Synthesis and Characterization of New Thermally Stable Polyamides Based on 2,5-Pyridine Dicarboxylic Acid and Hydantoin Derivatives

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Abstract

Introduction: Aromatic polyamides 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. However their application are restricted because of their poor solubility in organic solvents and too high glass transition temperatures that make them very difficult to be processed by spin coating or thermoforming techniques. Much effort has been made to create structurally modified aromatic polymers having increased solubility and processability with retention of their high thermal stability. It is known that the solubility of polymers is often increased when flexible bonds such as [-O-, -SO_2-, -CH_2-, -$C(CF_3\text{-})_2$], bulky pendent groups (such as t-butyl, adamantyle and naphtyl), large pendent groups or polar constituents such as heterocyclic segments are incorporated into the polymer backbone due to the altering crystallinity and intermolecular interactions.

Aim: In this article, synthesis and characterization of six new polyamides 3**a-f** containing pyridyl and hydantoin moieties in the main chain from the polycondensation reaction of 2,5-pyridine dicarboxylic acid **1** with six different of hydantoins derivatives **2a-f** such as hydantoin **2a**, 5,5-dimethyl hydantoin 2**b**, 5-ethyl, 5-methyl hydantoin **2c**, 5,5-diethyl hydantoin **2d,** 5,5-spirocyclopantyl hydantoin **2e,** spirocyclohyxyl hydantoin **2f** by using N-methyl-2-pyrrolidone (NMP), triphenylphosphite and pyridine as condensing agents was reported.

Materials and Methods: All chemicals were purchased from Fluka and Merck Chemical Company. The ^{1}H-NMR spectrum (300 MHz) was recorded on a Bruker Avance 300 spectrometer (Germany). Fourier transform infrared (FT-IR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England).

Results: Six new thermally stable polyamides **3a-f** were synthesized through the polycondensation reaction of 2,5-pyridine dicarboxylic acid **1** with six different derivatives of hydantoins **2a-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 and hydantoin moieties in the main chain in high yield with inherent viscosities between 0.56-0.80 dL/g. The resulting polymers were fully characterized by means of FT-IR spectroscopy, elemental analyses, inherent viscosity, and solubility tests. Thermal properties of these polymers were investigated by using thermal gravimetric analysis (TGA), differantional thermal gravimetric (DTG).

Conclusion: This work involved the syntheses of several new PAs **3a-f** through the direct polycondensation reaction of diacid **1** with six hydantoin compounds **2a-f** by 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 pridyl segments as a hetrocyclic ring into 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.

***Keywords*:** Polyamides. pyridyl moiety. hydantoin derivatives. direct polycondensation

Introduction

Aromatic polyamides 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.[1-3] However their application are restricted because of their poor solubility in organic solvents and too high glass transition temperatures that make them very difficult to be processed by spin coating or thermoforming techniques.[4-5] Much effort has been made to create structurally modified aromatic polymers having increased solubility and processability with retention of their high thermal stability. It is known that the solubility of polymers is often increased when flexible bonds such as [-O-, -SO_2-, -CH_2-, -$C(CF_3\text{-})_2$], bulky pendent groups (such as t-butyl, adamantyle and naphtyl), large pendent groups or polar constituents such as heterocyclic segments are incorporated into the polymer backbone due to the altering crystallinity and intermolecular interactions.[6-8] If the flexible segments are carefully chosen, it is possible to promote solubility without affecting thermal and mechanical properties to any great extent.[9-17] In our pervious papers we described synthesis of different polyamides and poly(amide-imide)s containing heterocyclic moieties in the main chain such as hydantoin derivatives with improved solubility and thermal properties.[18-23] In this article, synthesis and characterization of six new polyamides 3**a-f** containing pyridyl and hydantoin moieties in the main chain from the polycondensation reaction of 2,5-pyridine dicarboxylic acid **1** with six different of hydantoins derivatives **2a-f** such as hydantoin **2a**, 5,5-dimethyl hydantoin 2**b**, 5-ethyl, 5-methyl hydantoin **2c**, 5,5-diethyl hydantoin **2d,** 5,5-spirocyclopantyl hydantoin **2e,** spirocyclohyxyl hydantoin **2f** by using N-methyl-2-pyrrolidone (NMP), triphenylphosphite and pyridine as condensing agents was reported. These polymers have a heterocyclic aromatic ring such as pyridyl moiety in main chain for improving solubility in organic solvents in 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 of weatherproof high-temperature-stable epoxy resins. [24]

