

# New Polyamides Derived from 2,5-Bis[(4-carboxyanilino) carbonyl] Pyridine and Hydantoin Derivatives: Synthesis and Characterization

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We synthesized 2,5-bis[(4-carboxyanilino) carbonyl] pyridine (**4**) as a new monomer containing pyridyl moiety by using a 2-step reaction. At first 2,5-pyridine dicarboxylic acid (**1**) was converted to 2,5-pyridine dicarbonyl dichloride (**2**). Then, diacid **4** was prepared by a condensation reaction of diacid chloride (**2**) with p-aminobenzoic acid (**3**). Then, 6 new polyamides (**6a-f**) were synthesized through the polycondensation reaction of 2,5-bis[(4-carboxyanilino) carbonyl] pyridine (**4**) with 6 different derivatives of hydantoins (**5a-f**) in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. The polycondensation reaction produced a series of novel polyamides containing pyridyl moiety in the main chain in high yield, with inherent viscosities between 0.64 and 1.50 dL g<sup>-1</sup>. The resulting polymers were fully characterized by means of FT-IR spectroscopy, elemental analysis, inherent viscosity, and solubility tests. Thermal properties of these polymers were investigated using thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG). All the polymers were soluble at room temperature in polar solvents such as N,N'-dimethylacetamide, N,N'-dimethyl formamide, dimethyl sulfoxide, and N-methyl-2-pyrrolidone.

**Key Words:** Polyamides, pyridyl moiety, hydantoin derivatives, direct polycondensation.

## Introduction

Aromatic polyamides (PAs) have received considerable attention with regard to the production of high performance materials due to their outstanding thermal stability, chemical resistance, and electrical and mechanical properties.<sup>1-3</sup> However, their use is restricted because of poor solubility in organic solvents and excessively high glass transition temperatures, which make them very difficult to be processed by spin

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coating or thermoforming techniques.<sup>4,5</sup> Great effort has been made to create structurally modified aromatic polymers with increased solubility and processability, while retaining their high thermal stability. It is known that the solubility of polymers often increases when flexible bonds, large pendent groups, or polar constituents are incorporated into the polymer backbone.<sup>6–8</sup> If the pendent groups are carefully chosen, it is possible to promote solubility without affecting thermal and mechanical properties to any great extent. Furthermore, in many cases the introduction of various heterocyclic aromatic rings into the main chain of polyamides leads to polymers with improved solubility and superior thermal stability.<sup>9–12</sup> In our previous works we described the synthesis of different PAs and poly(amide-imide)s containing heterocyclic moieties in the main chain, such as hydantoin derivatives with improved solubility and thermal properties.<sup>13–20</sup>

In this article we describe the synthesis of a series of novel PAs (**6a–f**), containing pyridyl and hydantoin moieties in the main chain, from the polycondensation reaction of 2,5-bis[(4-carboxyanilino)carbonyl] pyridine (**4**) with 6 different hydantoin derivatives (**5a–f**): hydantoin (**5a**), 5,5-dimethyl hydantoin (**5b**), 5-ethyl, 5-methyl hydantoin (**5c**), 5,5-diethyl hydantoin (**5d**), 5,5-spirocyclopantyl hydantoin (**5e**), and spirocyclohexyl hydantoin (**5f**), using N-methyl-2-pyrrolidone (NMP), triphenylphosphite, and pyridine as condensing agents. These polymers have a heterocyclic aromatic ring, such as pyridyl moiety, in the main chain for better solubility in organic solvents as compared to aromatic polyamides. 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 weatherproof hightemperature-stable epoxy resins.<sup>21</sup>

## Experimental

### Materials

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

### Techniques

<sup>1</sup>H-NMR spectra were recorded on a Bruker 500 MHz instrument. Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (UK). Spectra of the solids were recorded using KBr pellets. Vibrational transition frequencies are reported in wave number (cm<sup>-1</sup>). Band intensities are denoted as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Technico<sup>®</sup> viscometer. Thermal gravimetric analysis (TGA and DTG) of the polymers was performed on a Mettler TA4000 system under N<sub>2</sub> atmosphere at a rate of 10 °C min<sup>-1</sup>. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran.

