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Synthesis and Properties of New Polyamides Based on 4-Phenylenediacrylic Acid and Hydantoin Derivatives in the Main Chain

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Six new polyamides (**5a-f**) containing p-phenylenediacrylic and hydantoin moieties in the main chain were prepared by direct polycondensation reaction of 4-phenylenediacrylic acid (**3**) with 6 different hydantoin derivatives (**4a-f**) using thionyl chloride and pyridine as condensing agents and N-methyl-2-pyrrolidone as solvent. These new polymers (**5a-f**) were obtained in high yield and inherent viscosity between 0.35-0.55 dL/g. The resulting polyamides were characterized by elemental analysis, viscosity measurements, thermal gravimetric analysis (TGA and DTG), solubility test, and FT-IR and UV-vis spectroscopy. 4-Phenylenediacrylic acid (**3**) was prepared by the reaction of terephthal aldehyde (**1**) with malonic acid (**2**) in the presence of pyridine.

Key Words: Polyamides; 4-phenylenediacrylic acid; hydantoin derivatives.

Introduction

Thermally stable polymers have received extensive interest in recent decades because of increasing demands for high temperature polymers as the 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, more studies have 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, and 4) Preventing 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 produce a high yield of polymers at a high molecular weight.^{20–21}

In this paper we used Yamazaki method for synthesis of a series of novel polyamides containing p-phenylenediacrylic and hydantoin moieties in the main chain from the direct polycondensation reaction of 4-phenylenediacrylic acid (**3**) with hydantoin (**4a**), 5,5-dimethyl hydantoin (**4b**), 5-ethyl-5-methyl hydantoin (**4c**), 5,5-diethyl hydantoin (**4d**), 5,5-spirocyclopantyl hydantoin (**4e**) and 5,5-spirocyclohexyl hydantoin (**4f**) using thionyl chloride and pyridine as condensing agents and N-methyl-2-pyrrolidone as solvent. These polymers have the vinyl moiety and heterocyclic segment such as hydantoin ring in the main chain for improving solubility in organic solvents in comparison to aromatic polyamides. On the other hand, there is a considerable attention for synthesis of polymers containing p-phenylenediacrylic moiety in the main chain, because they can be used for preparing photosensitive liquid crystalline polymers. There are some reported papers about synthesis polyester, polyimides, polyamides, and poly(amid-co-imide)s containing p-phenylenediacrylic 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 (England). Spectra of solids were performed by KBr pellets. Vibrational transition frequencies are reported in wave number (cm⁻¹). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Technico®. 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. Differential scanning calorimetric analysis was performed on differential scanning calorimeter (Du Pont 910) at a heating rate of 10 °C min⁻¹. Inherent viscosity was measured in DMF solution at a concentration of 0.5 g dL⁻¹ at 25 °C.

Monomer synthesis

4-Phenylenediacrylic acid (**3**)

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

p-Phenylenediacrylic acid (**3**)

In a 100 mL round-bottomed flask, 3.48 g of terephthal aldehyde (**1**) (26 mmol) and 8.27 g of malonic acid (**2**) (94mmol) were added to 30 mL of pyridine containing small amount of pipyridine. 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, in that order, and dried in a vacuum oven at room temperature to give 5.16 g (91 %) of white 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.

Hydantoin derivatives (4a-f)

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

5,5-Dimethylhydantoin (4b)

Acetone cyanohydrin (4.25 g, 0.05 mol) and freshly powdered ammonium carbonate (7.5 g, 0.078 mol) were added to a 250 mL round-bottomed flask, which contained a stirring bar. The mixture was heated to 50 °C for 30 min, and then heated to 70-80 °C for 3 h. Next, it was heated to 90 °C and was maintained at this point until the mixture was quiescent. The colorless residue was solidified on cooling. Then the crude product was recrystallized with hot water and the yield of pure product **4b** was 2.9 g (45%).

