

New Polyamides Based on Bis(p-amidobenzoic acid)-p-phenylene diacrylic acid and Hydantoin Derivatives: Synthesis and Characterization

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Bis(p-amidobenzoic acid)-p-phenylene diacrylic acid (**6**) as a new monomer containing p-phenylene-diacryloyl moiety was synthesized by using a 3-step reaction. At first p-phenylenediacrylic acid (**3**) was prepared by reaction of terephthal aldehyde (**1**) with malonic acid (**2**) in the presence of pyridine, and 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**). Then 6 new polyamides (**8a-f**) containing p-phenylenediacryloyl and hydantoin moiety in the main chain were prepared by the direct polycondensation reaction of bis(p-amidobenzoic acid)-p-phenylene diacrylic acid (**6**) with 6 different hydantoin derivatives (**7a-f**) by 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 0.32-0.50 dL/g. The resulting polyamides were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test, FT-IR, and UV-vis spectroscopy.

Key Words: Polyamides, p-phenylenediacryloyl moieties, bis(p-amidobenzoic acid)-p-phenylene diacrylic acid, hydantoin derivatives.

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 difficulty due to their infusibility and poor solubility in organic solvents.^{8,9} Therefore, much research has been focused on maintaining considerable

thermal stability and improving their solubility. These studies include: 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; 4) Destroying the hydrogen bonding by N-substitution with certain groups such as methyl.^{10–19}

The conventional method for synthesis of polyamides begins with having diamine react with a diacid chloride monomer by low temperature solution polycondensation. In another method, Yamazaki and co-workers 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.^{20–21}

In the present study, 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 hydantoin (**7a**), 5,5-dimethyl hydantoin (**7b**), 5-ethyl-5-methyl hydantoin (**7c**), 5,5-diethyl hydantoin (**7d**), 5,5-spirocyclopantyl hydantoin (**7e**), and 5,5-spirocyclohexyl hydantoin (**7f**) by using thionyl chloride, N-methyl-2-pyrrolidone, and pyridine as condensing agents. These polymers have a soft segment such as vinyl moiety in the main chain for improving solubility in organic solvents in comparison to aromatic polyamides. On the other hand, considerable attention is paid to the synthesis of polymers containing p-phenylenediacryloyl moiety in the main chain, because they can be used for preparing photosensitive liquid crystalline polymers. There are some reported papers about the synthesis of polyester, polyimides, polyamides, and poly(amid-co-imide)s containing p-phenylenediacryloyl moiety in the main chain.^{22–25}

Experimental

Materials

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

Techniques

¹H-NMR spectra were recorded on a Bruker 500 MHz instrument. UV-vis absorption were recorded at 25 °C in the 200–700 nm spectral region with a Perkin-Elmer Lambda 19 spectrophotometer on DMF solutions using cell path lengths of 1 cm. Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (UK). Spectra of solids were performed 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® Viscometer. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10 °C/min. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran. Weight-average (M_w) and number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC). The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm. Polystyrene was used as the standard.

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)

To a 100 ml round-bottomed flask containing 30 ml of pyridine containing small amount of piperidine were added 3.48 g of terephthal aldehyde (**1**) (26 mmol) and 8.27 g of malonic acid (**2**) (94 mmol). The reaction mixture was stirred for 2 h at 45 °C, 4 h at 80 °C, and 3 h at 110 °C, in that order. The solution was poured into a 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, FT-IR (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-d₆, 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 C₁₂H₁₀O₄: C, 66.07; H, 4.58; found: C, 66.2; H, 4.4.

Synthesis of p-phenylene diacryloyl chloride (4)

To a 50 ml round-bottomed flask were added 2.12 g of p-phenylenediacrylic acid (**3**) (10 mmol), 15 ml of thionyl chloride, and 0.1 ml of DMF (as a base). 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 twice to leave 2.27 g (89%) of yellow crystals of compound (**4**): mp 170-172 °C, FT-IR (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 C₁₂H₈O₂Cl₂: C, 56.49; H, 3.13; found: C, 56.6; H, 3.0.

