

Microwave Assisted Rapid Synthesis of Novel Optically Active Poly(amide-imide)s Based on *N*-Trimellitylimido-*L*-Leucine Diacid Chloride and Hydantoin Derivatives

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Received October 2, 2003; Revised April 23, 2004

Abstract: We have developed facile and rapid polycondensation reactions of *N*-trimellitylimido-*L*-leucine 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, by using a domestic microwave oven. The polycondensation reactions proceeded rapidly—they were complete within 7-9 min—to produce a series of novel optically active poly(amide-imide)s (**3a-h**) in high yield with inherent viscosities of 0.33-0.51 dL/g. We characterized the resulting poly(amide-imide)s by elemental analysis, thermal gravimetric analysis (DSC, TGA, and DTG), and FTIR spectroscopy, and by measuring their viscosities, specific rotations, and solubilities. All of the polymers were soluble at room temperature in polar solvents such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethylsulfoxide, tetrahydrofuran, and *N*-methyl-2-pyrrolidone.

Keywords: microwave-assisted rapid polycondensation, optically active polymers, poly(amide-imide)s, hydantoin derivatives, *N*-trimellitylimido-*L*-leucine diacid chloride.

Introduction

Recently, there has been growing interest in applying microwave energy to synthetic organic chemistry,¹⁻⁴ sample preparation for analysis,⁵ extraction of natural products from plants,⁶ waste treatment⁷ and polymer synthesis.⁸⁻¹¹ 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.¹²⁻¹⁷

Recently more attention has been paid to the synthesis and application of optically active polymers. Polymers with chiral structures are biologically very important.¹⁸ 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.¹⁹⁻²² Recently, we have synthesized optically active polymers by different methods.^{12-17,23-24}

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*-trimellitylimido-*L*-leucine diacid chloride **1** with eight different deriv-

atives of hydantoin compounds **2a-h** as heterocyclic moieties 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.²⁵

Experimental

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 Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were performed 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 using a Technico Regd Trad Merk Viscometer. Specific Rotations were measured by an A-Kruss polarimeter. Thermal Gravimetric Analysis (TGA) data for polymers were taken on a Mettler TA4000 System under N₂ atmosphere at a rate of 10 °C/min. Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument under N₂ atmosphere at a rate of 20 °C/min. Elemental analyses were performed by the Research Institute

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

Monomer Synthesis. N-trimellitylimido-L-leucine diacid chloride **1** was prepared by a procedure reported elsewhere.^{26,27} Hydantoin derivatives **2a-h** were prepared according to a typical procedure that was shown in scheme I.^{15,24}

Polymer Synthesis. An equimolar mixture of diacid chloride **1** (0.342 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 grounded until fine powder formed. Then 1 mL of o-cresol was added to the mixture and mixed up until homogeneous solution formed. Then the reaction mixture was irradiated in microwave oven at full power for 10 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 0.36 g (90%) of solid polymer **3d**.

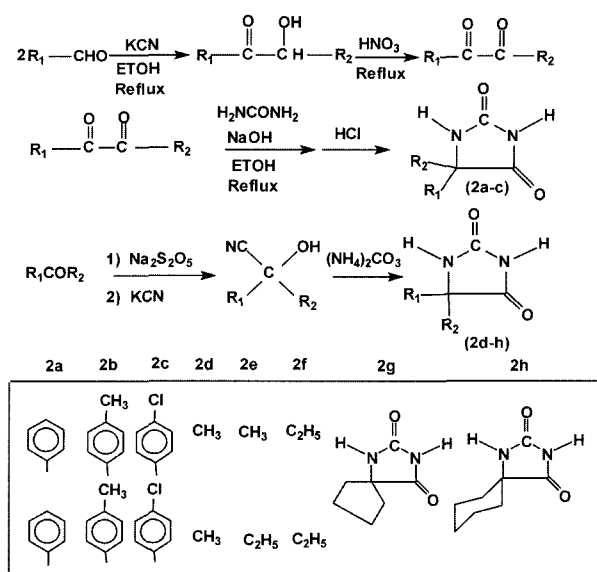
Results and Discussion

Monomer Synthesis. Hydantoin derivatives 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.²⁸ 5,5-disubstituted hydantoin derivatives were synthesized by two different methods. The compounds of **2a-c** were prepared from condensation reactions of benzil and benzil derivatives with urea. 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 proper cyanohydrin derivatives and ammonium carbonate (Scheme I).

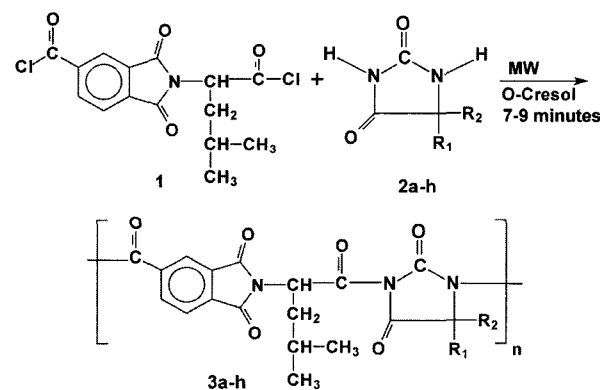
Polymer Synthesis. According to our previous results¹²⁻¹⁷ poly(amide-imide)s **3a-h** were synthesized by microwave assisted polycondensation reactions of an equimolar mixture of monomer **1** with six different derivatives of 5,5-disubstituted hydantoin **2a-h** in the presence of o-cresol as shown in Scheme II. The o-cresol was used as a 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 effective homogeneous heating of the reaction mixture and thereby subsequent polycondensation reaction occurs leading to the polymer formation. The optimum period of reaction time (irradiation time) was found between 7-9 minutes. Below this time given polymers showed lower inherent viscosities and above this time the materials degraded.

