

## POLYMERIZATION OF *N,N'*-(PYROMELLITOYL)-BIS-*L*-LEUCINE DIACID CHLORIDE WITH HYDANTOIN DERIVATIVES BY MICROWAVE IRRADIATION\*

Khalil Faghihi\*\*

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

**Abstract** Facile and rapid polycondensation reactions of *N,N'*-(pyromellitoyl)-bis-*L*-leucine diacid chloride **1** with eight different derivatives of hydantoin compounds **2a–h** were developed by using a domestic microwave oven in the presence of a small amount of polar organic medium such as *o*-cresol. The polycondensation reactions proceeded rapidly, compared with the conventional solution polycondensation, and was completed within 7–10 min, producing a series of novel optically active poly(amide-imide)s **3a–h** with high yield and inherent viscosity of 0.35–0.65 dL/g. All of the above polymers were fully characterized by FT-IR, elemental analyses, inherent viscosity ( $\eta_{inh}$ ), solubility test and specific rotation. Some structural characterization and physical properties of these optically active poly(amide-imide)s are reported.

**Keywords** Microwave-assisted rapid polycondensation, Optically active polymers, Poly(amide-imide)s, Hydantoin derivatives, *N,N'*-(Pyromellitoyl)-bis-*L*-leucine diacid chloride

### INTRODUCTION

Recently, there has been growing interest in applying microwave energy to 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 involved in these applications 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>[14–17]</sup>.

Recently more attention has been paid to the synthesis and application of optically active polymers. Polymers with chiral structures are biologically very important<sup>[18]</sup>. The other 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>[19–22]</sup>. Recently, we have synthesized optically active polymers by different methods<sup>[14–17, 23, 24]</sup>.

This paper reports a rapid and highly efficient method for the synthesis of new optically active poly(amide-imide)s **3a–h** from the polycondensation reactions of *N,N'*-(pyromellitoyl)-bis-*L*-leucine 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 basis of new generation of weatherproof high-temperature-stable epoxy resins<sup>[25]</sup>.

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\*\* Corresponding author: Khalil Faghihi, E-mail: k-faghihi@araku.ac.ir

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## EXPERIMENTAL

### Materials and Characterization

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI) and Merck Chemical Co. (Germany). Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrometer (England). Spectra of solid samples were performed using KBr pellets. Inherent viscosities were measured by a standard procedure using a Technico Regd Trad Merk Viscometer. Specific rotations were measured by an A. Krüss polarimeter. Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler TA 4000 System under N<sub>2</sub> atmosphere at a rate of 10 K/min. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, I. R. Iran. A Samsung domestic microwave oven (2450 MHz, 900 W) was used for carrying out polycondensation reactions.

### Monomer Synthesis

*N,N'*-(Pyromellitoyl)-bis-*L*-leucine diacid chloride **1** was prepared by a procedure reported elsewhere<sup>[26]</sup>. Hydantoin derivatives **2a–h** were prepared according to a typical procedure that is shown in Scheme 1<sup>[17, 24]</sup>.

### Polymerization Method

All of the polymers were synthesized by two different methods.

#### Method A: Polymerization by microwave technique in porcelain dish

Optically active poly(amide-imide)s (PAIs **3a–h**) were prepared by the following general procedure (using polymer **3d** as an example). An equimolar mixture of diacid chloride **1** (0.40 g,  $8.3 \times 10^{-4}$  mol) and 5,5-dimethyl hydantoin **2d** (0.10 g,  $8.3 \times 10^{-4}$  mol) were placed in a porcelain dish and the mixture was ground to a fine powder. Then 0.5 mL of *o*-cresol was added to the mixture and was mixed to form a homogeneous solution. Then the reaction mixture was irradiated in microwave oven at full power for 7 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 (90%) of solid polymer **3d**.