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

To a 100 ml round-bottomed flask with 50 ml THF in an ice bath was added 2.55 g of p-phenylene diacryloyl chloride (**4**) (10 mmol). Then a solution of p-aminobenzoic acid (**5**) (2.74 g, 20mmol) in 40 ml THF was added to the mixture over 20 min. The reaction mixture was stirred 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 of compound (**6**). mp > 300 °C, FT-IR (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-d₆, 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.

Hydantoin derivatives (7a-f)

These compounds were prepared according to a typical procedure that is shown in Scheme 2.²⁶

Polymer Synthesis

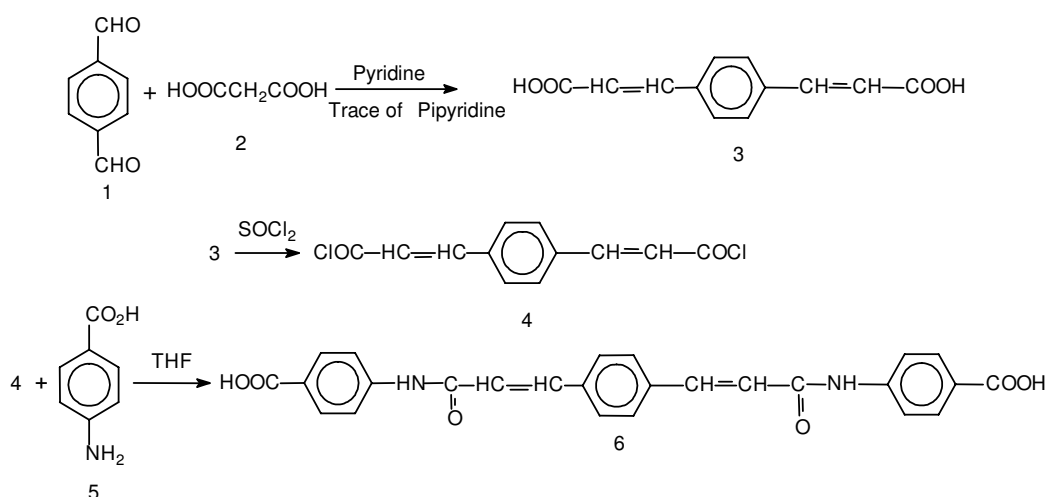
The polyamides **8a-f** were prepared using the following general procedure: Taking polymer **8a** as an example: The diacid **6** (0.456 g, 1 mmol) was dissolved in 10 ml N-methyl pyrrolidone in a dry 3-necked flask. The solution was cooled to -10 °C, then thionyl chloride (0.298 g, 2.5 mmol) was added and stirred for 5 min. Hydantoin **7a** (0.100 g, 1 mmol) and pyridine (0.198 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 0.45 g (87%) of solid.

Results and Discussion

Monomer Synthesis

Bis(p-amidobenzoic acid)-p-phenylene diacryloic acid (**6**) as a new monomer containing p-phenylenediacyloyl moiety was synthesized using a 3-step reaction as shown in Scheme 1. At first, p-phenylenediacyrylic 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-phenylenediacyloyl chloride (**4**) by reaction with thionyl chloride. Finally bis(p-amidobenzoic acid)-p-phenylene diacryloic acid (**6**) was prepared by condensation reaction of **4** with p-aminobenzoic acid (**5**) as a yellow solid with high yield.



Scheme 1

The chemical structure and purity of compounds **3** and **6** were proved using elemental analysis, FT-IR, and ¹H-NMR. The ¹H-NMR spectrum of diacid **3** showed 2 doublet peaks at 6.54-6.57 ppm 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, which 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 (Figure 1). The FT-IR spectrum of compound **3** showed a broad peak between 2800 and 3500 cm⁻¹, which was assigned to the COOH group. Several absorption bands at 1692, 1595, 1525 cm⁻¹ were observed, which were characteristic peaks for carbonyl bond, vinyl segment, and aromatic ring, respectively.