Materials and Method

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

Techniques

^{1}H-NMR spectra were recorded on a Bruker 500 MHz instrument. 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 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 by 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. Weight–average (Mw) and number–average molecular weights (Mn) 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

Hydantoin derivatives 2a-f

These compounds were prepared according to a typical procedure that was shown in Scheme 1. [25]

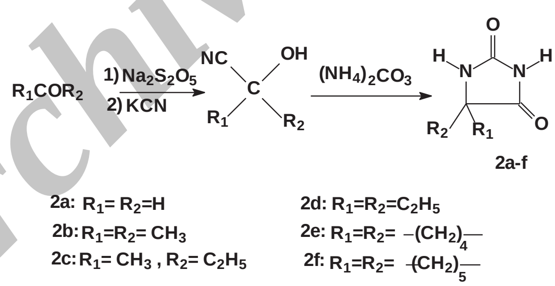
Polymer synthesis

The PAs **3a-f** were prepared by the following general procedure (using polymer **3a** as an example). Into a 25 ml round-bottomed flask which was fitted with a stirring bar were placed hydantoin **2a** (0.064 g, 0.64 mmol), diacid **1** (0.106 g, 0.64 mmol), calcium chloride (0.20 g, 1.80 mmol), triphenyl phosphite (1.68 ml, 6.00 mmol), pyridine (0.36 ml) and *NMP* (1.6 ml). The reaction mixture was heated under reflux on an oil bath at 60˚C for 1 h, then 90˚C for 2 hrs, and 130˚C for 8 hrs. Then the reaction mixture was poured into 25 ml of methanol and the precipitated polymer was collected by filtration and washed thoroughly with methanol and was dried at 60˚C for 12 hrs under vacuum to leave 0.133 g (91%) of yellow solid polymer **3a**.

Results and discussion

Monomer synthesis

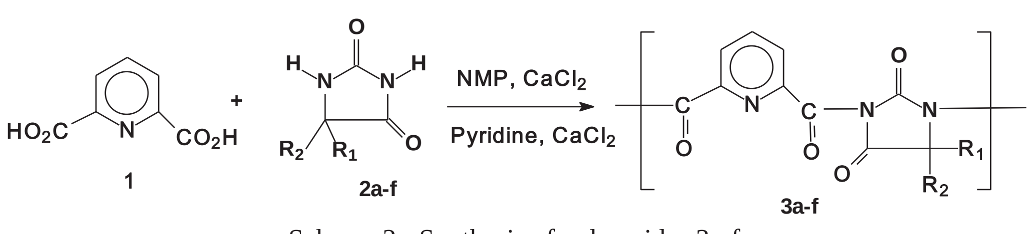
Hydantoin constitute an impotant class of heterocyclic compounds in medicinal chemistry because many derivatives have been identified to display interesting activities against a broad range of biological targets.[24] 5,5-Disubstituted hydantoin derivatives were synthesized by the Bucherer-Berg method. By using this method, hydantoin compounds **2a-f** (scheme 1) were prepared through the reaction of cyanohydrin derivatives with ammonium carbonat.



Scheme 1- Synthesis of hydantoin derivatives **2a-f**

Polymer synthesis

PAs **3a-f** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **1** with six hydantoin compounds **2a-f** in a medium consisting of *NMP*, triphenyl phosphite, calcium chloride and pyridine (Scheme 2).



Scheme 2 - Synthesis of polyamides 3a-f

The syntheses and some physical properties of these new PAs **3a-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 PAs solution was obtained in good yields.

Table 1- Synthesis and some physical properties of PAs **3a-f**

Hydantoins	Polymer	Yield(%)	η_{inh}(dL/g) [a]	$\bar{M}_n$ [b] (10^4)	$\bar{M}_w$ [b] (10^4)	PDI
2a	**3a**	91	0.80	2.2	3.4	1.54
2b	**3b**	90	0.65	1.7	3.4	2.00
2c	**3c**	86	0.56	1.4	3.6	2.57
2d	**3d**	83	0.78	2.1	4.5	2.14
2e	**3e**	91	0.60	1.9	3.9	2.05
2f	**3f**	89	0.72	1.8	3.6	2.00

[a] Measured at a concentration of 0.5g /dL in DMF at 25°C. [b] Measured by GPC in THF, polystyrene was used as standard

Polymer characterization

The syntheses and some physical properties of PAs **3a-f** are summarized in Table 1. These polymers had inherent viscosities around 0.56-0.80 dL/g and showed white crystal. These polymers were confirmed to be PAs with FT-IR spectroscopy and elemental analyses. A representative FT-IR spectrum of polymer **3a** is shown in Figure 1. FT-IR spectrum shows that the carbonyl peak of polymer shift to lower frequency in comparison with diacid **1** and OH peak at 2500-3100 cm^{-1} of diacid disappeared (Table 2).