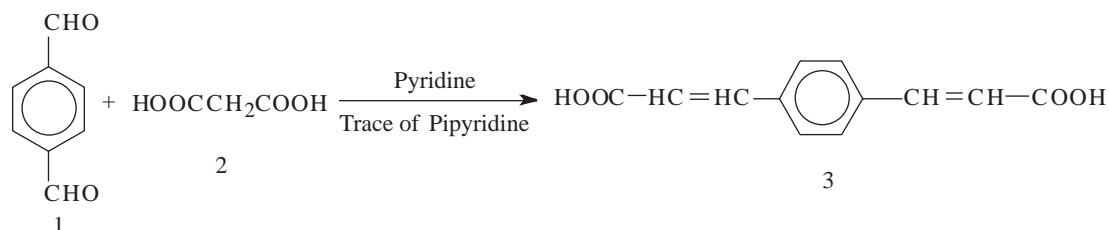
Polymer Synthesis

Polyamides **5a-f** were prepared using the following general procedure: Taking polymer **5a** as an example, diacid **3** (0.218 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 **4a** (0.1008 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 **5a** was collected by filtration and dried at 80 °C for 8 h under vacuum to leave 0.25 g (88 %) of solid.

Results and Discussion

Monomer Synthesis

p-Phenylenediacrylic acid **3** was synthesized by reaction of terephthal aldehyde **1** with malonic acid **2** in the presence of pyridine as a white solid in high yield as shown in Scheme 1.



Scheme 1

The chemical structure and purity of compound **3** was proved by elemental analysis and FT-IR and $^1\text{H-NMR}$ spectroscopic techniques. The FT-IR spectrum of compound **3** showed a broad peak between $2800\text{-}3500\text{ cm}^{-1}$, which was assigned to the COOH group. Several absorption bands at 1665 , 1610 , and 1501 cm^{-1} were observed, which are characteristic peaks for carbonyl bond, vinyl segment, and aromatic ring (Figure 1).

The $^1\text{H-NMR}$ spectrum of diacid **3** showed 2 doublet peaks at $6.54\text{-}6.57$ and $7.56\text{-}7.59$ ppm were assigned to the H_a and H_b protons of vinyl group. The peak at 7.70 ppm was assigned to the H_c protons of aromatic ring. Finally the broad peak between $12.80\text{-}13.00$ ppm was assigned to H_d protons of COOH groups (Figure 2). The measured results in elemental analyses of compound **3** are closely corresponded to the calculated ones, demonstrating that the expected compound was obtained.

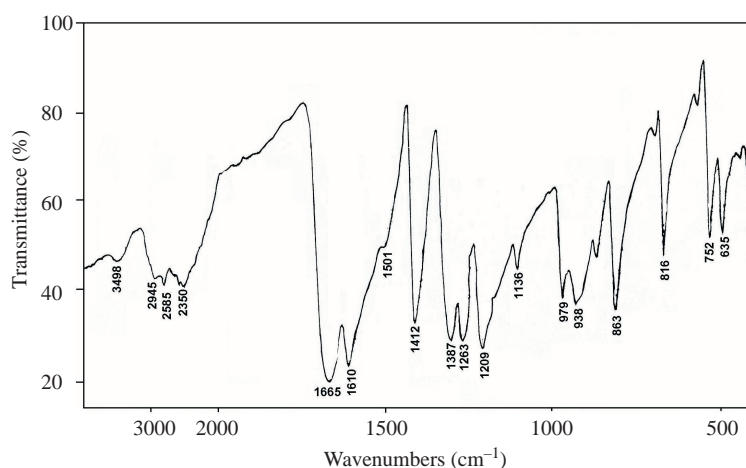
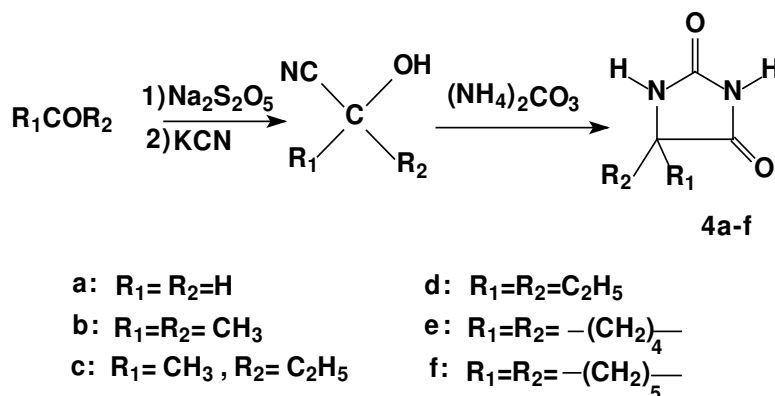


Figure 1. FT-IR Spectrum of diacid **3**.

