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NEW POLYAMIDES BASED ON 1,3-BIS(4-CARBOXY PHENOXY) PROPANE AND HYDANTOIN DERIVATIVES: SYNTHESIS AND PROPERTIES

Khalil Faghihi* and Nasim Valikhani

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak, 38156, Iran

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ABSTRACT. Six new polyamides **5a-f** containing flexible trimethylene segments in the main chain were synthesized through the direct polycondensation reaction of 1,3-bis(4-carboxy phenoxy) propane **3** with six derivatives of hydantoins **4a-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 in high yield with inherent viscosities between 0.30-0.47 dL/g. The resulted polymers were fully characterized by means of FT-IR, ^{1}H-NMR spectroscopy, elemental analyses, inherent viscosity, solubility tests and gel permeation chromatography (GPC). Thermal properties of these polymers were investigated by using thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG). The glass-transition temperatures of these polyamides were recorded between 130 and 155 ^{o}C by differential scanning calorimetry (DSC), and the 5% weight loss temperatures were ranging from 325 to 415 ^{o}C under nitrogen. 1,3-bis(4-Carboxy phenoxy) propane **3** was prepared from the reaction of 4-hydroxy benzoic acid **1** with 1,3-dibromo propane **2** in the presence of NaOH solution.

KEY WORDS: Polyamides, 1,3-bis(4-Carboxy phenoxy) propane, Hydantoin derivatives, Inherent viscosity

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 applications 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-)$_2$], bulky pendent groups (such as *t*-butyl, adamantyle and naphthyl), 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 previous 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 [18-26].

In this article, synthesis and characterization of novel polyamides **5a-f** containing trimethylene segments by the direct polycondensation reaction of 1,3-bis(4-carboxy phenoxy) propane **3** with hydantoin **4a** and its five derivatives; 5,5-dimethyl hydantoin **4b**, 5-ethyl-5-methyl hydantoin **4c**, 5,5-diethyl hydantoin **4d**, 5-spiro cyclopantyl hydantoin **4e**, 5-spiro cyclohexyl hydantoin **4f** in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine are described. Results showed these novel polymers with a flexible segment in the main chain have better solubility in organic solvents in compared to aromatic polyamides.

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*Corresponding author. E-mail: k-faghihi@araku.ac.ir, khfaghihi@yahoo.com

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 weather proof high-temperature-stable epoxy resins. Also hydantoin constitutes an important class of heterocyclic compounds in the medicinal chemistry because many derivatives have been identified to display interesting activities against a broad range of biological targets [27].

Materials

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

Techniques

^{1}H-NMR spectra were recorded on a Bruker 500 MHz instrument (Germany). 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 wavenumber (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 Regd Trad Merk Viscometer (Germany). 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 ^{o}C/min (Germany). Differential scanning calorimetric analysis was performed on differential scanning calorimeter (Du Pont 910) at a heating rate of 10 ^{o}C/min (USA). 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) (USA). The eluents were monitored with a UV detector (JMST Systems, USA, VUV-24) at 254 nm. Polystyrene was used as the standard.

Monomer synthesis

*1,3-bis(4-Carboxy phenoxy) propane **3***

Diacid 3 was prepared according to a typical procedure shown in Scheme 1. Into a 250 mL round bottomed flask with dropping funnel and provided with stirring bar (4.60 g, 33.3 mmol) of 4-hydroxy benzoic acid **1** and a solution of (2.60 g, 65.0 mmol) sodium hydroxide in 14.0 mL H_2O were placed. The mixture well-stirred and (3.40 g, 16.8 mmol) of 1,3-dibromo propane **2** was slowly added. The mixture was refluxed for 3.5 h, then (0.66 g, 16.5 mmol) of sodium hydroxide was added. After that the mixture was continuously refluxed for 2 h, and stirred for over night at room temperature. The white precipitate was filtered and washed with 10 mL of methanol. The crude product was purified by dissolving in 34 mL H_2O, reprecipitated by 3 M H_2SO_4 solution and washed with cold water, then filtered and dried to obtain 6.32 g (60%) of white precipitate of pure 1,3-bis (4-carboxy phenoxy) propane **3** with m.p. 318–320 ºC.

