

## RAPID SYNTHESIS OF NOVEL OPTICALLY ACTIVE POLY(AMIDE-IMIDE)S DERIVED FROM *N,N'*-(PYROMELLITOYL)-BIS-*L*-ALANINE DIACID CHLORIDE AND HYDANTOIN DERIVATIVES UNDER MICROWAVE IRRADIATION\*

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**Abstract** Eight novel poly(amide-imide)s were synthesized under microwave irradiation by using a domestic microwave oven from the polycondensation reactions of *N,N'*-(pyromellitoyl)-bis-*L*-alanine diacid chloride (**1**) with eight different derivatives of hydantoin compounds (**2a–h**) in the presence of a small amount of a polar organic medium such as *o*-cresol. The polycondensation proceeded rapidly, compared with the conventional solution polycondensation and was completed within 8–10 min, producing a series of new poly(amide-imide)s (**3a–h**) with inherent viscosities about 0.35–0.68 dL/g in high yields. The obtained PAIs (**3a–h**) were fully characterized by means of FT-IR spectroscopy, elemental analyses, inherent viscosity ( $\eta_{mh}$ ), solubility and specific rotation measurements. All of the resulting polymers show optical rotation and are optically active. Thermal properties of the poly(amide-imide)s were investigated by using thermal gravimetric analysis (TGA).

**Keywords:** Microwave-assisted polycondensation; Optically active polymers; 5,5-Disubstituted hydantoin derivatives.

### INTRODUCTION

Recently, there is growing interest in applying microwave energy in synthetic organic chemistry<sup>[1–4]</sup>, sample preparation for analysis<sup>[5]</sup>, extraction of natural products from plants<sup>[6]</sup>, waste treatment<sup>[7]</sup> and polymer synthesis<sup>[8–13]</sup>. The reactions are very fast and are completed within a short period of time. Recently we have used microwave irradiation for the synthesis of poly(amide-imide)s and poly(ester-imide)s<sup>[14–16]</sup>.

The synthesis and application of optically active polymers are the new exciting topics, which have attracted more attention recently. Polymers with chiral structures have biological significance<sup>[17]</sup>. Some noticeable applications are: (1) constructing chiral media for asymmetric synthesis, (2) chiral stationary phases for resolution of enantiomers in chromatographic techniques, (3) chiral liquid crystals in ferroelectric and nonlinear optical devices<sup>[18–21]</sup>. Recently, we have synthesized some optically active polymers by different methods<sup>[14–16, 22, 23]</sup>.

This paper describes the synthesis and characterization of new optically active PAIs (**3a–h**) through the polycondensation reactions of *N,N'*-(pyromellitoyl)-bis-*L*-alanine diacid chloride (**1**) with eight different derivatives of hydantoin compounds (**2a–h**) as a heterocyclic unit under microwave irradiation. Hydantoin and hydantoin derivatives are important intermediates in the synthesis of several amino acids. In the chemical industry various 5,5-disubstituted hydantoins are the base of new generation of weather proof heat-stable epoxy resins<sup>[24]</sup>.

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## EXPERIMENTAL

### Materials

All reagents were available from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Merck Chemical Co. (Germany).

### Apparatus

A Samsung domestic microwave oven (2450 MHz, 900 W) was used for carrying out polycondensation reactions.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrometer (England). Inherent viscosities were measured by a standard viscometer. Specific rotations were measured by an A-Kruss polarimeter. Thermal gravimetric analysis (TGA) data of polymers were taken on a Mettler TA4000 system under N<sub>2</sub> atmosphere at a heating rate of 10 K/min. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, I. R. Iran.

### Monomer Synthesis

*N,N'*-(pyromellitoyl)-bis-*L*-alanine diacid chloride (**1**) was prepared by a procedure reported elsewhere<sup>[25]</sup>. 5,5-Disubstituted hydantoin derivatives (**2a–h**) were prepared according to our previous work<sup>[23]</sup>.

### Polymer Synthesis

All of the polymers were synthesized by two different methods.

Method A: Polymerization by microwave technique in porcelain dish; The PAIs (**3a–h**) were prepared by the following general procedure (using polymer **3d** as an example). An equimolar mixture of diacid chloride (**1**) (0.397 g, 1.0 mmol) and 5,5-dimethyl hydantoin **2d** (0.128 g, 1.0 mmol) were placed in a porcelain dish and the mixture was ground until fine powder was formed. Then 0.5 mL of *o*-cresol was added to the mixture and mixed up until a homogeneous solution was formed. Then the reaction mixture was irradiated in microwave oven at full power for 8 min. The reaction mixture was poured into 50 mL of methanol and the resulting polymer was filtered off, and dried at 80°C for 12 h under vacuum to leave 0.40 g (88%) of solid polymer **3d**.