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. By using this method, hydantoin compounds **4a-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 for the new generation of weatherproof thermally stable epoxy resins.²⁸



Scheme 2

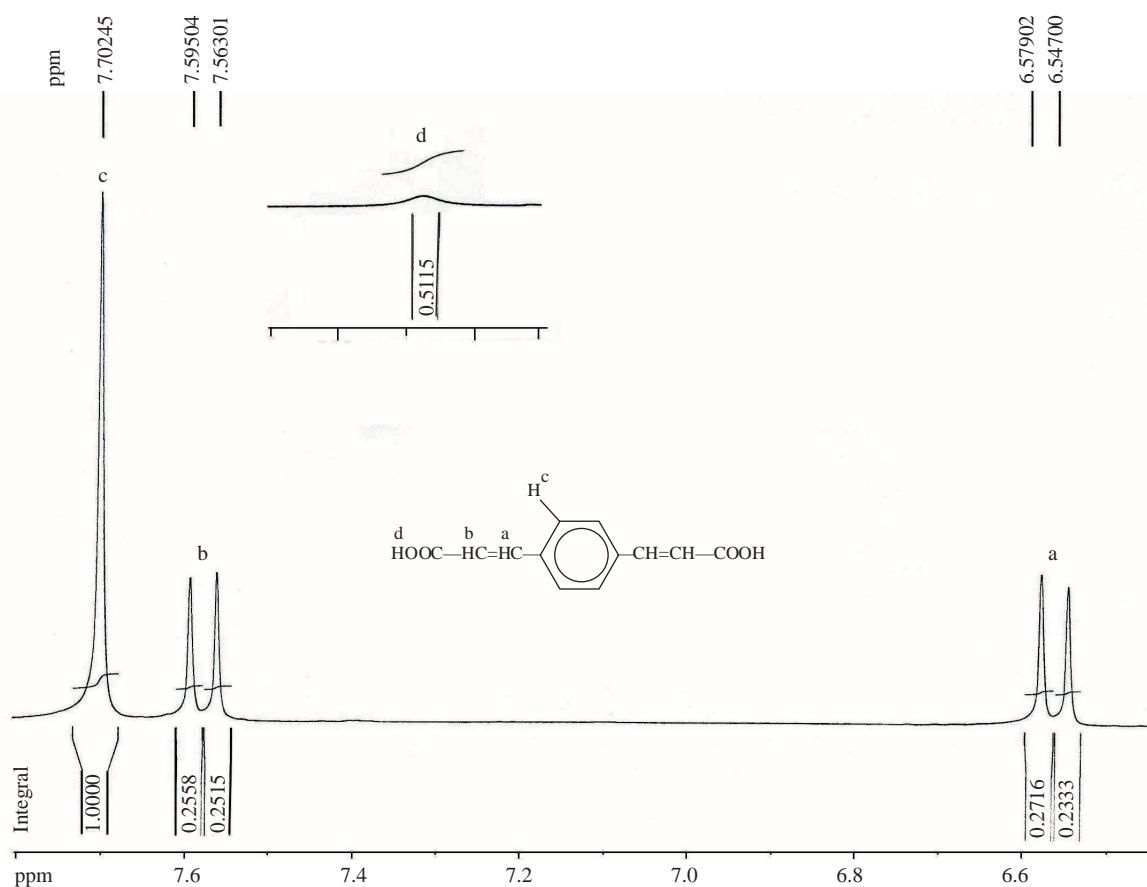
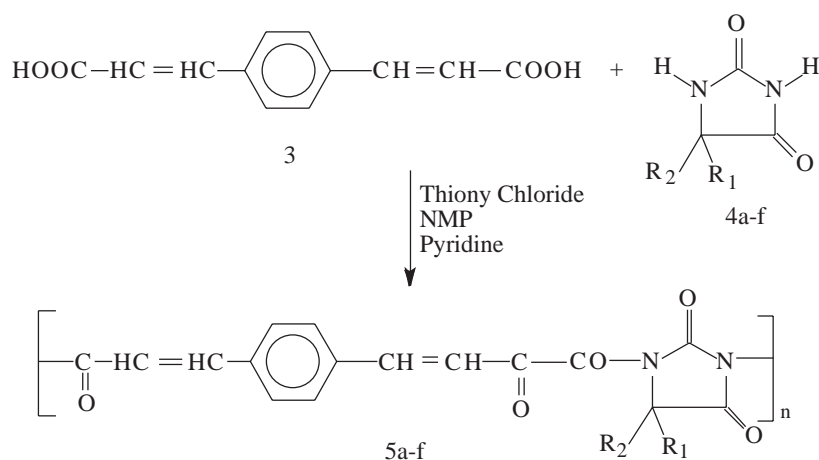


Figure 2. ¹H-NMR Spectrum of diacid **3**.