The structure of diacid **6** is also confirmed by its NMR spectrum (Figure 2). In the ¹H-NMR spectrum, the protons H_a and H_b of vinyl bond appear at 6.62-6.65 ppm and 6.92-6.95 ppm 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 shows 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 (Figure 2). 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.

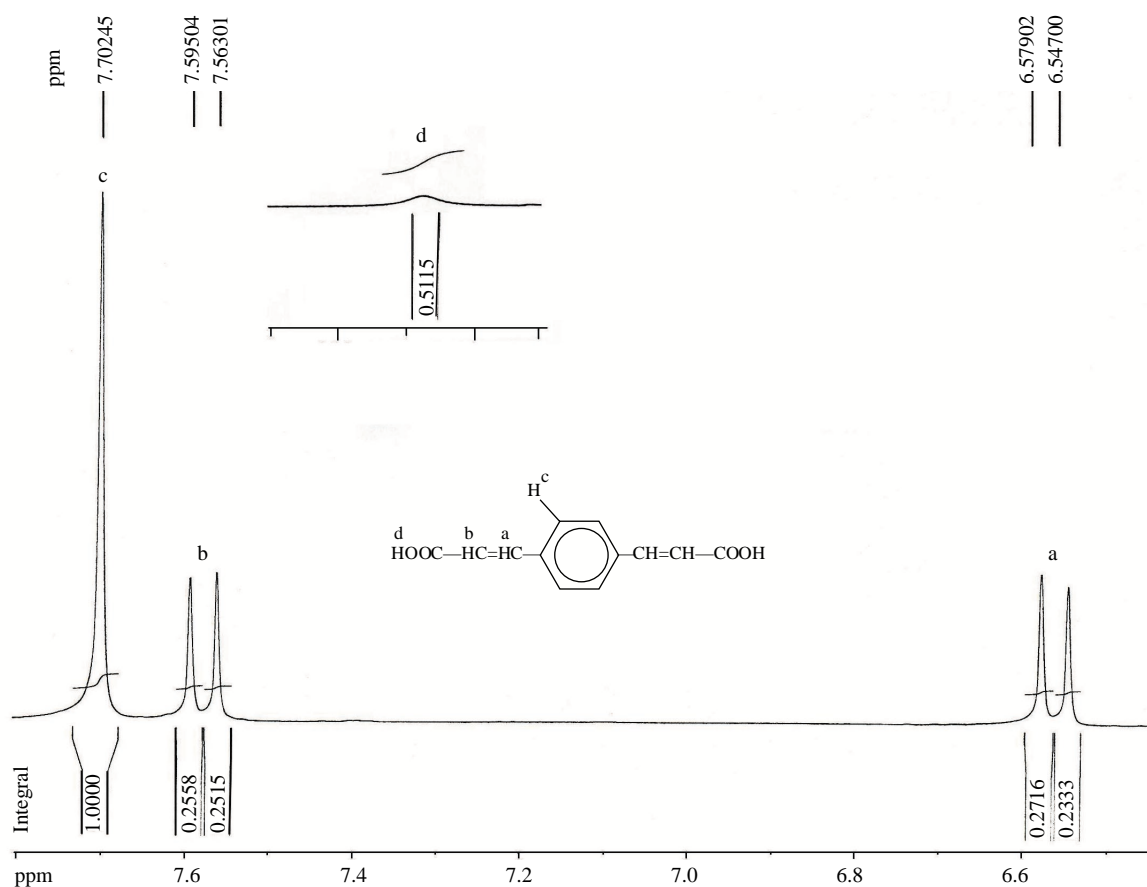
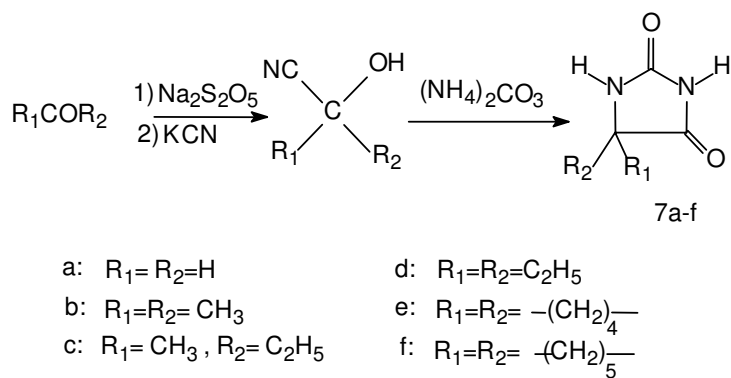