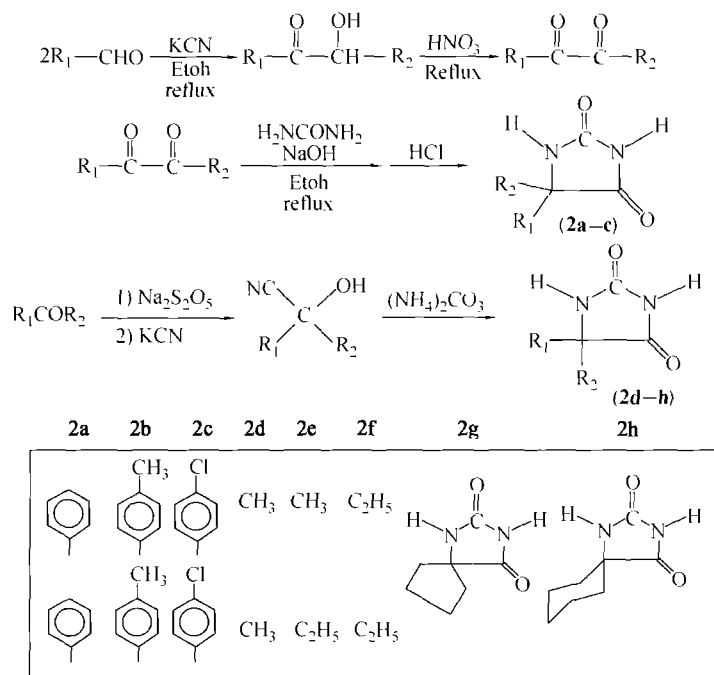
Method B: Solution polycondensation with pyridine as a base; The PAIs (**3a–h**) were prepared by the following general procedure (using polymer **3d** as an example). Into a 25 mL round-bottomed flask which was fitted with a stirring bar were placed 5,5-dimethyl hydantoin **2d** (0.128 g, 1.0 mmol) and 1.5 mL of DMAc. The mixture was cooled in an ice-water bath, to this solution, (0.06 g, 0.8 mmol) of pyridine was added. Then (0.397 g, 1.0 mmol) of diacid chloride **1** was added all at once. The polymerization proceeded as the acid chloride was dissolved. The reaction mixture was stirred in an ice-water bath for 1 h and the stirring was continued at room temperature overnight and then was heated at 80°C for 12 h. The reaction mixture was poured into 50 mL of methanol. The precipitated polymer was collected by filtration and washed thoroughly with methanol and was dried at 80°C for 12 h under vacuum to leave 0.31 g (68%) of solid polymer **3d**.

The PAIs **3a–h** were then analyzed by using FT-IR, the results as following: Polymer **3a**, FT-IR (KBr, cm<sup>-1</sup>): 1764 (s), 1724 (s), 1491 (m), 1458 (w), 1384 (s), 1370 (s), 1222 (s), 1170 (s), 1109 (m), 1076 (m), 839 (w), 752 (m), 729 (m). Polymer **3b**, FT-IR (KBr, cm<sup>-1</sup>): 1766 (s, br), 1724 (s, br), 1491 (w), 1458 (w), 1383 (s), 1369 (s), 1222 (s), 1170 (s), 1109 (m), 1076 (m), 1020 (w), 752 (m), 729 (m). Polymer **3c**, FT-IR (KBr, cm<sup>-1</sup>): 1761 (s), 1718 (s, br), 1616 (w), 1487(m), 1454 (m), 1384 (s), 1370 (s, sh) 1303 (m), 1226 (s), 1159 (s), 1076 (s), 1022 (m), 912 (w), 839 (w), 727 (m). Polymer **3d**, FT-IR (KBr, cm<sup>-1</sup>): 1764 (s), 1724 (s, br), 1491 (w), 1458(w), 1384 (s), 1370 (s, sh) 1222 (s), 1170 (s), 1111 (m), 1076 (m), 1020 (w), 839 (w), 752 (w), 729 (m). Polymer **3e**, FT-IR (KBr, cm<sup>-1</sup>): 1774 (s, sh), 1720 (s, br), 1450 (w), 1384 (s, br), 1370 (m), 1228 (w), 1170 (w), 1080 (w), 752 (w), 729 (w). Polymer **3f**, FT-IR (KBr, cm<sup>-1</sup>): 1764 (s), 1724 (s, br), 1491 (m), 1458 (w), 1384 (s), 1370 (s), 1222 (s), 1170 (s), 1170 (m), 1111 (m), 1076 (m), 839 (w), 750 (m), 729 (m). Polymer **3g**, FT-IR (KBr, cm<sup>-1</sup>): 1763 (s, br), 1724 (s, br), 1491 (w), 1465 (w), 1383 (s, br), 1370 (s), 1242 (w), 1221 (s), 1170 (s, br), 1109 (s), 1085 (w), 750 (m), 725 (m). Polymer **3h**, FT-IR (KBr, cm<sup>-1</sup>): 1776 (s, br), 1724 (s, br), 1491 (w), 1465 (w), 1383 (s, br), 1370 (s), 1242 (w), 1221 (s), 1170 (s, br), 1109 (s), 1085 (w), 754 (m), 734 (m).

