NOTES

New Optically Active Poly(amide-imide)s Containing *N*-Trimellitylimido-*L*-phenylalanine and Hydantoin Moieties: Synthesis and Properties

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Poly(amide-imide)s (PAIs) are useful high-performance materials that show more special characteristic in the processing with polyimides that have analogous structures.^{1,2} They are finding numerous applications in adhesives, electronic wire enamel, injection-molding, extrusion products and membranes.^{3–5} They inherit desirable characteristics from both polyamides and polyimides and possess good thermal properties compared to polyamides and better melt processability than polyimides.

The synthesis and application of optically active polymers are the newly considerable topics, that recently there has been more consideration on them. Because the polymers with chiral structures are biologically very important. Most of the natural polymers are optically active and have special chemical activities such as catalytic properties that exist in genes, proteins and enzymes.^{6–8} Recently, we have synthesized optically active polymers by different methods.^{9–12}

This paper reports the synthesis and characterization of a series of new optically active poly(amide-imide)s (**5a–f**) containing hydantoin moieties in the main chain in the presence of triphenyl phosphite. The triphenyl phosphite activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides have been reported by Yamazaki *et al.*¹³ Recently, this technique has been used for the preparation of high molecular weight polyamides as well as PAIs as reported in the literature.^{14,15}

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland) and Merck Chemical Co. (Ger-

many).

N-Trimellitylimido-*L*-phenylalanine (**3**). Into a 250 mL round-bottomed flask 3.84 g (20 mmol) of trimellitic anhydride (1,2,4-benzenetricarboxylic anhydride) (**1**) 3.30 g (20 mmol) of *L*-phenylalanine (**2**), 80 mL of mixture of acetic acid and pyridine (3:2) and a stirring bar were placed. The mixture was stirred at room temperature for overnight and was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was dissolved in 100 mL of cold water, then 5 mL of concentrated HCl was added. The solution was stirred until a white precipitate was formed, then the precipitate filtered off and dried to give 6.10 g (90%) of compound (**3**): Recrystallization from methanol/water gave white crystals with mp 217–220 °C, $[\alpha]_D^{25} = -2.0$ (C 0.5, DMF); FT-IR (KBr): 3500–2800 (m, br), 2650 (m), 2450 (m), 1775 (m), 1710 (s, br), 1620 (m), 1600 (m), 1415 (m), 1380 (s), 1350 (m, sh), 1280 (m), 1250 (m), 1180 (m), 1100 (s), 1060 (w), 990 (w), 950 (m), 870 (m), 790 (w), 740 (w), 720 (m) cm^{-1} . *Anal.* Calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_6$: C, 63.7; H, 3.8; N, 4.1. Found: C, 63.6; H, 4.0; N, 4.00.

5,5-Dialkylhydantoin Derivatives (4a–f). 5,5-Dialkylhydantoin derivatives (**4a–f**) were prepared according to a typical procedure that was shown in Scheme 1.¹⁶

Polymer Synthesis (5a–f)

The PAIs (**5a–f**) were prepared by direct polycondensation by use of the following general procedure: Taking polymer (**5a**) as a sample. Into a 100-mL round-bottomed flask fitted with water cooled condenser and a magnetic stirrer, were placed 0.2 g (0.59 mmol) of diacid (**3**), 0.12 g of calcium chloride, 0.39 mL (1.47 mmol) of triphenyl phosphite, 0.36 mL

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Scheme 1.

(4.40 mmol) of pyridine, 0.06 g (0.59 mmol) of hydantoin (**4a**) and 1.4 mL of *N*-methyl-2-pyrrolidone. The stirrer was started and the mixture was heated under an atmosphere of nitrogen in an oil bath at 70 °C for 1 h, then at 90 °C for 2 h and finally at 130 °C for 10 h. The viscous reaction mixture was poured into 50 mL methanol. The precipitated polymer was collected by filtration and dried at 100 °C for 8 h under vacuum to give 0.22 g (95%) of PAI (**5a**).

All of the other **PAIs** (**5b–f**) were synthesized by the above method.

Polymer 5a. FT-IR (KBr): 1763 (s), 1724 (s, br), 1458 (w), 1384 (s, br), 1369 (s), 1222 (m), 1170 (m), 1111 (w), 1078 (w), 729 (m) cm^{-1} .

Elemental Anal. **5a** ($C_{21}H_{13}N_3O_6$); calcd C: 62.55; H: 3.22; N: 10.41; found C: 63.00; H: 3.40; N: 9.90.

Polymer 5b. FT-IR (KBr): 1764 (s), 1724 (s, br), 1491 (w), 1458 (w), 1384 (s), 1369 (s, sh), 1222 (s), 1170 (s), 1111 (m), 1076 (m), 1020 (w), 839 (w), 752 (w), 729 (m) cm^{-1} .

Elemental Anal. **5b** ($C_{23}H_{17}N_3O_6$); calcd C: 64.05; H: 3.94; N: 9.74; found C: 64.90; H: 4.20; N: 9.10.

Polymer 5c. FT-IR (KBr): 1767 (s), 1724 (s, br), 1491 (w), 1458 (w), 1384 (s, br), 1369 (s, br), 1222 (m), 1170 (m), 1111 (m), 1070 (m), 1020 (w), 840 (w), 752 (w), 735 (m) cm^{-1} .

Elemental Anal. **5c** ($C_{24}H_{19}N_3O_6$); calcd C: 64.73; H: 4.26; N: 9.43; found C: 65.30; H: 4.10; N: 8.90.