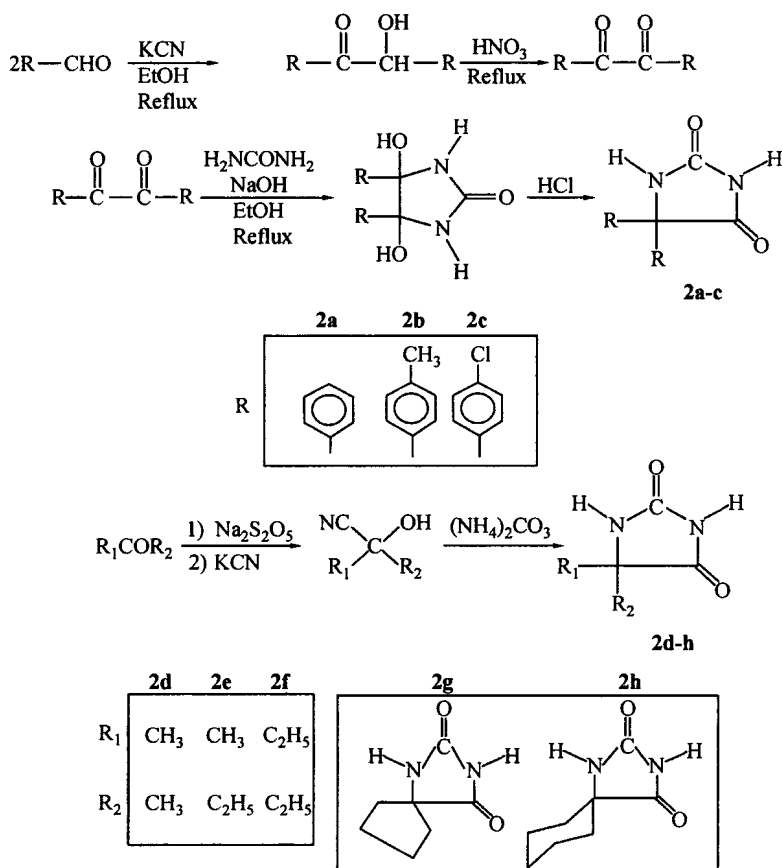
#### Method B: Solution polycondensation with pyridine as a base

PAIs **3a–h** were prepared by the following general procedure (using polymer **3d** as an example). Into a 25 mL round-bottomed flask fitted with a stirring bar was placed 5,5-dimethyl hydantoin **2d** (0.10 g,  $8.3 \times 10^{-4}$  mol) and 1.2 mL of DMAc. The mixture was cooled in an ice-water bath and pyridine (0.06 g,  $7.98 \times 10^{-4}$  mol) was added. Then 0.40 g,  $8.3 \times 10^{-4}$  mol 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 stirring was continued at room temperature overnight. Thereafter it 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 dried at 80°C for 12 h under vacuum to leave 0.32 g (72 %) of solid polymer **3d**.