Polyamides **5a-f** were synthesized by direct solution polycondensation reactions of an equimolar diacid **3** with 6 different hydantoin derivatives (**4a-f**) using thionyl chloride and pyridine as condensing agents and N-methyl-2-pyrrolidone as solvent (Scheme 3). The entire polycondensation readily proceeded to 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 0.35-0.55 dL/g as solid.



Scheme 3

Polymer characterization

Synthesis and some physical properties of polyamides **5a-f** are summarized in Table 1. These polymers have inherent viscosities in a range between 0.35-0.55 dL/g. These polymers exhibited number-average molecular weights (M_n) and weight-average molecular weights (M_w) in the range of $1.0-2.2 \times 10^4$ and $2.3-6.0 \times 10^4$, respectively, as measured by GPC, relative to polystyrene standards.

Table 1. Some physical properties of polyamides **5a-f**.

Hydantoin	Polymer	Yield (%)	η_{inh} (dL/g) ^a	\bar{M}_n^b (10^4)	\bar{M}_w^b (10^4)	PDI
4a	5a	88	0.55	2.2	6.0	2.72
4b	5b	87	0.45	1.0	3.1	3.1
4c	5c	90	0.40	1.2	3.0	2.5
4d	5d	83	0.41	1.0	2.3	2.3
4e	5e	91	0.37	2.2	3.6	1.63
4f	5f	90	0.35	2.1	4.5	2.14

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

The structures of these polymers were confirmed as polyamides by FT-IR spectroscopy and elemental analyses (Table 2).

The representative FT-IR spectrum of polyamide **5a** is shown in Figure 3. The polymer shows absorption bands at 1668 cm^{-1} due to carbonyl of amide group. Also absorption bands around $1450-1600 \text{ cm}^{-1}$ show the presence of the aromatic ring and vinyl moiety in this polymer. The other spectra show a similar pattern.