### Monomer synthesis

#### 2,5-Pyridine dicarbonyl dichloride (**2**)

Into a 100-mL round-bottomed flask were placed 2 g (11.9 mmol) of 2,5-pyridine

dicarboxylic acid (**1**), 20 mL of thionyl chloride, and 0.1 mL of pyridine as a base. The reaction mixture was heated in an oil bath at 70 °C until the suspension mixture was converted into a clear solution. Then, unreacted thionyl chloride was removed by distillation and the residue was placed under vacuum to

leave 2 g (83%) of 2,5-pyridine dicarbonyl dichloride (**2**). FT-IR (KBr): 1726 (s), 1602 (w, sh), 1402 (s), 1234 (s, sh), 1128 (s), 748 (s), 491 (m), 277 (m)  $\text{cm}^{-1}$ .

### 2,5-Bis[(4-carboxyanilino) carbonyl] pyridine (**4**)

Into a 100-mL round-bottomed flask were added (2.04 g, 10 mmol) diacid chloride and 20 mL of dry THF; the reaction mixture was cooled in an ice-water bath and then a solution of 4-amino benzoic acid (**3**) (2.6874 g, 20 mmol) in 20 mL of dry THF was slowly added over 10 min. The reaction mixture was stirred overnight at room temperature and after cooling the excess solvent was removed by distillation and the residue was washed twice with hot water to give the pure diacid (**4**) (3.72 g, 92% yield); mp 380 °C (dec). 3331 (m), 2500-3100 (s, br), 1687 (s, br), 1593 (s), 1523 (s), 1441 (s), 1294 (s, br), 1178 (s), 1022 (m), 947 (w), 856 (m), 771 (m), 678 (m), 551 (m). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, TMS),  $\delta$ : 7.91-7.96 (m, 4H), 8.04-8.12 (m, 5H), 8.33-8.35 (d, 2H), 9.09 (s, 2H), 10.94 (s, 2H). Analysis: Calculated for C<sub>21</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>: C, 62.24; H, 3.70; N, 10.36; found: C, 62.0; H, 3.6; N, 10.0.

### Hydantoin derivatives (**5a-f**)

These compounds were prepared according to a typical procedure that is shown in Scheme 2.<sup>13</sup>

### Polymer synthesis

The PAs (**6a-f**) were prepared by the following general procedure (using polymer **6a** as an example). Into a 25-mL round-bottomed flask that was fitted with a stirring bar were placed hydantoin (**5a**) (0.03 g, 0.32 mmol), diacid (**4**) (0.13 g, 0.32 mmol), calcium chloride (0.10 g, 0.90 mmol), triphenyl phosphite (0.84 ml, 3.00 mmol), pyridine (0.18 ml), and N-methyl-2-pyrrolidone (0.8 mL). The reaction mixture was heated under reflux in an oil bath at 60 °C for 1 h, then at 90 °C for 2 h and 130 °C for 8 h. Afterwards, the reaction mixture was poured into 25 mL of methanol and the precipitated polymer was collected by filtration, washed thoroughly with methanol, and then dried at 60 °C for 12 h under vacuum to leave 0.12 g (78%) of yellow solid polymer **6a**. The PAs (**6a-f**) were analyzed using FT-IR spectroscopy.

### Polymer **6a**, FT-IR (KBr)

3327 (m), 3081 (w), 1732 (s), 1678 (s), 1606 (s), 1523 (s), 1410 (s), 1300 (s), 1269 (s), 1176 (s), 1078 (s), 1024 (m), 943 (m), 854 (m), 763 (s), 688 (s), 551 (w), 507 (m).

### Polymer **6b**, FT-IR (KBr):

3327 (m), 3087 (m), 2858 (w), 2580 (w), 1984 (w, br), 1778 (w), 1730 (s), 1678 (s), 1606 (s), 1528 (s), 1481 (s), 1332 (s), 1286 (s), 1176 (s), 1116 (w), 1078 (m), 945 (w), 854 (m), 788 (m), 688 (m), 640 (w), 551 (w), 505 (w).

### Polymer **6c**, FT-IR (KBr):

3321 (m), 3059 (w), 1730 (s), 1666 (s), 1593 (s), 1523 (s), 1410 (s), 1321 (s), 1269 (s), 1078 (m), 1024 (m), 941 (m), 852 (m), 763 (m), 686 (m), 640 (w), 507 (w).

**Polymer 6d, FT-IR (KBr):**

3321 (w), 3057 (w), 1730 (s), 1678 (s), 1606 (s), 1523 (s), 1491 (s), 1411 (s), 1321 (s), 1296 (s), 1195 (s), 1078 (m), 1026 (w), 943 (w), 854 (w), 763 (m), 688 (m).