## RESULTS AND DISCUSSION

### Monomer Synthesis

Hydantoins constitute 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>[26]</sup>. 5,5-Disubstituted hydantoin derivatives were synthesized by two different methods. The compounds **2a-c** were prepared from condensation reactions of benzil and benzil derivatives with urea. Benzil and benzil derivatives were obtained from the oxidation of benzoin and benzoin derivatives with concentrated nitric acid, which in turn were obtained from benzoin condensation of benzaldehyde and benzaldehyde derivatives. Hydantoin derivatives of **2d-h** were synthesized by the Bucherer-Berg method, in which hydantoin compounds **2d-h** were prepared from the reactions of proper cyanohydrin derivatives and ammonium carbonate (Scheme 1).

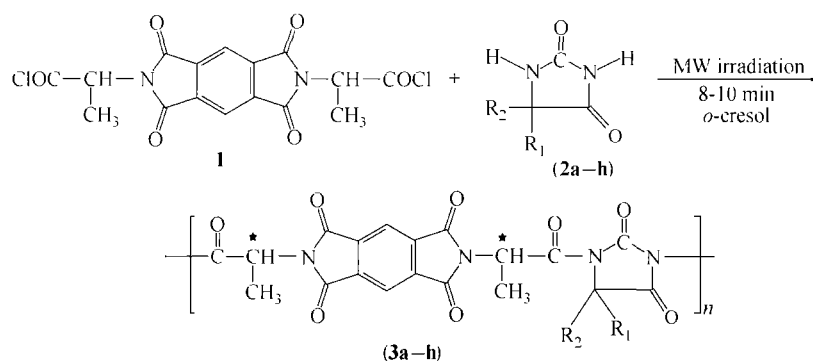


Scheme 1

### Polymer Synthesis

Poly(amide-imide)s (**3a-h**) were synthesized by microwave-assisted polycondensation as well as solution polycondensation reactions of an equimolar mixture of monomer (**1**) with eight different derivatives of hydantoin compounds (**2a-h**) as shown in Scheme 2. The microwave-assisted polycondensation reactions were carried out in a porcelain dish in the presence of small amount of a polar organic medium such as *o*-cresol that acted as a primary microwave absorber, then the reaction mixture was irradiated for 7–10 min. The resulting PAIs (**3a-h**) having higher inherent viscosities were obtained in higher yield in a shorter period of irradiation. The reaction yields and some physical data are listed in Table 1.

To compare the microwave-assisted polycondensation method with the conventional solution polycondensation method, polymerization of diacid chloride (**1**) with **2a-h** was performed in DMAc solution in the presence of pyridine as a base. Although we obtained high yield of PAIs (**3a-h**), but lower inherent viscosities were resulted. Therefore microwave-assisted polycondensation proceeds rapidly and produces polymers with higher inherent viscosities in a shorter period of time in comparison with the solution polycondensation. The reaction yields and some physical data of the solution polycondensations are listed in Table 2.



Scheme 2

**Table 1.** Synthesis and some physical properties of PAIs (**3a-h**) prepared by microwave technique (method A)

| Polymer   | Irradiation time (min) | Temperature (°C) <sup>a</sup> | Yield (%) | $\eta_{\text{inh}}(\text{dL/g})^b$ | $[\alpha]_{\text{D}}^{25, \text{c}}$ |
|-----------|------------------------|-------------------------------|-----------|------------------------------------|--------------------------------------|
| <b>3a</b> | 8.5                    | 160                           | 85        | 0.35                               | -5.0                                 |
| <b>3b</b> | 9                      | 160                           | 83        | 0.35                               | -7.0                                 |
| <b>3c</b> | 9                      | 160                           | 88        | 0.55                               | -6.0                                 |
| <b>3d</b> | 8                      | 120                           | 87        | 0.60                               | -6.5                                 |
| <b>3e</b> | 8                      | 120                           | 90        | 0.68                               | -6.7                                 |
| <b>3f</b> | 8                      | 120                           | 92        | 0.56                               | -7.5                                 |
| <b>3g</b> | 10                     | 140                           | 78        | 0.35                               | -4.0                                 |
| <b>3h</b> | 10                     | 140                           | 85        | 0.40                               | -4.5                                 |