Figure 1. ¹H-NMR Spectrum of diacid **3**.

In the FT-IR spectrum of diacid **6**, a broad peak at 2700-3200 cm^{-1} , which was assigned to the COOH groups, was observed.

Hydantoin constitutes an important class of heterocycles in medicinal chemistry because many derivatives have been identified to display interesting activities against a broad range of biological targets.²⁷ 5,5-Disubstituted hydantoin derivatives were synthesized by the Bucherer-Berg method. Using this method, hydantoin compounds **5a-f** (Scheme 2) were prepared through the reaction of cyanohydrin derivatives with ammonium carbonate. Hydantoin and hydantoin derivatives are important intermediates in the synthesis of several amino acids. In the chemical industry various hydantoin derivatives are the basis of new generation of weatherproof high-temperature-stable epoxy resins.²⁸

The polyamides **8a-f** were synthesized by the direct solution polycondensation reactions of an equimolar diacid (**6**) with 6 different derivatives of hydantoin (**7a-f**) by using thionyl chloride, N-methyl-2-pyrrolidone, and pyridine as condensing agents (Scheme 3). The entire polycondensation readily proceeded in a homogeneous solution. Tough and stringy precipitates formed when the viscous polymers solutions were trickled into stirred methanol. All of the polymers were obtained in quantitative yields with inherent viscosities between 0.32-0.50 dL/g.