**Polymer 6e, FT-IR (KBr):**

3329 (m), 3070 (m), 1786 (w), 1730 (s), 1680 (s), 1591 (s), 1521 (s), 1411 (s), 1321 (s), 1267 (s), 1178 (s), 1078 (s), 947 (w), 854 (m), 765 (w), 688 (m), 640 (w), 503 (w).

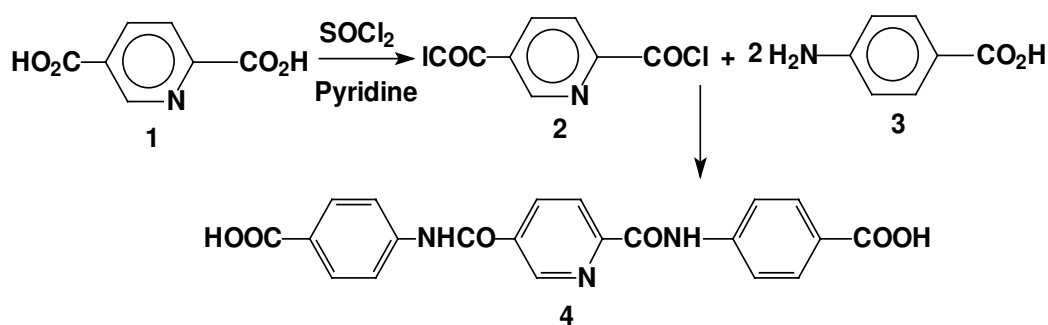
**Polymer 6f, FT-IR(KBr):**

3321 (m), 3080 (w), 2661 (w), 2544 (w), 1730 (s), 1680 (s), 1593 (s), 1523 (s), 1411 (s), 1321 (s), 1269 (s), 1178 (s), 1144 (w), 1080 (m), 1028 (w), 943 (w), 895 (w), 854 (w), 783 (m), 686 (m), 640 (w), 551 (w), 503 (w).

## Results and Discussion

### Monomer synthesis

2,5-Bis[(4-carboxyanilino) carbonyl] pyridine (**4**) was synthesized through the condensation reaction of 1 equivalent of 2,5-pyridine dicarbonyl dichloride (**2**) with 2 equivalents of 4-amino benzoic acid (**3**) in extra pure THF, as shown in Scheme 1. Then, diacid acid **4** was washed with hot water and purified by recrystallization from DMF.



**Scheme 1.** Synthesis of 2,5-bis[(4-carboxyanilino) carbonyl] pyridine (**4**).

The chemical structure and purity of this compound were proven with elemental analysis, and  $^1\text{H-NMR}$  and FT-IR spectroscopy. The measured results of elemental analysis of diacid **4** closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. The FT-IR spectrum of compound **4** showed a broad peak between 2500 and 3100  $\text{cm}^{-1}$ , which was assigned to the COOH group and the absorption band that appeared at 3321  $\text{cm}^{-1}$  was assigned to the NH groups (Figure 1).