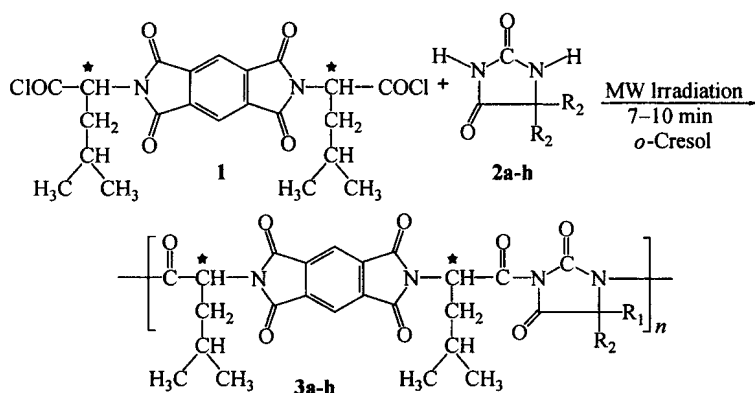
## RESULTS AND DISCUSSION

### Monomer Synthesis

Hydantoins constitute an important class of heterocyclics in medicinal chemistry because many derivatives have been identified that display interesting activities against a broad spectrum of biological targets<sup>[27]</sup>. 5,5-Disubstituted hydantoin derivatives were synthesized by two different methods. 5,5-Diaryl hydantoins of **2a–c** were prepared by condensation reactions of benzil and benzil derivatives with urea to give an intermediate heterocyclic pinacol which on acidification yields the hydantoin derivatives **2a–c** as the results of a pinacol rearrangement. Benzil and benzil derivatives were obtained from oxidation of benzoin and benzoin derivatives with concentrated nitric acid. Benzoin and benzoin derivatives were also obtained from benzoin condensation of benzaldehyde and benzaldehyde derivatives. Hydantoin derivatives of **2d–h** were synthesized by the Bucherer-Berg method. In this method hydantoin compounds **2d–h** were prepared from the reactions of appropriate cyanohydrin derivatives and ammonium carbonate (Scheme 1).



Scheme 1



Scheme 2

### Polymer Synthesis

PAIs **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 a small amount of a polar organic medium such as *o*-cresol that acts as a primary microwave absorber, then the reaction mixture was irradiated for 7–10 min. *o*-Cresol was used as polar organic medium that acts as a primary microwave absorber and as a solvent for both of the starting monomers and the resulting polymers. This allows the reaction mixture to be uniformly heated and thereby subsequent polycondensation

reaction occurs leading to the polymer formation. The optimum reaction time (irradiation time) was found to be 7–10 min. After shorter reaction times, the polymers obtained will have lower inherent viscosities and after longer times the materials will be degraded. The resulting PAIs **3a–h** have higher yields and higher inherent viscosities in a shorter period of irradiation. The reaction yields and some physical data are listed in Table 1.

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

| Polymer   | Irradiation time (min) | Temperature (°C) <sup>a</sup> | Yield (%) | $\eta_{inh}(\text{dL/g})^b$ | $[\alpha]_{\text{D}}^{25\text{ }^{\circ}\text{C}}$ <sup>c</sup> |
|-----------|------------------------|-------------------------------|-----------|-----------------------------|-----------------------------------------------------------------|
| <b>3a</b> | 8.5                    | 160                           | 87        | 0.42                        | + 1.5                                                           |
| <b>3b</b> | 9                      | 160                           | 90        | 0.40                        | + 2.0                                                           |
| <b>3c</b> | 9                      | 160                           | 92        | 0.45                        | + 1.0                                                           |
| <b>3d</b> | 7                      | 120                           | 90        | 0.65                        | + 1.8                                                           |
| <b>3e</b> | 8                      | 120                           | 85        | 0.55                        | + 1.5                                                           |
| <b>3f</b> | 8                      | 120                           | 82        | 0.41                        | + 0.5                                                           |
| <b>3g</b> | 10                     | 140                           | 78        | 0.35                        | + 1.0                                                           |
| <b>3h</b> | 10                     | 140                           | 85        | 0.40                        | + 1.0                                                           |

<sup>a</sup> Temperature of reaction mixture under microwave irradiation

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

To compare microwave-assisted polycondensation method with the conventional solution polycondensation method, polymerization of diacid chloride **1** with eight different derivatives of hydantoin compounds **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 resulted. Therefore microwave-assisted polycondensation proceeds rapidly and the products have higher inherent viscosities in a shorter period of time in comparison with solution polycondensation. The reaction yields and some physical data of the solution polycondensations are listed in Table 2.

**Table 2.** Synthesis and some physical properties of PAIs (**3a–h**) prepared by conventional solution polycondensation (method B)

| Polymer   | Yield (%) | $\eta_{inh}(\text{dL/g})^a$ | $[\alpha]_{\text{D}}^{25\text{ }^{\circ}\text{C}}$ <sup>b</sup> |
|-----------|-----------|-----------------------------|-----------------------------------------------------------------|
| <b>3a</b> | 80        | 0.22                        | + 1.3                                                           |
| <b>3b</b> | 75        | 0.18                        | + 1.8                                                           |
| <b>3c</b> | 87        | 0.27                        | + 1.0                                                           |
| <b>3d</b> | 72        | 0.31                        | + 1.6                                                           |
| <b>3e</b> | 81        | 0.22                        | + 1.5                                                           |
| <b>3f</b> | 78        | 0.29                        | + 0.6                                                           |
| <b>3g</b> | 70        | 0.30                        | + 1.1                                                           |
| <b>3h</b> | 70        | 0.23                        | + 1.4                                                           |