Scheme 2

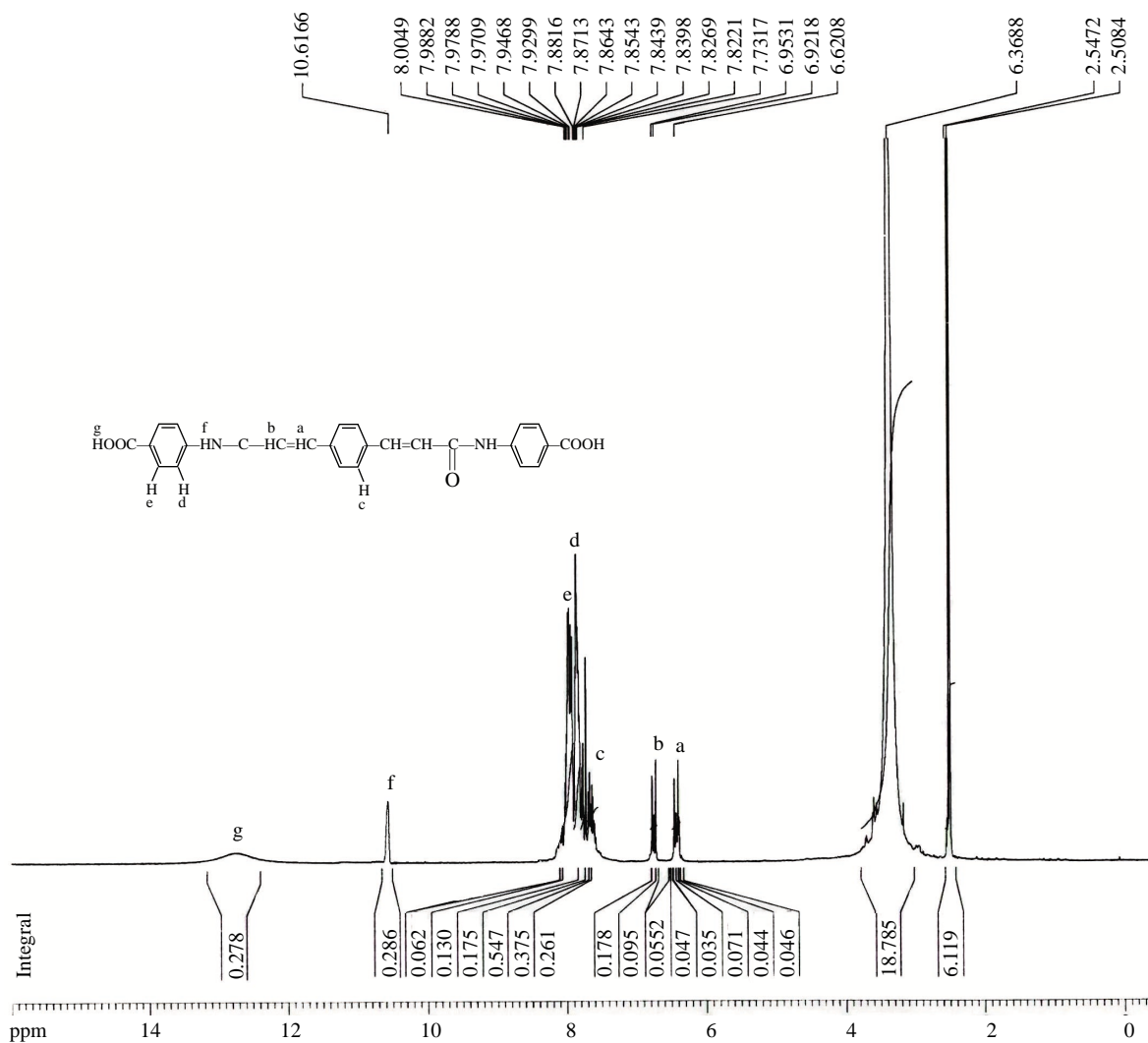
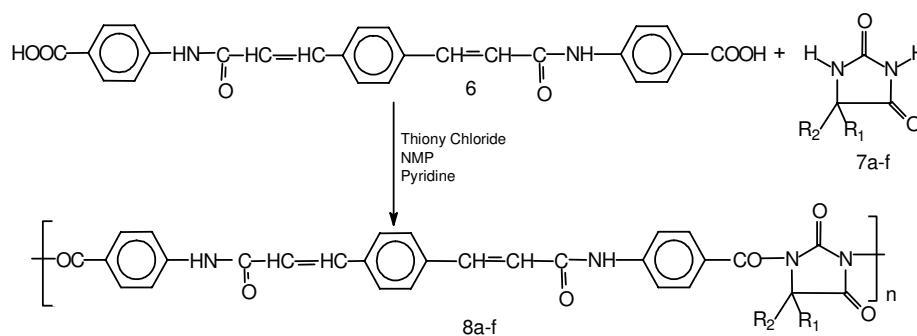


Figure 2. ¹H-NMR Spectrum of diacid 6.



Scheme 3

Table 1. Synthesis and some physical properties of polyamide **8a-f**.

Hydantoins	Polymer	Yield (%)	η_{inh} (dL/g) ^a	\bar{M}_n^b (10 ⁴)	\bar{M}_w^b (10 ⁴)	PDI
7a	8a	87	0.50	2.5	6.8	2.72
7b	8b	81	0.35	1.3	2.8	2.15
7c	8c	83	0.32	1.4	3.0	2.14
7d	8d	87	0.40	1.0	1.9	1.9
7e	8e	85	0.45	2.1	4.6	2.19
7f	8f	84	0.42	2.0	3.7	1.85

^aMeasured at a concentration of 0.5 g/dL in DMF at 25 °C. ^bMeasured by GPC in THF, polystyrene was used as standard.