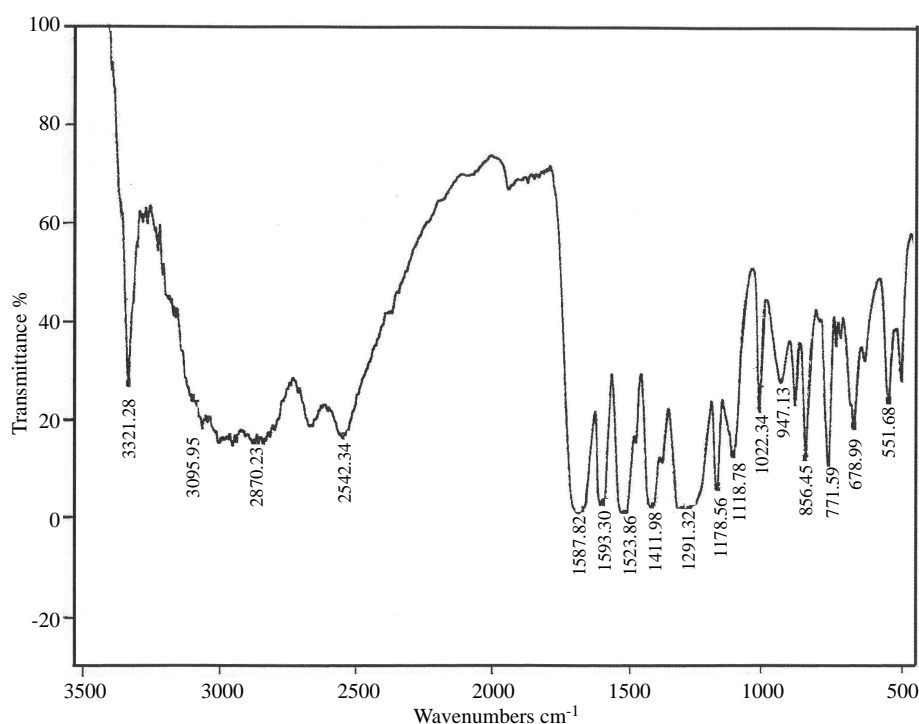
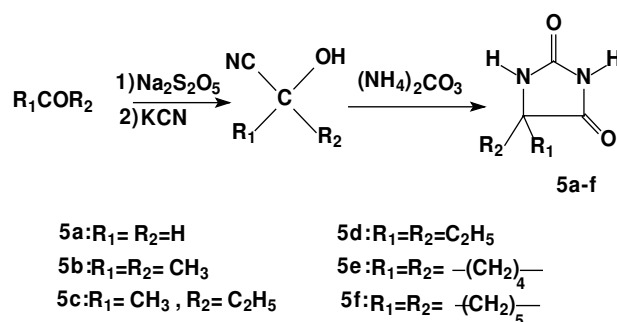


Figure 1. FT-IR spectrum of diacid 4.

The  $^1\text{H-NMR}$  spectrum of compound 4 showed a broad singlet peak at 10.94 ppm, which was assigned to the  $\text{H}_a$  proton of the  $\text{COOH}$  groups. The broad singlet peak at 9.09 ppm was assigned to the  $\text{H}_b$  and  $\text{H}_c$  protons of the  $\text{NH}$  groups. The peak between 8.33 and 8.35 ppm was assigned to the  $\text{H}_d$  and  $\text{H}_e$  protons of the pyridine ring. Peaks between 8.04 and 8.12 ppm were assigned to the  $\text{H}_f$  proton of the pyridine ring, and  $\text{H}_g$  and  $\text{H}_h$ , protons of the phenyl rings. Finally, a peak between 7.91 and 7.94 ppm was assigned to the  $\text{H}_i$  and  $\text{H}_j$  protons of the phenyl ring (Figure 2).

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.<sup>21</sup> 5,5-Disubstituted hydantoin derivatives were synthesized by the Bucherer-Berg method. By using this method hydantoin compounds (**5a-f**) (Scheme 2) were prepared through the reaction of cyanohydrin derivatives with ammonium carbonate.



Scheme 2. Synthesis of hydantoin derivatives (**5a-f**).