<sup>a</sup> Reaction temperature under microwave irradiation<sup>b,c</sup> Measured at a concentration of 0.5 g/dL in DMF at 25°C**Table 2.** Synthesis and some physical properties of PAIs (**3a-h**) prepared by conventional solution polycondensation (method B)

| Polymer   | Yield (%) | $\eta_{\text{inh}}(\text{dL/g})^a$ | $[\alpha]_{\text{D}}^{25, \text{h}}$ |
|-----------|-----------|------------------------------------|--------------------------------------|
| <b>3a</b> | 73        | 0.20                               | -5.0                                 |
| <b>3b</b> | 75        | 0.17                               | -6.5                                 |
| <b>3c</b> | 80        | 0.21                               | -5.7                                 |
| <b>3d</b> | 68        | 0.30                               | -6.5                                 |
| <b>3e</b> | 72        | 0.32                               | -6.7                                 |
| <b>3f</b> | 78        | 0.35                               | -7.1                                 |
| <b>3g</b> | 70        | 0.30                               | -4.0                                 |
| <b>3h</b> | 70        | 0.33                               | -4.0                                 |

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

### Polymer Characterization

The structures of PAIs were confirmed by means of FT-IR spectroscopy and elemental analyses. All the polymers show optical rotation and are optically active. The representative FT-IR spectrum of PAI **3a** is shown in Fig. 1. The absorption bands around 1780–1700  $\text{cm}^{-1}$  are due to amide and imide carbonyl linkages. Absorption bands around 1390–1380  $\text{cm}^{-1}$  and 730–710 show the presence of imide heterocyclic in this polymer. The other PAIs spectra show a similar pattern. These spectra show that the carbonyl peaks of polymers shift to lower frequency in comparison with diacid chloride (**4**). FT-IR spectrum of compound (**1**) shows that the carbonyl peak of diacid chloride appears at 1800–1820  $\text{cm}^{-1}$ . The elemental analysis of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 3). The solubility of PAIs (**3a-h**) was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All the polymers are soluble in organic solvents

such as DMF, DMAc, DMSO, NMP and acetone at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water. The introduction of 5,5-disubstituted hydantoin moieties into the polymer backbone would increase the solubility of these polymers.

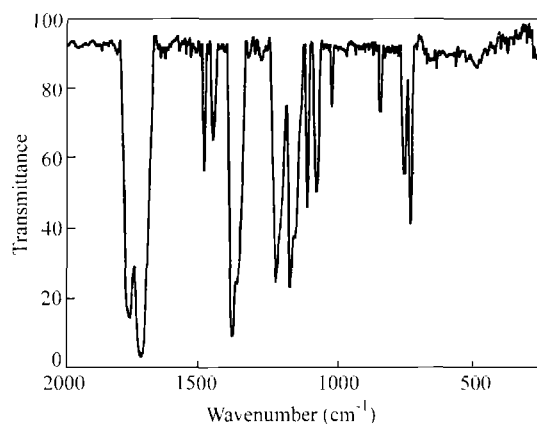


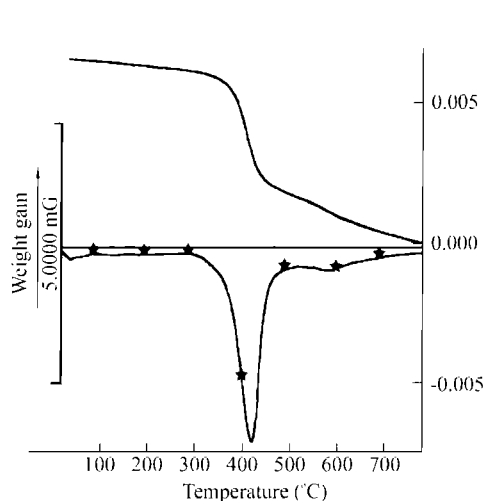
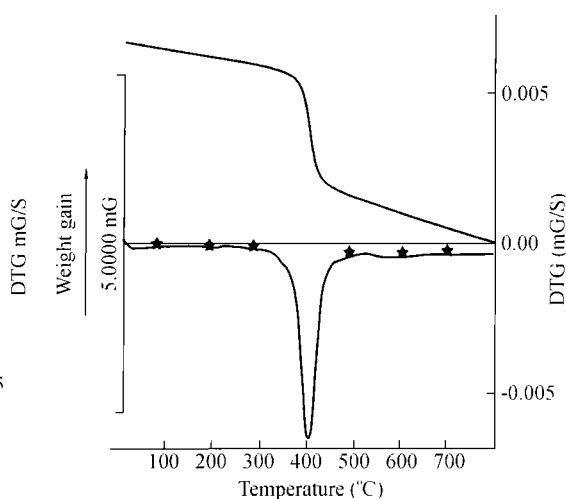
Fig. 1 FT-IR Spectrum of PAIs **3a**