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

### Polymer Characterization

PAIs **3a–h** derived from monomer **1** show different colors, from cream or off-white to brown. All of the resulting polymers show optical rotation and are optically active. The structures of these polymers were confirmed as PAIs by means of FT-IR spectroscopy and elemental analyses. The representative FT-IR spectrum of PAIs **3b** is shown in Fig. 1. The polymers show absorption bands near 1780–1700 cm<sup>-1</sup> which can be assigned as the amide and imide absorption vibration of carbonyl linkages. Absorption bands around 1390–1380 cm<sup>-1</sup> and 730–710 show the presence of imide heterocycle in this polymer. The other spectra of PAI polymers show a similar pattern. The spectra show that their carbonyl vibrations shift to lower frequency in comparison with diacid chloride **1**. The carbonyl peak of diacid chloride appears at 1800–1820 cm<sup>-1</sup>.

The elemental analyses of the resulting polymers are in good agreement with the calculated values for the proposed structures. The solubility of PAIs **3a–h** was investigated as 0.01 g of polymeric sample in 2 mL of

solvent. All of 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 increases the solubility of these polymers.

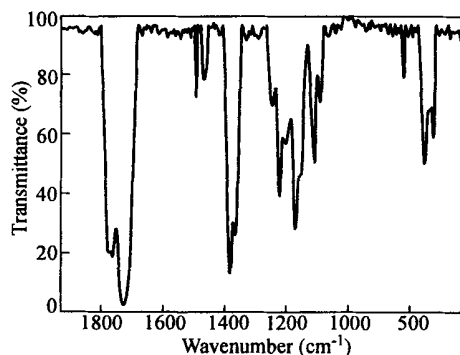


Fig. 1 FT-IR spectrum of PAIs 3b

### Thermal Properties

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

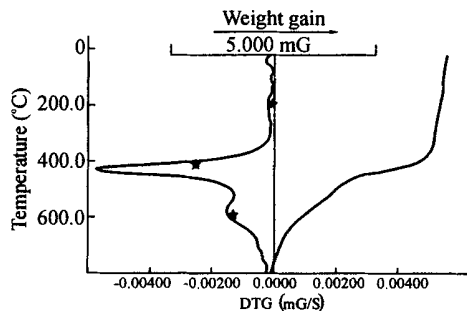


Fig. 2 TGA and DTG thermogram of PAIs (3a)

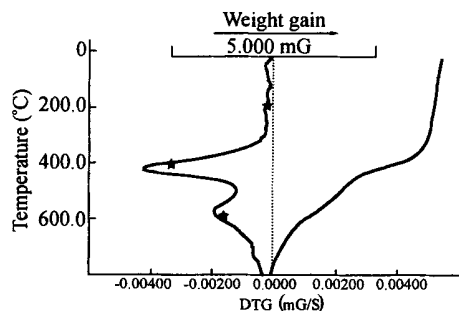


Fig. 3 TGA and DTG thermogram of PAIs (3d)

Table 3. Thermal behavior of PAIs 3a, 3d

| Polymer | $T_5$ (°C) <sup>a</sup> | $T_{10}$ (°C) <sup>b</sup> | Char yield <sup>c</sup> |
|---------|-------------------------|----------------------------|-------------------------|
| 3a      | 340                     | 390                        | 48.0                    |
| 3d      | 330                     | 390                        | 55.0                    |

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

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

### CONCLUSIONS

Eight novel 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 heterocycle unit. These aromatic PAIs are optically active and are soluble in various organic solvents. The introduction of hydantoin moieties into the backbone will increase the solubility of these polymers. These resulting novel polymers have the potential to be used in column chromatography for the separation of enantiomeric mixtures.