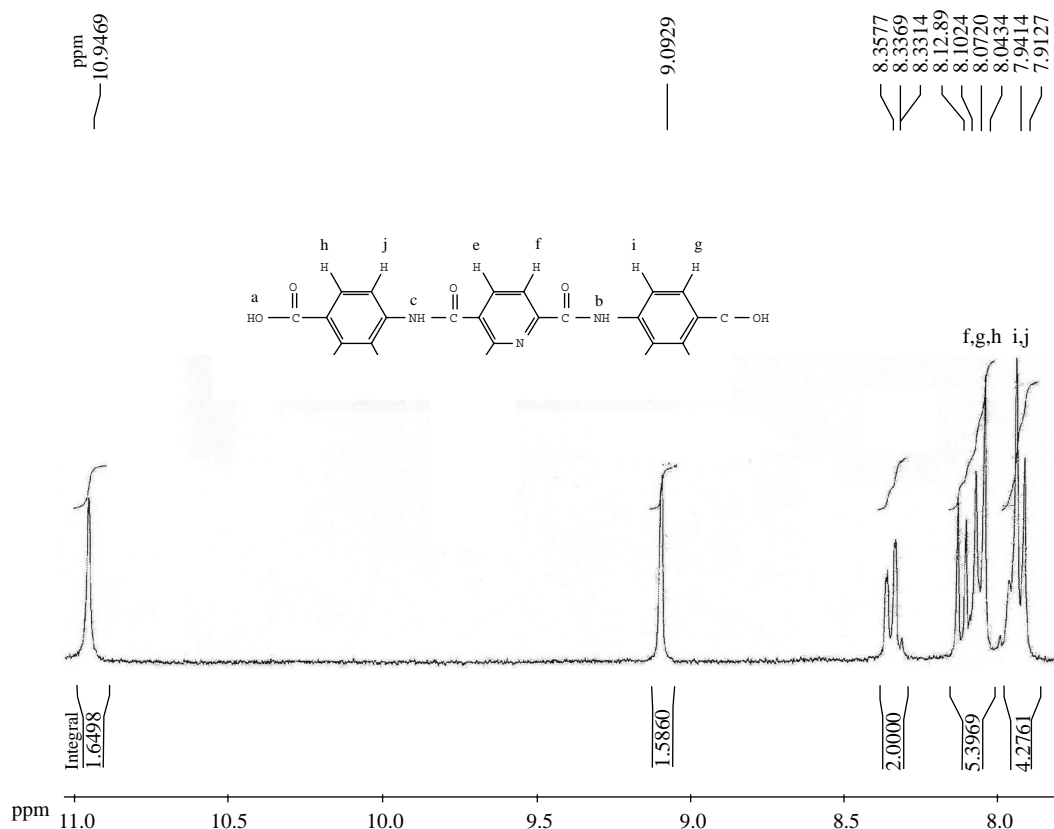
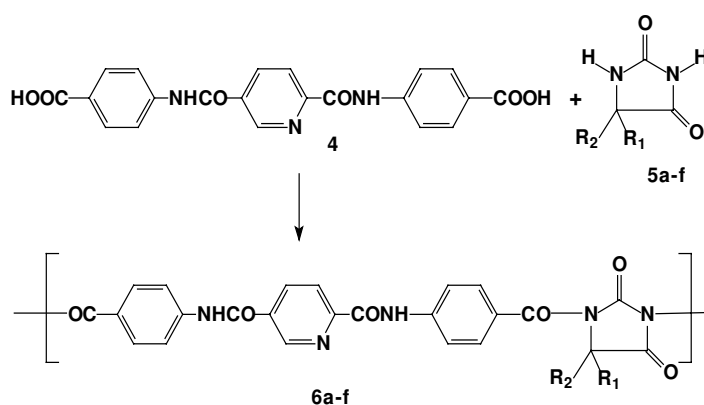


Figure 2.  $^1\text{H-NMR}$  spectrum of diacid **4**.

## Polymer synthesis

PAs **6a-f** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **4** with 6 hydantoin compounds (**5a-f**) in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine (Scheme 3).



Scheme 3. Synthesis of polyamides **6a-f**.

The synthesis and some physical properties of these new PAs (**6a-f**) are given in Table 1. The entire polycondensation reaction readily proceeded in a homogeneous solution, while tough and stringy precipitates formed as the viscous PA solutions were obtained in moderate to good yields.

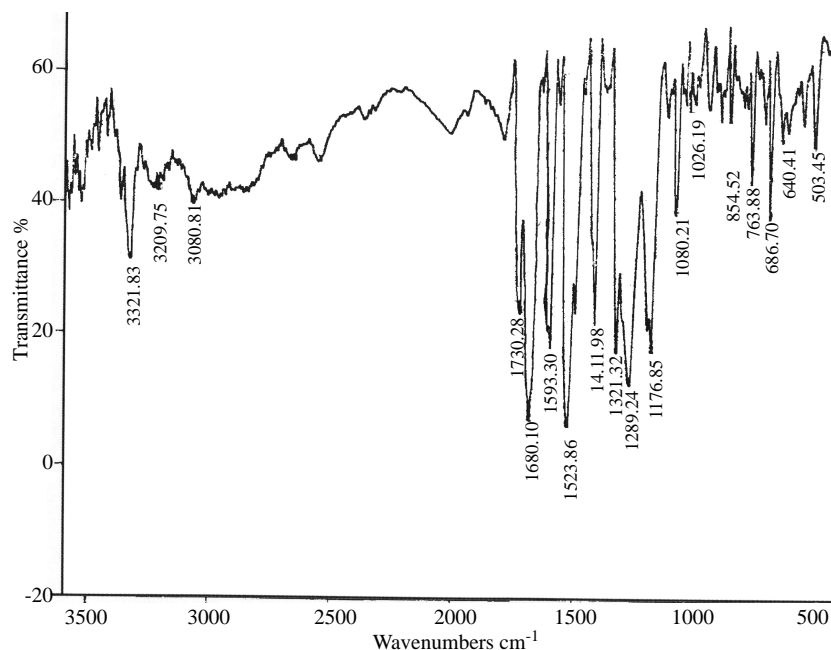
**Table 1.** Synthesis and some physical properties of the PAs (**6a-f**).