FT-IR (KBr): 2511–3016 (s, br), 1678 (s), 1606 (s), 1431 (s), 1303 (s), 1249 (s), 1170 (s), 1055 (m), 1514 (m), 999 (m), 848 (m), 766 (s), 542 (w), 549 (w) cm^{-1}. ^{1}H-NMR (DMSO-d_6), TMS) δ: 2.18-2.23 (q, 2H), 4.18-4.22 (t, 4H), 7.01-7.04 (d, 4H), 7.86-7.89 (d, 4H), 12.62 (s, br, 2H) ppm. Elemental anal. calcd for $C_{17}H_{16}O_6$: C, 64.58; H, 5.06; found: C, 64.2; H, 5.0.

*Hydantoin derivatives **4a-f***

These compounds were prepared according to a typical procedure shown in Scheme 2 [28].

Polymer synthesis

The PAs **5a-f** were prepared by the following general procedure (using polymer **5a** as an example). Into a 25 mL round-bottomed flask which was fitted with a stirring bar were placed hydantoin **4a** (0.064 g, 0.64 mmol), diacid **3** (0.202 g, 0.64 mmol), calcium chloride (0.200 g, 1.80 mmol), triphenyl phosphite (1.68 mL, 6.00 mmol), pyridine (0.36 mL) and N-methyl-2-pyrolidone (1.6 mL). The reaction mixture was gradually refluxed using an oil bath at 60 ˚C for 1 h, 90 ˚C for 2 h, and at 130 ˚C for 8 h. The reaction mixture was poured into 25 mL of methanol and the precipitated polymer was collected by filtration and washed thoroughly by methanol and dried at 60 ˚C for 12 h under vacuum to leave 0.208 g (86%) of yellow solid polymer **5a**. The PAs **5a-f** were analyzed by using FT-IR spectroscopy.

*Polymer **5a***. FT-IR (KBr): 2958(w), 1712(s), 1604(s), 1514(m), 1473(m), 1423(w), 1317(m), 1271(s), 1221(s), 1163(s), 1109(s), 1078(s), 985(m), 962(m), 848(m), 767(m), 744(m), 694(w) cm^{-1}.

*Polymer **5b***. FT-IR (KBr): 2950(w), 1714(s), 1604(s), 1514(m), 1489(w), 1423(w), 1317(m), 1273(s), 1221(m), 1163(s), 1109(m), 1078(m), 1055(w), 958(w), 848(w), 767(m) cm^{-1}.

*Polymer **5c***. FT-IR (KBr): 2962(w), 1715(s), 1610(s), 1514(m), 1489(w), 1423(w), 1317(m), 1273(s), 1221(m), 1163(s), 1110(m), 1078(m), 1055(w), 983(w), 848(w), 767(m), 707(w), 650(w) cm^{-1}.

*Polymer **5d***. FT-IR (KBr): 2958(w), 1714(s), 1604(s), 1514(m), 1489(w), 1423(w), 1317(m), 1273(s), 1221(m), 1163(s), 1109(m), 1078(m), 1055(w), 985(w), 848(w), 767(m), 707(w), 650(w) cm^{-1}.

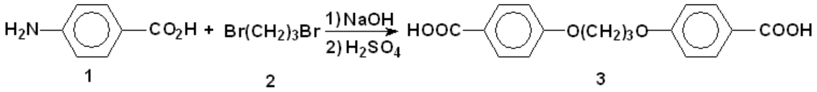
*Polymer **5e***. FT-IR (KBr): 3203(w), 3057(w), 2958(w), 1714(s), 1604(s), 1514(m), 1489(m), 1423(w), 1317(m), 1273(s), 1221(m), 1163(s), 1109(s), 1078(s), 1055(m), 985(w), 848 (m), 744(m), 694(w), 650(w), 516(w) cm^{-1}.

*Polymer **5f***. FT-IR (KBr): 2957(w), 2876(w), 1714(s), 1604(s), 1514(m), 1491(m), 1473(w), 1423(w), 1317(m), 1259(s), 1221(m), 1165(s), 1109(m), 1078(m), 985(w), 962(w), 848(m), 767(m), 744(m) cm^{-1}.

RESULTS AND DISCUSSION

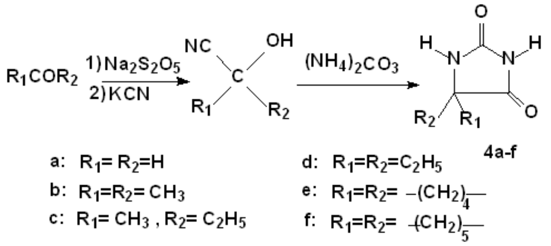
Monomer synthesis

1,3-bis(4-Carboxy phenoxy) propane **3** was prepared from the reaction of 4-hydroxy benzoic acid **1** with 1,3-dibromo propane **2** in the presence of NaOH solution. The chemical structure of diacid **3** was proved with elemental analysis, ^{1}H-NMR, and FT-IR spectroscopy [29].