Polymer characterization

Synthesis and some physical properties of polyamides **8a-f** are summarized in Table 1. These polymers have inherent viscosities in a range between 0.32-0.50 dL/g. The structures of these polymers were confirmed as polyamides by means of FT-IR spectroscopy and elemental analyses (Table 2). The representative FT-IR spectrum of polyamide **8a** is shown in Figure 3. The polymer shows absorption bands at 1685 and 1660 cm^{-1} due to carbonyl of amide groups. Also absorption bands around 1450-1600 cm^{-1} show the presence of the aromatic ring and vinyl moiety in this polymer. The other spectra show a similar pattern. These polymers exhibited number-average molecular weights (M_n) and weight-average molecular weights (M_w) in the range of $1.0\text{--}2.0 \times 10^4$ and $1.9\text{--}6.82 \times 10^4$, respectively, as measured by GPC, relative to polystyrene standards.

The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table 2). The UV-vis absorption spectra of diacid **6** and polyamide **8e** in N,N-dimethyl formamide are shown in Figures 4 and 5. The spectrum of diacid **6** exhibited 2 typical peaks at 269 nm ($\pi \rightarrow \pi^*$) and 328 nm ($n \rightarrow \pi^*$). Also the spectrum of polyamide **8e** exhibited the same 2 typical peaks at 265 nm ($\pi \rightarrow \pi^*$) and 325 nm ($n \rightarrow \pi^*$). By comparing of the 2 spectra, a slightly blue shift was shown in polyamide **8e**.

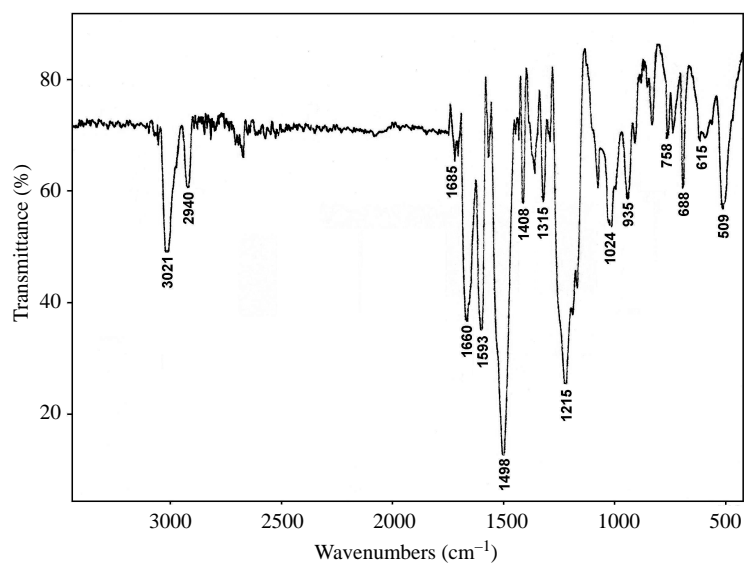


Figure 3. FT-IR Spectrum of polyamide **8a**.

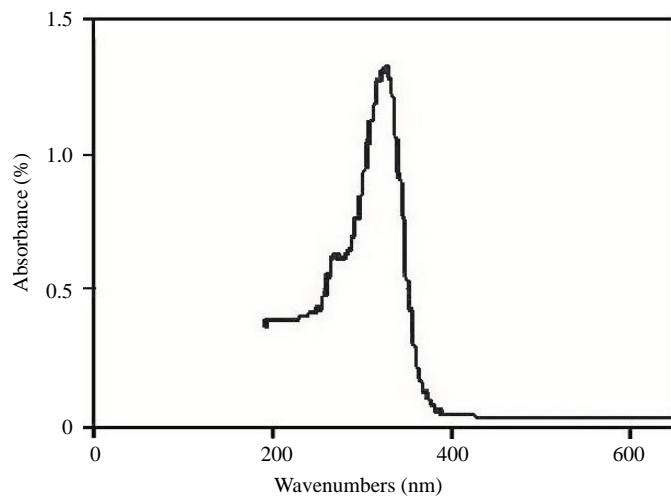


Figure 4. UV Spectrum of diacid **6**.