Table 3. Elemental analysis of PAIs (**3a-h**)

| Polymer   | Formula                  |       | C%    | H%   | N%    |
|-----------|--------------------------|-------|-------|------|-------|
| <b>3a</b> | $C_{31}H_{20}N_4O_8$     | Calcd | 64.58 | 3.49 | 9.71  |
|           | $(576.5)_n$              | Found | 65.0  | 4.2  | 9.1   |
| <b>3b</b> | $C_{33}H_{24}N_4O_8$     | Calcd | 65.56 | 4.00 | 9.26  |
|           | $(604.5)_n$              | Found | 66.1  | 4.2  | 8.9   |
| <b>3c</b> | $C_{31}H_{18}N_4O_8Cl_2$ | Calcd | 57.69 | 2.79 | 8.68  |
|           | $(645.31)_n$             | Found | 58.2  | 3.1  | 8.2   |
| <b>3d</b> | $C_{21}H_{16}N_4O_8$     | Calcd | 55.75 | 3.56 | 12.38 |
|           | $(452.3)_n$              | Found | 56.1  | 4.1  | 11.8  |
| <b>3e</b> | $C_{22}H_{18}N_4O_8$     | Calcd | 56.65 | 3.88 | 12.01 |
|           | $(466.4)_n$              | Found | 57.0  | 4.2  | 11.6  |
| <b>3f</b> | $C_{23}H_{20}N_4O_8$     | Calcd | 57.50 | 4.19 | 11.66 |
|           | $(480.4)_n$              | Found | 58.4  | 4.8  | 10.9  |
| <b>3g</b> | $C_{23}H_{18}N_4O_8$     | Calcd | 57.76 | 3.76 | 11.71 |
|           | $(478.23)_n$             | Found | 57.1  | 3.8  | 11.2  |
| <b>3h</b> | $C_{24}H_{20}N_4O_8$     | Calcd | 58.53 | 4.09 | 11.37 |
|           | $(498.4)_n$              | Found | 59.1  | 4.5  | 10.9  |

### Thermal Properties

The thermal decomposition temperatures of two PAIs **3a** and **3c** were evaluated by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 K/min (Table 4). All these polymers show similar decomposition behavior (Figs. 2, 3). Initial decomposition temperature, 5% and 10% weight loss ( $T_5$ ,  $T_{10}$ ), char yield at 600 °C for PAIs **3a** and **3c** are summarized in Table 4.

Fig. 2 TGA and DTG thermogram of PAIs **3a**Fig. 3 TGA and DTG thermogram of PAIs **3c**Table 4. Thermal behavior of PAIs **3a, 3d**

| Polymer   | $T_5$ (°C) <sup>a</sup> | $T_{10}$ (°C) <sup>b</sup> | Char yield <sup>c</sup> |
|-----------|-------------------------|----------------------------|-------------------------|
| <b>3a</b> | 290–295                 | 360–370                    | 17.8                    |
| <b>3d</b> | 250–255                 | 360–365                    | 16.0                    |

<sup>a, b</sup>Temperature at which 5% and 10% weight loss was recorded by TGA at heating rate of 10 K/min in N<sub>2</sub> respectively.

<sup>c</sup>Percentage weight of material left undecomposed after TGA analysis at 600°C in N<sub>2</sub>

## CONCLUSIONS

Eight novels optically active PAIs (**3a-h**) were synthesized by microwave-assisted polycondensation reaction using the optically active monomer (**1**) with eight different derivatives of hydantoin compounds (**2a-h**) as a heterocyclic unit in main chain. The obtained polymers are optically active and soluble in various organic solvents. The introduction of hydantoin moieties into the backbone would increase the solubility of these polymers. The above results demonstrate that microwave heating is an efficient method (shorter reaction time and higher efficiency of energy) for the polycondensation reactions. We are currently using this method for the synthesis of novel polymers and modification of polymers.

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