Table 2 - FTIR Spectra of PAs 3a-f

FTIR Spectroscopic Data
Polymer (3a): 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 (3b): 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 (3c): 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 (3d): 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 (3e): 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 (3f): 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).

The GPC data of the PAs **3a-f** are shown in Table 1, Mn and Mw values available in the range of 1.4– 2.2 × 10^4 and 3.4–4.5 ×10^4 respectively, as measured by GPC, relative to polystyrene standards. The polydispersity index (PDI) Mw/Mn values were 1.54–2.57.

The elemental analysis of the resulting polymers is in good agreement with the calculated values for the proposed structures (Table 3).

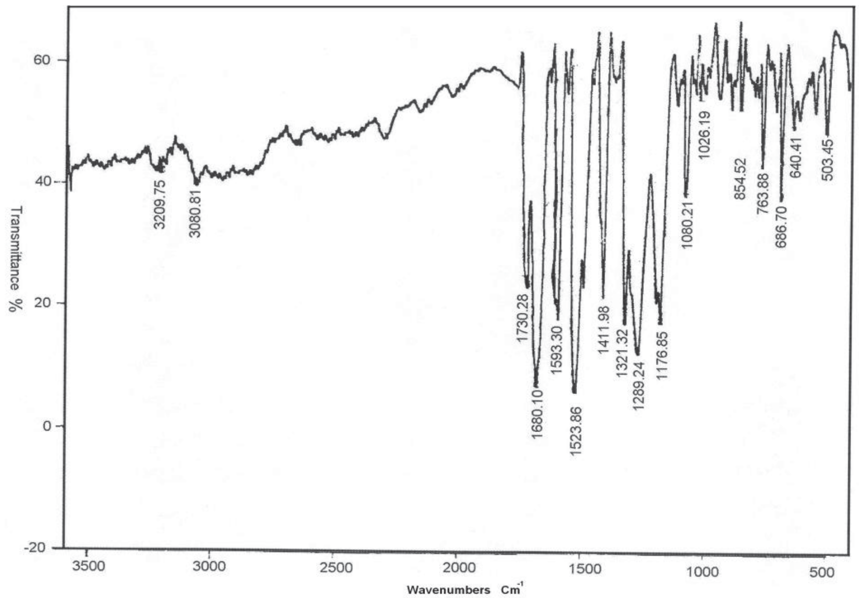


Fig. 1 FTIR Spectrum of PA 3a

Table 3- Elemental Analysis of PAs **3a-f**

Polymer	Formula		C%	H%	N%
	$C_{10}H_5N_3O_4$	Calcd	51.96	2.16	18.17
3a	$(231.10)_n$	found	50.60	2.00	17.80
	$C_{12}H_9N_3O_4$	Calcd	55.61	3.47	16.20
3b	$(259.12)_n$	found	54.90	3.00	15.80
	$C_{13}H_{11}N_3O_4$	Calcd	57.16	4.02	15.37
3c	$(273.13)_n$	found	56.80	3.70	14.60
	$C_{14}H_{13}N_3O_4$	Calcd	58.55	4.52	14.62
3d	$(287.14)_n$	found	58.00	4.10	14.00
	$C_{14}H_{11}N_3O_4$	Calcd	58.96	3.85	14.72
3e	$(285.14)_n$	found	58.10	3.30	14.00
	$C_{15}H_{13}N_3O_4$	Calcd	60.22	4.34	14.03
3f	$(299.15)_n$	found	60.90	4.00	13.70

The solubility of PAs **3a-f** was investigated with 0.01g polymeric samples in 2 ml of solvent. All of the polymers are dissolved in organic solvents such as DMF, DMAC, DMSO and NMP at room temperature and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Table 4- Solubility of PAs **3a-f**

Solvents	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	-	-	_ -	-_	-	-_
Acetone	-	-	_ -	-_	-	-_
$CHCl_3$	-	-	_ -	-_	-	-_
EtOH	-	-	_ -	-_	-	-_
MeOH	-	-	_ -	-_	-	-_
CH_2Cl_2	-	-	_ -	-_	-	-_
H_2O	-	-	_ -	-_	-	-_