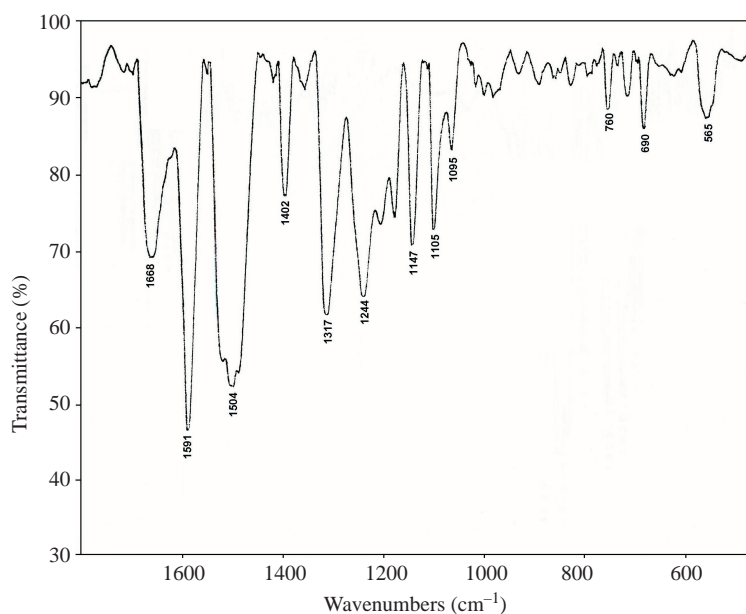


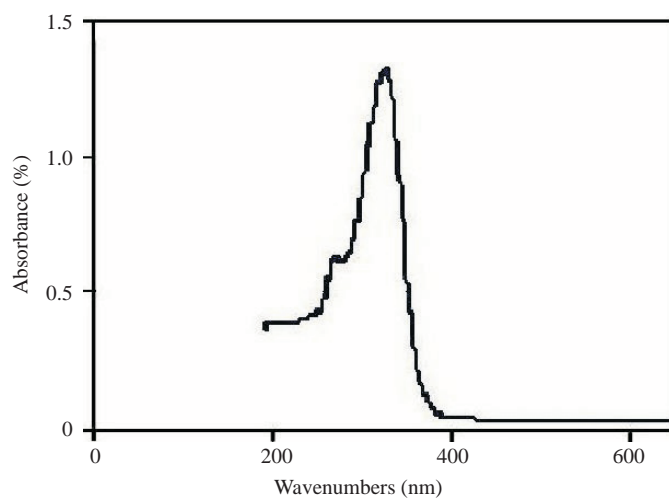
Figure 3. FT-IR Spectrum of polyamide **5a**.

The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Table 2).

Table 2. Elemental Analysis of Polyamides **5a-f**.

Polymer	Formula		C%	H%	N%
5a	$C_{15}H_{10}N_2O_4$	calcd	63.84	3.54	9.92
	$(282.12)_n$	found	63.0	3.1	9.0
5b	$C_{17}H_{14}N_2O_4$	calcd	65.82	4.51	9.02
	$(310.17)_n$	found	64.9	4.1	8.8
5c	$C_{18}H_{16}N_2O_4$	calcd	66.68	4.93	8.63
	$(324.18)_n$	found	65.9	4.2	8.2
5d	$C_{19}H_{18}N_2O_4$	calcd	67.47	5.32	8.27
	$(338.19)_n$	found	66.8	5.0	7.9
5e	$C_{19}H_{16}N_2O_4$	Calcd	67.87	4.75	7.13
	$(336.19)_n$	Found	67.0	4.0	6.9
5f	$C_{20}H_{18}N_2O_4$	calcd	68.58	5.13	7.99
	$(350.2)_n$	found	67.8	4.9	7.0

The UV-vis absorption spectra of diacid **3** and polyamide **5a** 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 **5a** exhibited the same 2 typical peaks at 265 nm ($\pi \rightarrow \pi^*$) and 325 nm ($n \rightarrow \pi^*$). By comparing the 2 spectra, a slightly blue shift was shown in polyamide **5a**.

**Figure 4.** UV Spectrum of diacid **3**.

The solubility of polyamides **5a-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, and NMP at room temperature, and are insoluble in solvents such as THF, acetone, chloroform, methylene chloride, methanol, ethanol, and water.

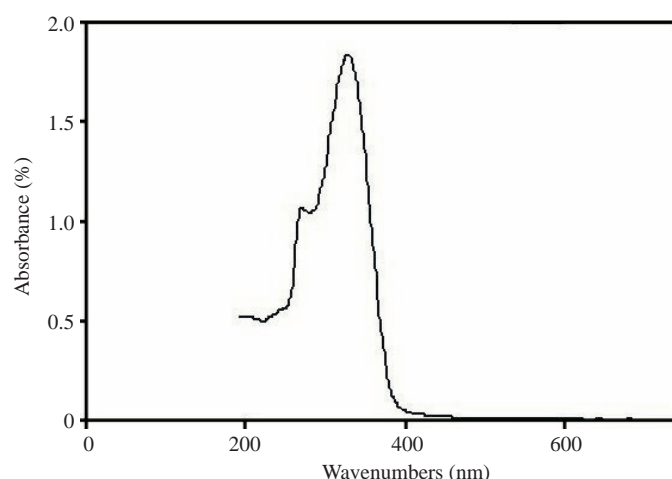


Figure 5. UV Spectrum of polyamide **5b**.

Thermal properties

The thermal properties of 2 samples of these polymers (**5a** and **5e**) were investigated by means of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min and results such as initial decomposition temperature, 5% and 10% weight loss (T_5 , T_{10}), and char yields at 600 °C are summarized in Table 3 (Figures 6 and 7). These polymers exhibited good resistance to thermal decomposition up to 350-365 °C in nitrogen and began to decompose gradually above that temperature. The residual weights for these polymers at 600 °C were 22 and 61% in nitrogen. Results showed that polyamide **5e** with spiro structure in C-5 of hydantoin ring has higher residual weight at 600 °C compared to polyamide **5a** with hydrogen in C-5 of hydantoin ring. In the DSC experiments, there is no melting endotherm in the DSC thermograms. Glass transition temperatures of these polyamides were in the range of 156-162 °C. Also polyamide **5e** has higher Tg compared to polyamide **5a**.