Polymer 5d. FT-IR (KBr): 1764 (s), 1724 (s, br), 1491 (m), 1458 (m), 1384 (s, br), 1369 (s), 1222 (s), 1170 (s), 1109 (m), 1074 (m), 1020 (w), 841 (w), 752 (m), 729 (m) cm^{-1} .

Elemental Anal. **5d** ($C_{25}H_{21}N_3O_6$); calcd C: 65.37; H: 4.57; N: 9.14; found C: 64.80; H: 3.90; N: 8.80.

Polymer 5e. FT-IR (KBr): 1764 (s), 1726 (s, br), 1491 (m), 1460 (m), 1383 (s), 1369 (s, sh), 1222 (s), 1170 (s), 1108 (m), 1076 (m), 1020 (w), 841 (m), 752 (m), 729 (w) cm^{-1} .

Elemental Anal. **5e** ($C_{25}H_{19}N_3O_6$); calcd C: 65.66; H: 4.15; N: 9.18; found C: 66.10; H: 4.60; N: 8.80.

Polymer 5f. FT-IR (KBr): 2958 (m), 1774 (s), 1724 (s, br), 1491 (w), 1383 (s, br), 1369 (s), 1221 (m),

1170 (s), 1109 (m), 752 (w), 729 (m) cm^{-1} .

Elemental Anal. **5a** ($C_{26}H_{21}N_3O_6$); calcd C: 66.26; H: 4.45; N: 8.91; found C: 61.70; H: 5.00; N: 8.90.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on Galaxy series FT-IR 5000 spectrophotometer (England). Spectra of solids were performed by 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 by using a Technico Regd Trad Merk Viscometer. Specific rotations were measured by an A-Kruss polarimeter. DSC (Differential Scanning Calorimetry) and Thermal Gravimetric Analysis (TGA) 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 Research Institute of Petroleum Industry, Tehran, Iran.

RESULTS AND DISCUSSION

Monomer Synthesis

Hydantoins constitute an important class of heterocycles in medicinal chemistry because many derivatives have been identified that display interesting activities against a broad range of biological targets.¹⁷ Hydantoin derivatives of (**4a–f**) were synthesized by the Bucherer–Berg method. In this method hydantoin compounds (**4a–f**) were prepared by the reactions of proper cyanohydrin derivatives with ammonium carbonate (Scheme 1).

Polymer Synthesis

The **PAIs** (**5a–f**) were synthesized by the direct solution polycondensation reactions of an equimolar imidedicarboxylic acid (**3**) with a series of hydantoin derivatives (**4a–f**) using triphenyl phosphite, *N*-methyl-2-pyrrolidone and pyridine as condensing agents (Scheme 2). Synthesis and some of the physical properties of these **PAIs** (**5a–f**) were given in Table I. The entire polycondensation readily proceeded in a homogeneous solution. Tough and stringy precipitates formed when the viscous **PAIs** solutions were trickled into stirred methanol. All the polymers were obtained in quantitative yields with moderate inherent viscosities between 0.53–0.62 dL/g.

Polymer Characterization

The structures of these polymers were confirmed as **PAIs** by means of FT-IR spectroscopy and elemental analyses (Experimental section). The FT-IR spectra of **PAIs** **5a–f** showed absorption bands around 1780–

Scheme 2.

Table I. Synthesis and some physical properties of PAIs (**5a-f**)

Hydantoin compound	Polymer	Yield (%)	η_{inh}^a (dL/g)	$[\alpha]^{25}_D^b$
4a	5a	95	0.59	-5.0
4b	5b	90	0.53	-6.0
4c	5c	93	0.62	-6.5
4d	5d	89	0.55	-7.0
4e	5e	90	0.58	-8.0
4f	5f	93	0.60	-11.0

^{a,b}Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

1700 cm⁻¹ due to amide and imide carbonyl linkages. Absorption bands around 1390–1380 cm⁻¹ and 730–710 cm⁻¹ showed the presence of the imide heterocycle in these polymers. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures (Experimental section).

The solubility of PAIs (**5a-f**) was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in DMF, DMAc, DMSO, NMP and THF at room temperature, and are insoluble in solvents such as acetone, chloroform, methylene chloride, methanol, ethanol and water.

Thermal Properties

The thermal properties of two PAIs (**5a**) and (**5d**) were investigated by means of differential scanning calorimetry (DSC) as well as the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min. The T_g values and the temperatures of 5 and 10% weight loss (T_5 , T_{10}) and char yields at 600 °C for PAIs (**5a**) and (**5d**) were summarized in Table II. These polymers exhibited good resistance to thermal decomposition up to 245–270 °C in nitrogen and began to decompose gradually above that temperature. The temperatures of 5% weight loss for

Table II. Thermal behavior of PAIs (**5a**, **5d**)

Polymer	T_g	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield ^c
5a	145	270–275	295–300	43.0
5d	156	245–250	285–290	49.0

^{a,b}Temperature at which 5 or 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in N₂. ^cWeight percentage of material left after TGA analysis at maximum temperature 600 °C in N₂.

these polymers ranged from 250 to 275 °C and the residual weight at 600 °C ranged from 43.0 to 49.0% in nitrogen.

CONCLUSIONS

A series of new optically active PAIs having inherent viscosities of 0.53–0.62 dL/g were synthesized by direct polycondensation reaction of optically active *N*-trimellitylimido-L-phenylalanine (**3**) with six hydantoins. These aromatic PAIs are optically active and are soluble in various organic solvents. The introduction of hydantoin moieties into the backbone increased solubility of these polymers. These resulting novel polymers have the potential to be used in column chromatography technique for separation of the enantiomeric mixtures.

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