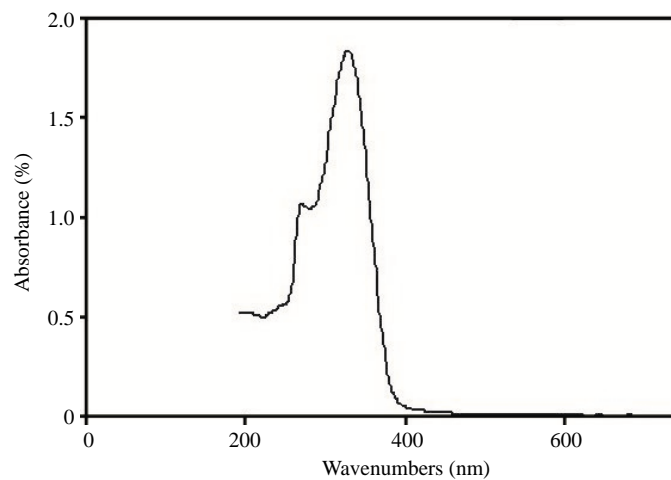


Figure 5. UV Spectrum of polyamide **8e**.

Table 2. Elemental analysis of polyamides **8a-f**.

Polymer	Formula		C%	H%	N%
8a	$C_{29}H_{20}N_4O_6$	calcd	66.94	3.84	10.76
	$(520.29)_n$	found	66.00	3.10	9.90
8b	$C_{31}H_{24}N_4O_6$	calcd	67.90	4.37	10.21
	$(548.31)_n$	found	67.10	4.00	9.80
8c	$C_{32}H_{26}N_4O_6$	calcd	68.34	4.62	9.95
	$(562.32)_n$	found	67.90	4.00	9.10
8d	$C_{33}H_{28}N_4O_6$	calcd	68.76	4.85	9.71
	$(576.33)_n$	found	68.00	4.20	9.00
8e	$C_{33}H_{26}N_4O_6$	Calcd	69.00	4.52	9.75
	$(574.33)_n$	Found	68.60	4.60	9.10
8f	$C_{34}H_{28}N_4O_6$	calcd	69.40	4.75	9.51
	$(588.34)_n$	found	68.90	4.00	9.20

The solubility of polyamides **8a-f** was investigated as 0.01 g of polymeric sample in 2 ml of solvent. All of these PAIs are soluble in organic solvents such as DMF, DMAc, DMSO, NMP, THF and acetone at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water (Table 3).

Table 3. Solubility of polyamides **8a-f**.

Solvents	8a	8b	8c	8d	8e	8f
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
CHCl ₃	-	-	-	-	-	-
EtOH	-	-	-	-	-	-
MeOH	-	-	-	-	-	-
CH ₂ Cl ₂	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-

+: Soluble at room temperature, -: Insoluble at room temperature.

Thermal properties

The thermal properties of some polyamides (**8a**, **8d**, and **8f**) were investigated by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min and thermal data are summarized in Table 4. These polymers show almost similar decomposition behavior (Figures 6 and 7). Initial decomposition temperature, 5% and 10% weight loss (T_5 and T_{10}) and

char yields at 600 °C for these polyamides are summarized in Table 4. These polymers exhibited good resistance to thermal decomposition up to 340-390 °C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 340 to 390 °C and the residual weight for these polymers at 600 °C ranged from 24% to 57% in nitrogen.