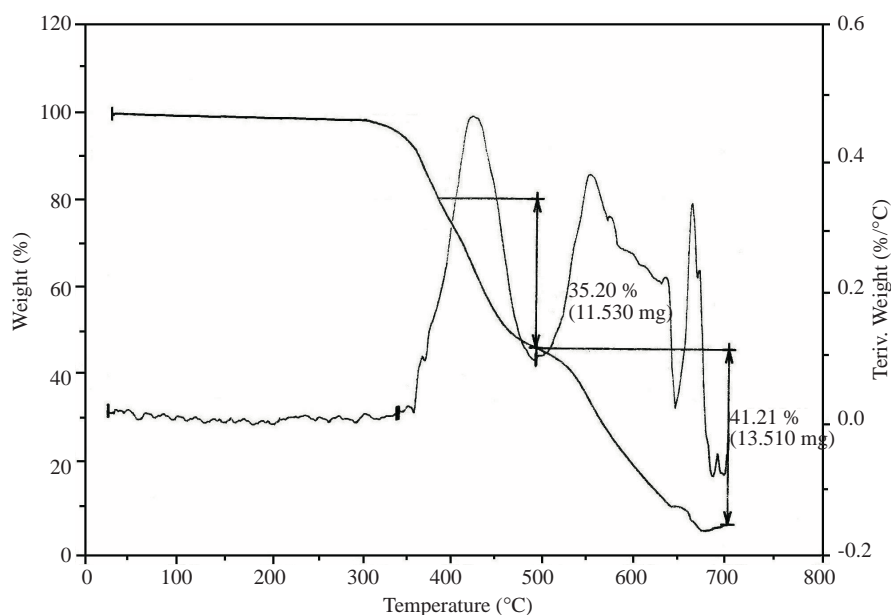


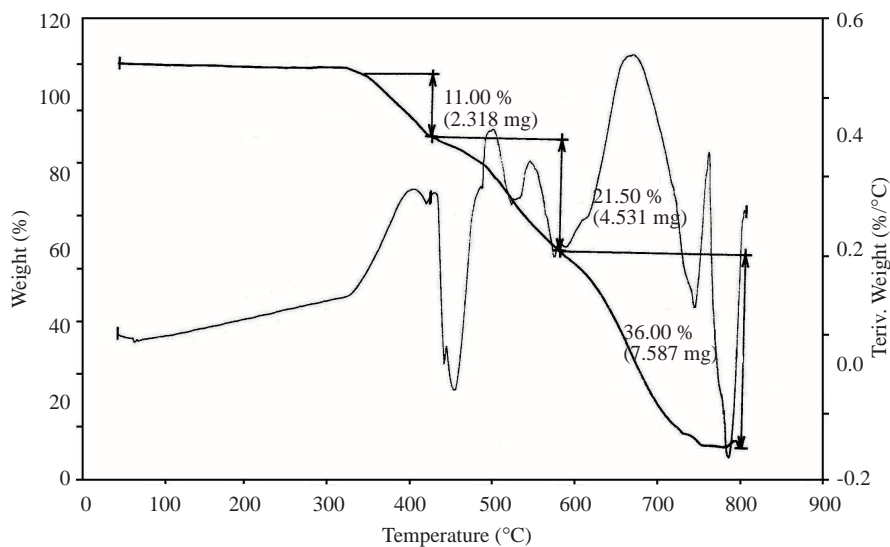
Figure 6. TGA and DTG thermogram of polyamide **5a**.

Table 3. Thermal behavior of polyamides **5a** and **5e**.

Polymer	T _g	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c (%)
5a	156	350-355	365-370	22
5e	162	365-370	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 at 600 °C.

**Figure 7.** TGA and DTG thermogram of polyamide **5d**.

Conclusion

In this article, several new polyamides (**5a-f**) by direct polycondensation reaction of monomer **3** with 6 different hydantoin derivatives (**4a-f**) using thionyl chloride and pyridine as condensing agents and N-methyl-2-pyrrolidone as a solvent were synthesized. These new polyamides are soluble in various organic solvents and have satisfactory thermal stability. These properties can make these polyamides attractive for practical applications such as processable high-performance engineering plastics.

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