Furthermore, the above results demonstrate that microwave heating is an efficient method (shorter reaction time and high efficiency of energy) for the polycondensation reactions. We are currently using this method for the synthesis of novel polymers and modification of polymers.

## REFERENCES

- 1 Varma, S.R., *Green Chemistry*, 1999, 43
- 2 Gong, Y.D., Sohn, H.Y. and Kurth, M.J., *J. Org. Chem.*, 1998, 63: 4854
- 3 Bogdal, D., *Molecules*, 1999, 4: 333
- 4 Varma, S.R. and Kumar, D., *Org. Lett.*, 1999, 1
- 5 Pylypiw, H.M., Jr, Arsenault, T.L., Thetford, C.M. and Mattina, M.J.I., *J. Agric. Food Chem.*, 1997, 45: 3522
- 6 Yaylayan, V.A. and Matni, G., *J. Agric. Food Chem.*, 1997, 45: 149
- 7 Vazques, M.J., Carro, A.M., Lorenzo, R.A. and Cela, R., *Anal. Chem.*, 1997, 69: 221
- 8 Jullien H. and Valot H., *Polymer*, 1985, 26: 506
- 9 Silinski, B., Kuzmycz C. and Gourdenne, A., *Eur. Polym. J.*, 1987, 23: 273
- 10 Van, L.Q. and Gourdenne, A., *Eur. Polym. J.*, 1987, 23: 777
- 11 Wei, J., Hawley, M.C. and Delong, J.D., *Poly. Engineer. Sci.*, 1993, 33: 1132
- 12 Imai, Y., Nemoto, H., Watanabe, S. and Kakimoto, M.A., *Polymer J.*, 1996, 28: 256
- 13 Liu, Y., Sun, X.D., Xie, X.Q. and Scola D.A., *J. of Polym. Sci., Part A, Polym. Chem.*, 1998, 36: 2653
- 14 Mallakpour, S.E., Hajipour, A.R. and Faghihi, Kh., *Polym. Int.*, 2000, 49: 1383
- 15 Mallakpour, S.E., Hajipour, A.R. and Faghihi, Kh., *Eur. Polym. J.*, 2001, 37: 119
- 16 Mallakpour, S.E., Hajipour, A.R., Faghihi, Kh., Foroughifar, N. and Bagheri, J., *J. Appl. Polym. Sci.*, 2001, 80: 2416
- 17 Faghihi, Kh., Zamani, Kh., Mirsamie, A. and Sangi, M.R., *Eur. Polym. J.*, 2003, 39: 247
- 18 Okamoto, Y. and Nakano, T., *Chem. Rev.*, 1994, 94: 349
- 19 Farina, M., *Top Stereochem.*, 1987, 17: 1
- 20 Ciardelli, F., *Encycl. Polym. Sci. Engng.*, 1987, 10: 463
- 21 Wulff, G., *Angew. Chem. Int. Ed.*, 1989, 28: 21
- 22 Fontanille, M. and Guyot, A., "Recent Advances in Synthetic and Mechanistic Aspects of Polymerization Dordrecht", Kluwer, the Netherlands, 1987
- 23 Mallakpour, S.E., Dabbagh, H.A. and Faghihi, Kh., *Iranian Polym. J.*, 2000, 9: 41
- 24 Faghihi, Kh., Zamani, Kh. and Mallakpour, S., *Iranian Polym. J.*, 2002, 11: 339
- 25 "Kirk-Othmer Encyclopedia of Chemical Technology", 3<sup>rd</sup> Ed., John Wiley and Sons, New York, 1983, Vol.12, p.692-700
- 26 Mallakpour, S.E., Hajipour, A.R. and Habibi, S., *Eur. Polym. J.*, 2001, 37: 2435
- 27 Lamothe, M., Lannuzel, M. and Perez, M., *J. Comb. Chem.*, 2002, 4: 73