Hydantoin derivatives	Polymer	Yield (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>
<b>5a</b>	<b>6a</b>	78	1.50
<b>5b</b>	<b>6b</b>	74	0.80
<b>5c</b>	<b>6c</b>	81	0.64
<b>5d</b>	<b>6d</b>	83	0.78
<b>5e</b>	<b>6e</b>	73	1.03
<b>5f</b>	<b>6f</b>	77	0.96

<sup>a</sup>Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

### Polymer characterization

The synthesis and some physical properties of the PAs (**6a-f**) are summarized in Table 1. These polymers had inherent viscosities around 0.64-1.50 dL/g and showed yellow crystals. These polymers were confirmed to be PAs with FT-IR spectroscopy and elemental analysis (Table 2). A representative FT-IR spectrum of polymer **6d** is shown in Figure 3. FT-IR spectra show that the carbonyl peak of the polymer shifted to a lower frequency in comparison to diacid **4** and that the OH peak at 2500-3100  $\text{cm}^{-1}$  of diacid disappeared.

**Figure 3.** FT-IR spectrum of PA **6f**.

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

The solubility of the PAs (**6a-f**) was investigated with 0.01 g of polymeric samples in 2 mL of solvent. All of the polymers were dissolved in organic solvents, such as DMF, DMAC, DMSO, and NMP, at room

temperature and were insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

**Table 2.** Elemental analysis of the PAs (**6a-f**).

Polymer	Formula		C%	H%	N%
<b>6a</b>	C <sub>24</sub> H <sub>15</sub> N <sub>5</sub> O <sub>6</sub> (469.41)n	Calcd	61.41	3.22	14.92
		found	61.90	3.00	13.90
<b>6b</b>	C <sub>26</sub> H <sub>19</sub> N <sub>5</sub> O <sub>6</sub> (497.46)n	Calcd	62.77	3.85	14.08
		found	61.40	3.10	13.50
<b>6c</b>	C <sub>27</sub> H <sub>21</sub> N <sub>5</sub> O <sub>6</sub> (511.5)n	Calcd	63.40	4.14	13.69
		found	62.50	3.50	12.90
<b>6d</b>	C <sub>28</sub> H <sub>23</sub> N <sub>5</sub> O <sub>6</sub> (525.52)n	Calcd	63.99	4.41	13.33
		found	62.80	3.40	12.80
<b>6e</b>	C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> O <sub>6</sub> (535.51)n	Calcd	65.04	3.95	13.08
		found	64.00	3.10	12.80
<b>6f</b>	C <sub>30</sub> H <sub>23</sub> N <sub>5</sub> O <sub>6</sub> (549.54)n	Calcd	65.57	4.22	12.74
		found	66.10	3.20	11.50

**Table 3.** Solubility of the PAs (**6a-f**).

Solvents	<b>6a</b>	<b>6b</b>	<b>6c</b>	<b>6d</b>	<b>6e</b>	<b>6f</b>
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	+	+	+	+	+	+
Acetone	+	+	+	+	+	+
CHCl <sub>3</sub>	-	-	-	-	-	-
EtOH	-	-	-	-	-	-
MeOH	-	-	-	-	-	-
CH <sub>2</sub> Cl <sub>2</sub>	-	-	-	-	-	-
H <sub>2</sub> O	-	-	-	-	-	-

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

## Thermal properties

The thermal properties of the PAs (**6a-f**) were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup> and the thermal data are summarized in Table 4 (Figures 4 and 5). The initial decomposition temperatures of 5% and 10% weight loss (T<sub>5</sub> and T<sub>10</sub>), and the char yield at 600 °C for **6c**, **6d**, and **6e** are summarized in Table 4. These polymers exhibited good resistance to thermal decomposition up to 280-310 °C in nitrogen and began to decompose gradually above that temperature. T<sub>5</sub> for polymers **6a**, **6c**, and **6d** ranged from 285 to 310 °C, T<sub>10</sub> for all polymers ranged from 300 to 315 °C, and the residual