Scheme 1

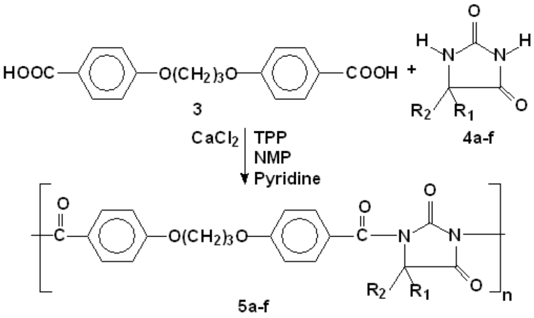
5,5-Disubstituted hydantoin derivatives were synthesized by the Bucherer-Berg method. The hydantoin compounds **(4a-f)** (Scheme 2) were prepared through the reaction of cyanohydrin derivatives with ammonium carbonate [28].



Scheme 2

Polymer synthesis

PAs **5a-f** were synthesized by the direct polycondensation reaction of an equimolar mixture of diacid **3** with six aromatic diamines **5a-f** in a medium consisting of N-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride and pyridine (Scheme 3). The syntheses and some physical properties of these new PAs **5a-f** are given in Table 1. The entire polycondensation reaction readily proceeded in a homogeneous solution, tough and stringy precipitates formed when the viscous PAs solution was obtained in moderate to good yields.



Scheme 3

Polymer characterization

The syntheses and some physical properties of PAs **5a-f** are summarized in Table 1. The resulting white to yellow crystal polymers had inherent viscosities around 0.30-0.47 dL/g.

Table 1. Synthesis and some physical properties of polyamide **5a-f**.

Hydantoin	Polymer	Yield (%)	η_{inh} (dL/g)[a]	M_n (10^4)[b]	M_w (10^4)[b]	PDI
4a	**5a**	92	0.47	2.1	5.8	2.76
4b	**5b**	86	0.42	1.9	5.7	3.00
4c	**5c**	85	0.35	1.4	4.3	3.07
4d	**5d**	76	0.38	2.0	5.9	2.95
4e	**5e**	89	0.40	2.2	4.8	2.18
4f	**5f**	94	0.30	2.2	5.4	2.45

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

These polymers were confirmed to be PAs with FT-IR spectroscopy and elemental analyses. FT-IR spectrum shows the carbonyl peaks of hydantoin moiety at 1700-1714 cm^{-1} and the carbonyl peaks of amide group in polymer shifted to lower frequency in comparison with diacid **4** at 1695 cm^{-1} and disappearance of –OH di-acid peak at 2500-3100 cm^{-1}. The ^{1}H-NMR spectrum of PA **5a** shows two doublets between 7.01-7.04 ppm and 7.86-7.89 ppm which were assigned to the H_d and H_e protons of the phenyl ring. A multiplet between 2.18-2.23 ppm was assigned to the H_a and a triplet between 4.1-4.2 ppm was assigned to the H_c of methylene group. Also the singlet at 2.75 ppm was assigned to the H_b of hydantoin ring.

These polymers exhibited number-average molecular weights M_n and weight-average molecular weights M_w in the range of 1.4-2.2 × 10^4 and 4.3-5.9 x 10^4 g/mol, respectively, as measured by GPC, relative to polystyrene standards.

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

Table 2. Elemental analysis of the resulting polyamide **5a-f**.

Polymer	Formula		C%	H%	N%
5a	$C_{20}H_{16}N_2O_6$	Calcd	63.17	4.20	7.36
	$(380.20)_n$	found	62.10	3.50	7.00
5b	$C_{22}H_{20}N_2O_6$	Calcd	64.72	4.90	6.85
	$(408.22)_n$	found	65.40	4.00	5.90
5c	$C_{23}H_{22}N_2O_6$	Calcd	65.42	5.21	6.63
	$(422.23)_n$	found	64.90	5.00	6.10
5d	$C_{24}H_{24}N_2O_6$	Calcd	66.07	5.50	6.41
	$(436.24)_n$	found	65.30	4.50	7.30
5e	$C_{24}H_{22}N_2O_6$	Calcd	66.37	5.06	6.44
	$(434.24)_n$	found	65.30	4.70	5.80
5f	$C_{25}H_{24}N_2O_6$	Calcd	66.98	5.35	6.24
	$(448.25)_n$	found	66.20	5.10	6.70

The solubility behavior of PAs **5a-f** was investigated with 0.01 g polymeric samples in 2 mL of solvent. All the polymers 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.

