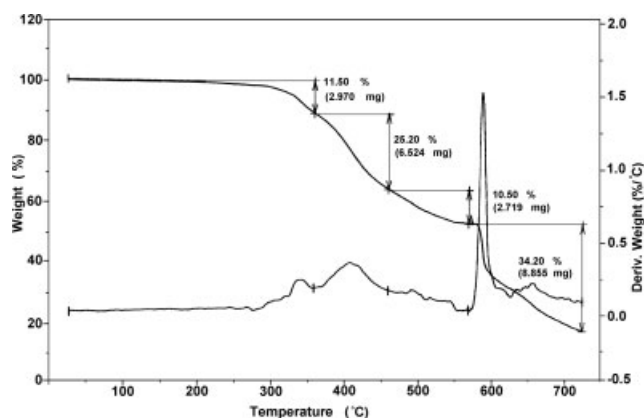


Figure 5 TGA and DTG thermogram of polyamide 8d.

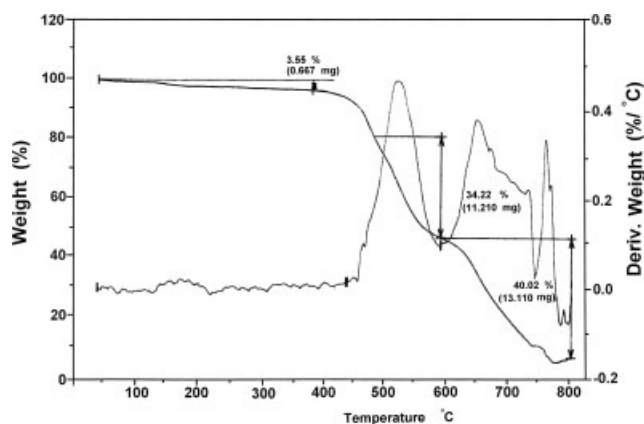


Figure 6 TGA and DTG thermogram of polyamide 8e.

in Figures 3 and 4. The spectrum of diacid 6 exhibited two typical peaks at 269 nm ($\pi \rightarrow \pi^*$) and 328 nm ($n \rightarrow \pi^*$). Also the spectrum of polyamide 8e exhibited same two typical peaks at 265 nm ($\pi \rightarrow \pi^*$) and 325 nm ($n \rightarrow \pi^*$). By comparing the two spectra, a slightly blue shift is shown in polyamide 8e.

The solubility of polyamides 8a–f was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All these PAIs were soluble in organic solvents such as DMF, DMAc, DMSO, NMP, THF, and acetone at room temperature, and were insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water (Table III).

Thermal properties

The thermal properties of resulted polyamides 8a–f were investigated by means of TGA and DTG analysis in a nitrogen atmosphere at a heating rate of 10°C/min. Initial decomposition temperature, 5 and 10% weight loss (T_5 , T_{10}), and char yields at 600°C for these polyamides are summarized in Table IV. All these polymers showed almost similar decomposition behavior (Figs. 5 and 6). These polymers exhibited good resistance to thermal decomposition up to 315–405°C in nitrogen, and began to decompose gradually above this temperature. The temperature of 5% weight loss for all the polymers ranged from 315 to 405°C, and the residual weight for these polymers at 600°C ranged from 35 to 62% in nitrogen. Polyamide 8e and 8f showed higher initial decomposition temperature in comparison with other polyamides, because these polymers have sulfonyl (SO₂) moiety in the main chain.

CONCLUSIONS

This work has synthesized several new polyamides 8a–f by the direct polycondensation reaction of the monomer 6 with six different derivatives of aromatic

diamine **7a–f** by using thionyl chloride, *N*-methyl-2-pyrrolidone, and pyridine as condensing agents. The resulting polyamides were soluble in various organic solvents and had good thermal stability. These properties can make these polyamides attractive for practical applications such as processable high-performance engineering plastics.

APPENDIX: THE POLYAMIDES **8a–f** ANALYSES USING FTIR

Polymer **8a**

FTIR (KBr): 3310 (m), 3056 (w), 3025 (m), 1690 (w), 1660 (s), 1593 (s), 1498 (s, br), 1408 (w), 1315 (w), 1215 (s), 1024 (m), 935 (w), 758 (w), 688 (m) cm^{-1} .

Polymer **8b**

FTIR (KBr): 3300 (m), 3051 (w), 3025 (m), 1690 (w), 1664 (s), 1592 (s), 1490 (s, br), 1406 (w), 1310 (w), 1211 (s), 1020 (m), 935 (w), 758 (w), 680 (m) cm^{-1} .

Polymer **8c**

FTIR (KBr): 3313 (m), 3046 (w), 3020 (m), 1690 (w), 1658 (s), 1593 (s), 1516 (s), 1498 (s, br), 1406 (m), 1319 (w), 1244 (s), 1180 (m), 1024 (m), 815 (w), 760 (m), 688 (w) cm^{-1} .

Polymer **8d**

FTIR (KBr): 3335 (m), 3050 (w), 3015 (m), 1692 (w), 1660 (s), 1593 (s), 1496 (s, br), 1406 (m), 1315 (m), 1210 (s), 1024 (m), 930 (w), 752 (w), 680 (m) cm^{-1} .

Polymer **8e**

FTIR (KBr): 3342 (m), 3034 (w), 1692 (w), 1662 (s), 1591 (s), 1493 (s, br), 1402 (m), 1315 (w), 1242 (m), 1215 (s), 1147 (m), 1106 (m), 935 (w), 750 (m), 680 (m) cm^{-1} .

Polymer **8f**

FTIR (KBr): 3340 (m), 3030 (w), 1692 (w), 1666 (s), 1593 (s), 1493 (s, br), 1510 (s), 1417 (m), 1300 (s), 1238 (s), 1182 (m), 933 (w), 750 (w), 680 (m) cm^{-1} .

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