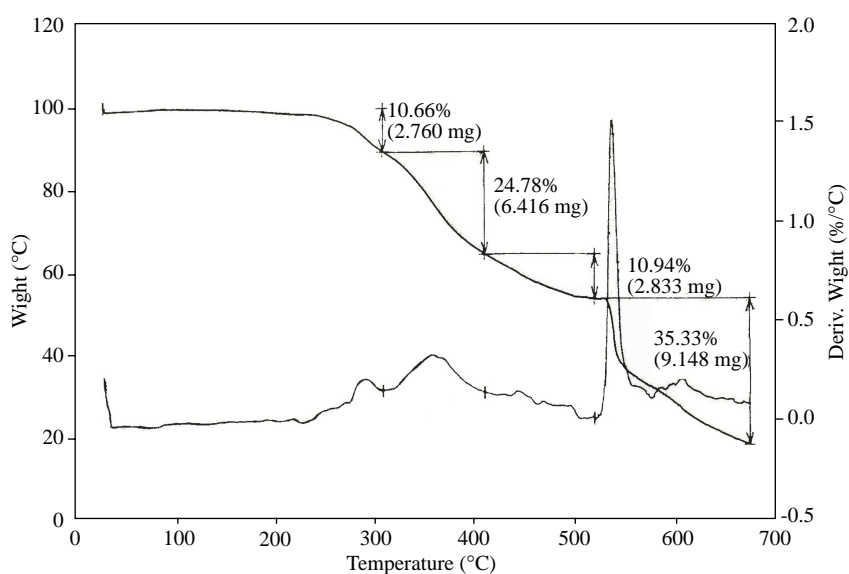


weight for these polymers at 600 °C ranged from 21% to 24% in nitrogen. These results show that the PAs (**6a-f**) have thermal resistance and can be used as engineering plastic in many applications.

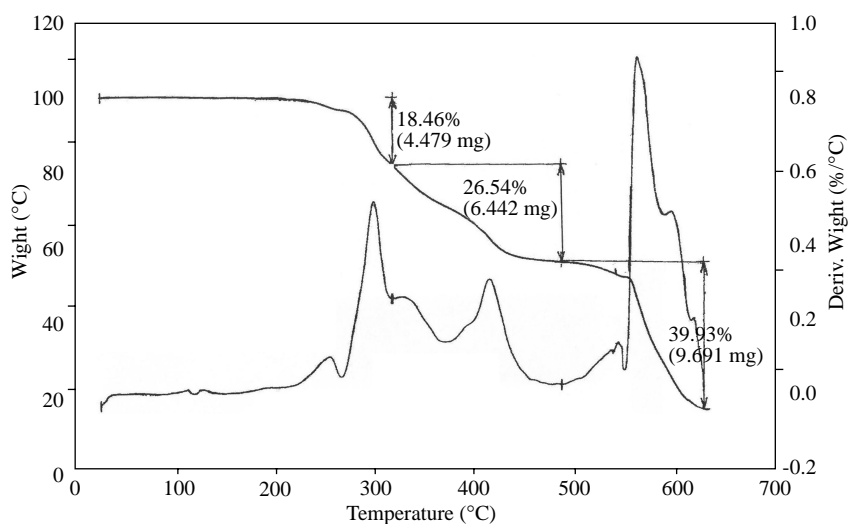
**Table 4.** Thermal behavior of the PAs (**6a,c,d**).

Polymer	T <sub>5</sub> (°C) <sup>a</sup>	T <sub>10</sub> (°C) <sup>b</sup>	Char Yield <sup>c</sup>
<b>6a</b>	270-275	305-310	21 %
<b>6c</b>	275-280	300-305	23 %
<b>6d</b>	280-285	290-295	24 %

<sup>a,b</sup>Temperature at which 5% and 10% weight loss was recorded by TGA at the heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub>, respectively. <sup>c</sup> Percentage weight of undecomposed material left after TGA analysis at 600 °C.



**Figure 4.** TGA and DTG thermogram of PA **6c**.



**Figure 5.** TGA and DTG thermogram of PA **6d**.

## Conclusion

This work involved the synthesis of several new PAs (**6a-f**) through the direct polycondensation reaction of diacid **4** with 6 hydantoin compounds (**5a-f**) using triphenyl phosphite, NMP, calcium chloride, and pyridine as condensing agents. These new PAs were soluble in various organic solvents and had good thermal stability. The presence of pyridyl segments as a heterocyclic ring in the backbone increased the solubility of these polymers. These properties could make these PAs attractive for practical applications, such as processable high-performance engineering plastics.

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