+: Soluble at room temperature, –: Insoluble at room temperature

Thermal properties

The thermal properties of PAs **3a-f** were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10^{o}C/min^{-1} and the thermal data are summarized in Table 5 (Fig. 2 and 3). The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600°C for these polymers are summarized in Table 5. These polymers exhibited good resistance to thermal decomposition, up to 400-530 ºC in nitrogen, and began to decompose gradually above that temperature. T_5 for these polymers ranged from 400 to 530 ºC and T_{10} for all polymers ranged from 430 to 550 ºC, and the residual weight for these polymers at 600 ºC ranged from 69 to 88 % in nitrogen. These results show PAs **3a-f** have thermal resistance and they can be used as engineering plastic in many applications. Results show polyamides **3e** and **3f** containing spirocyclopantyl and spirocyclohexyl substituents in C-5 of hydantoin ring exhibited higher resistance to thermal decomposition at T_5 and T_{10} in comparison than other polyamides. Also polyamides **3a-d** show lower thermal stability in compare to **3e-f** because they have aliphatic constituents such as CH_3 and C_2H_5 in C-5 of hydantoin ring.

Table 5- Thermal behavior of PAs 3a-f

Polymer	T_5 (^{o}C) [a]	T_{10} (^{o}C) [b]	Char Yield [c]
3a	495-500	525-530	76%
3b	450-455	465-470	70%
3c	440-445	470-475	69%
3d	400-405	430-435	71%
3e	570-575	585-590	88%
3f	530-535	550-560	80%

[a,b]Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10^{o}C/min in N_2 respectively. [c]Percentage weight of material left undecomposed after TGA analysis 600 ^{O}C.

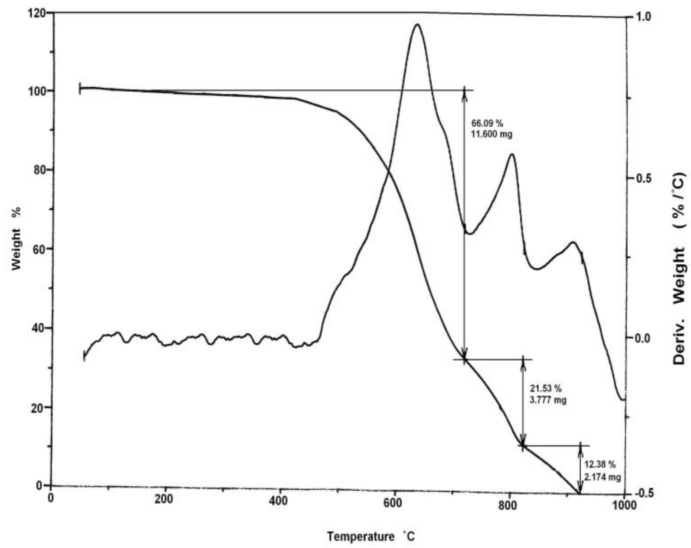


Fig. 2 TGA & DTG thermogram of PA 3a

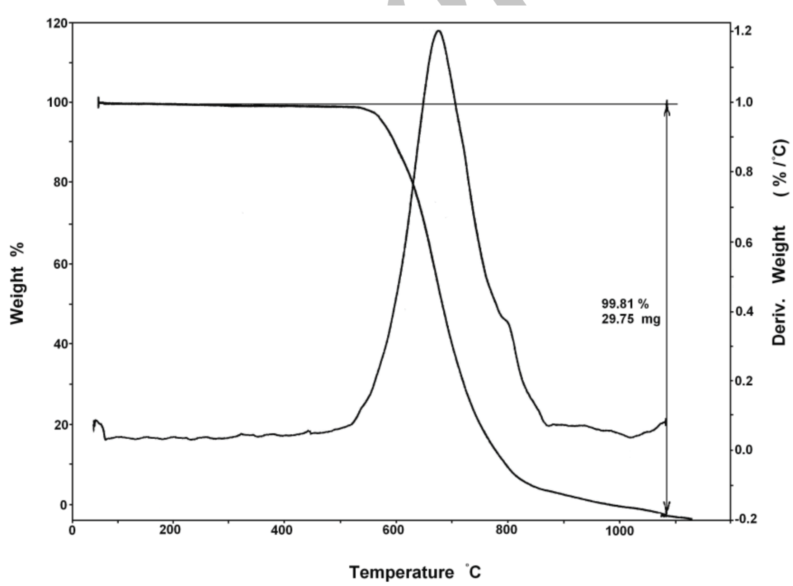


Fig. 3 TGA & DTG thermogram of PA 3e

Conclusion

This work involved the syntheses of several new PAs **3a-f** through the direct polycondensation reaction of diacid **1** with six hydantoin compounds **2a-f** by 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 pridyl segments as a hetrocyclic ring into 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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