Thermal properties

The thermal properties of resulting PAs **5a-f** were investigated with TGA and DTG in a nitrogen atmosphere at a heating rate of 10 $^oC/min^{-1}$ and the thermal data are summarized in Table 3 (Figure 1). The initial decomposition temperatures of 5 and 10% weight losses (T_5 and T_{10}) and the char yield at 600 °C for them are summarized in Table 3. These polymers exhibited good resistance to thermal decomposition, up to 325-415 ºC in nitrogen, and began to decompose gradually above that temperature. T_5 for these polymers ranged from 325-415 ºC and T_{10} for all polymers ranged from 365 to 430 ºC, and the residual weight for these polymers at 600 ºC ranged from 22 to 65% in nitrogen. In the DSC experiments, there is no melting endotherm in the DSC thermograms. Glass transition temperatures of these polymers were found to be in the range of 130-150 ^{o}C. Also polyamide **5e** and **5f** containing spirocyclopantyl and spirocyclohexyl in C-5 hydantoin ring exhibited higher thermal stability compared to other PAIs **5a-d**.

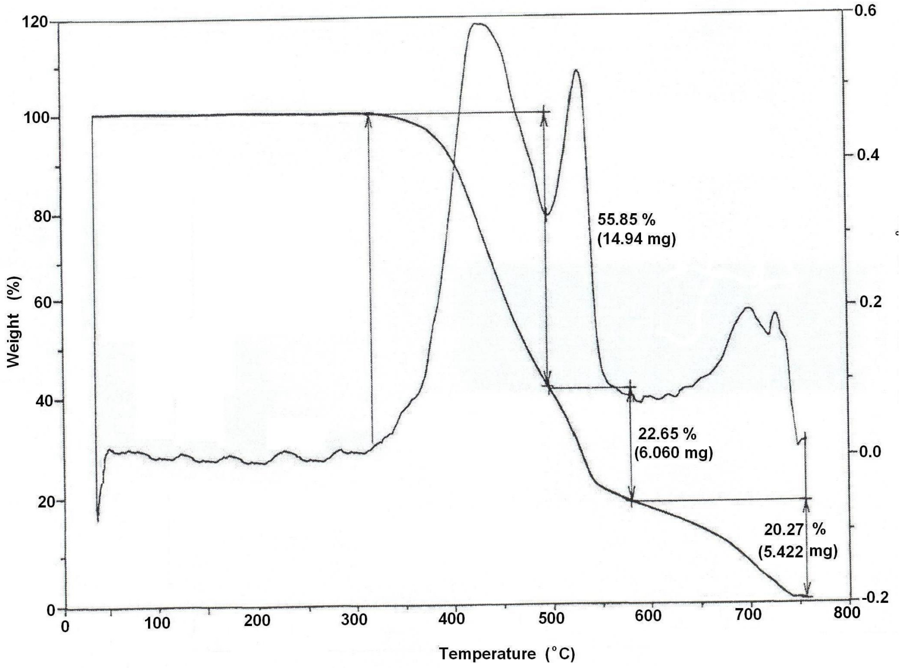


Figure 1. TGA and DTG thermograms of PA **5d**.

Table 3. Thermal behavior of polyamide **5a-f**.

Polymer	Tg^a	T_5 (°C)^b	T_{10} (°C)^c	Char yield^d (%)
5a	135	345-350	395-400	58
5b	140	325-330	365-370	62
5c	130	345-350	410-415	41
5d	150	400-405	430-435	22
5e	130	410-415	420-425	64
5f	145	415-420	425-430	65

The glass-transition temperatures (Tg) were measured by DSC. [b,c]Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 °C/min in N_2, respectively. [d]Percentage weight of material left undecomposed after TGA analysis 600 °C.

CONCLUSIONS

This work involved the syntheses of several new PAs **5a-f** through direct polycondensation reaction of diacid **3** with six hydantoin derivatives **4a-f** by using triphenyl phosphite, NMP, calcium chloride and pyridine as condensing agents. These new PAs were soluble in various organic solvents and had moderate thermal stability. The presence of trimethylene as a flexible segment into the backbone increased the solubility of these polymers in comparison to aromatic polyamides. These properties could make these PAs attractive for practical applications, such as processable high-performance engineering plastics.

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