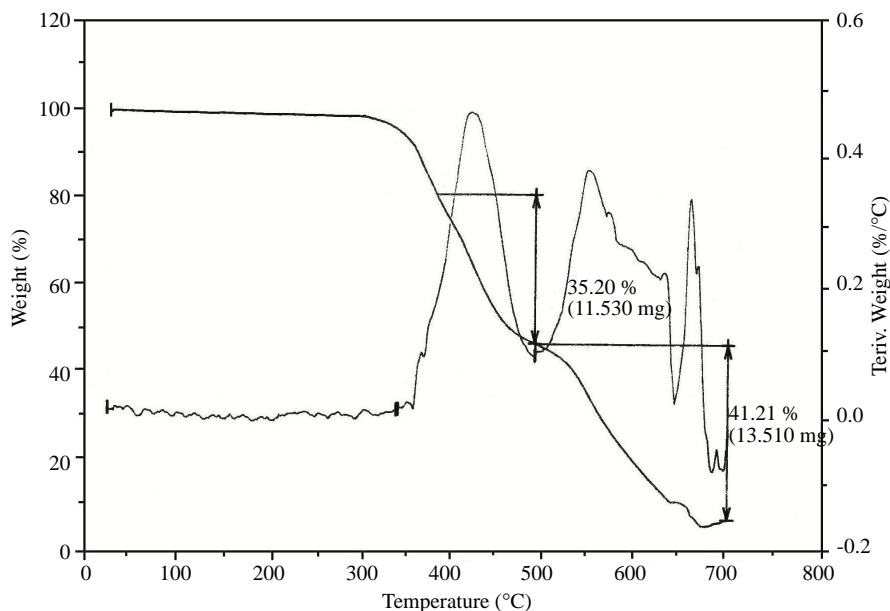


Figure 6. TGA and DTG thermogram of polyamide **8b**.

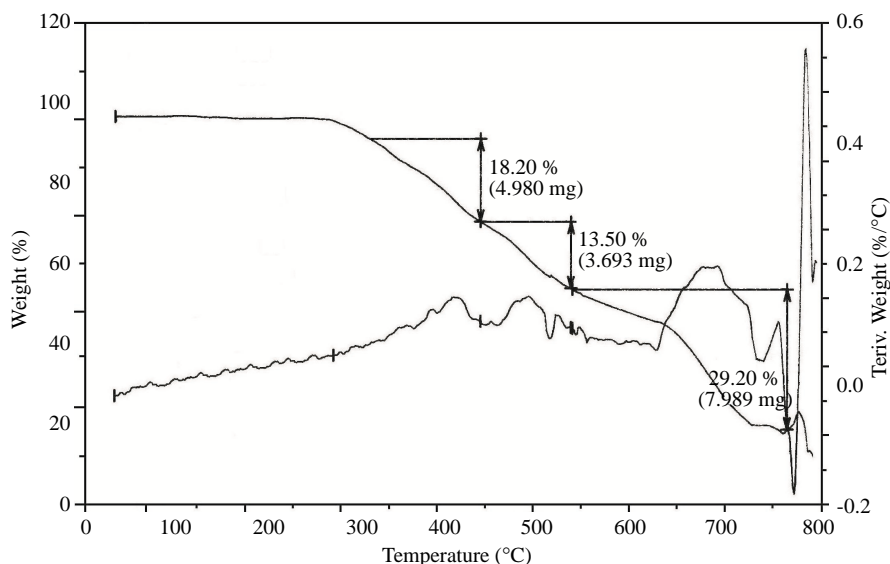


Figure 7. TGA and DTG thermogram of polyamide **8f**.

Table 4. Thermal behavior of polyamides **8a**, **d**, **f**.

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c (%)
8a	340-345	355-360	37
8d	350-355	360-365	24
8f	345-350	385-390	57

^{a,b}Temperature at which 5% and 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in N₂, respectively. ^cPercentage weight of material left undecomposed after TGA analysis at 600 °C.

Conclusion

This work has synthesized several new polyamides (**8a-f**) by direct polycondensation reaction of the monomer **6** with 6 different derivatives of hydantoin (**7a-f**) using thionyl chloride, N-methyl-2-pyrrolidone, and pyridine as condensing agents. These new polyamides are soluble in various organic solvents and have good thermal stability. These properties can make these polyamides attractive for practical applications such as processable high-performance engineering plastics.

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