Polymer Characterization. The structures of these polymers were confirmed as PAIs by means of FT-IR spectro-

Scheme I



Scheme II



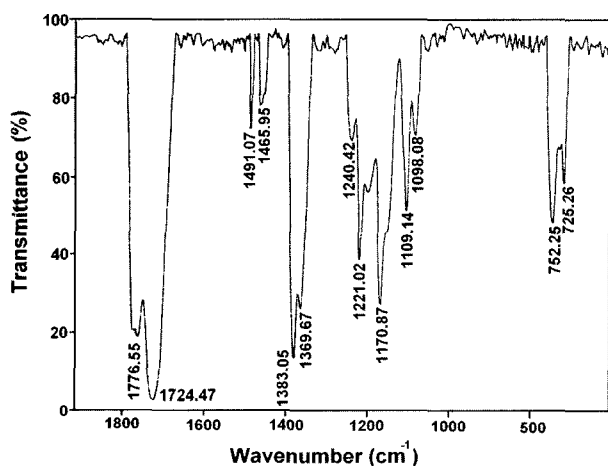
scopy and elemental analyses. The representative FT-IR spectrum of PAIs **3b** is shown in Figure 1. The polymers show absorption bands around 1780-1700 cm^{-1} due to amide and imide carbonyl linkages. Absorption bands around 1390-1380 cm^{-1} and 730-710 show the presence of the imide heterocycle in this polymer. The other spectra show a similar pattern. These spectra showed the carbonyl peaks in polymers shifted to lower frequency in comparison with diacid chloride **1**. FT-IR spectrum of compound **1** was showed the carbonyl peak of diacid chloride in 1800-1820 cm^{-1} . The elemental analysis values of the resulting polymers are in good agreement with the calculated values for the proposed structures (Table II).

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 THF at room temperature, and are insoluble in solvents such as acetone, chloroform, methylene

Table I. Synthesis and Some Physical Properties of PAIs 3a-h

Polymer	Irradiation time ^a (min.)	Temp. (°C) ^b	Yield ^c (%)	η_{inh} (dL/g) ^d	$[\alpha]_D^{25}$ ^e
3a	9	160	91	0.45	-12.0
3b	9	160	88	0.33	-8.0
3c	9	160	80	0.40	-16.0
3d	7	140	90	0.55	-7.0
3e	7	140	89	0.50	-9.0
3f	7.5	140	85	0.48	-11.0
3g	8	140	82	0.36	-12.0
3h	8	140	78	0.40	-10.0

^aTime of microwave irradiation. ^bTemperature of reaction mixture under microwave irradiation. ^cPower of microwave irradiation is 900 W. ^{d,e}Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

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

chloride, methanol, ethanol and water. The introduction of 5,5-disubstituted moieties into the polymer backbone increased solubility of these polymers.

Thermal Properties. The thermal properties of two PAIs **3a** and **3d** 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 rate of heating of 10 °C/min and thermal data are summarized in Table IV. All of these polymers show similar decomposition behavior (Figures 2, 3). Initial decomposition temperature, 5 and 10% weight loss (T_5 , T_{10}) and char yields at 600 °C for poly(amide-imide)s **3a** and **3d** are summarized in Table IV. These polymers exhibited good resistance to thermal decomposition up to 315-330 °C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged from 320 to 335 °C and the residual weight for these polymers at 600 °C ranged from 10.0 to 15.0% in

Table II. Elemental Analysis of PAIs 3a-h

Polymer	Formula		C%	H%	N%
3a	$C_{30}H_{23}N_3O_6$	Calcd	69.11	4.41	8.05
	$(521.3)_n$	Found	68.6	4.9	7.5
3b	$C_{32}H_{27}N_3O_6$	Calcd	69.96	4.91	7.64
	$(549.32)_n$	Found	68.7	4.5	7.0
3c	$C_{30}H_{21}N_3O_6Cl_2$	Calcd	61.03	3.55	7.11
	$(590.3)_n$	Found	60.9	3.8	6.6
3d	$C_{20}H_{19}N_3O_6$	Calcd	60.47	4.78	10.57
	$(397.2)_n$	Found	59.2	4.0	9.7
3e	$C_{21}H_{21}N_3O_6$	Calcd	61.33	5.10	10.21
	$(411.21)_n$	Found	60.5	4.5	9.6
3f	$C_{22}H_{23}N_3O_6$	Calcd	62.13	5.40	9.87
	$(425.22)_n$	Found	61.7	5.0	8.9
3g	$C_{22}H_{21}N_3O_6$	Calcd	62.43	4.96	9.92
	$(423.22)_n$	Found	63.4	5.0	8.2
3h	$C_{30}H_{23}N_3O_6$	Calcd	63.17	5.26	9.60
	$(437.23)_n$	Found	62.6	5.1	9.0

Table III. Solubility of PAIs 3a-h

Solvents	3a	3b	3c	3d	3e	3f	3g	3h
DMAC	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+	+
THF	+	+	+	+	+	+	+	+
CHCl ₃	-	-	-	-	-	-	-	-
Acetone	-	-	-	-	-	-	-	-
EtOH	-	-	-	-	-	-	-	-
MeOH	-	-	-	-	-	-	-	-
CH ₂ Cl ₂	-	-	-	-	-	-	-	-
H ₂ O	-	-	-	-	-	-	-	-

+: Soluble at room temperature, -: Insoluble at room temperature.

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

Polymer	T_g	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield ^c
3a	165	330-335	355-360	15.0
3d	155	315-320	340-345	10.0

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

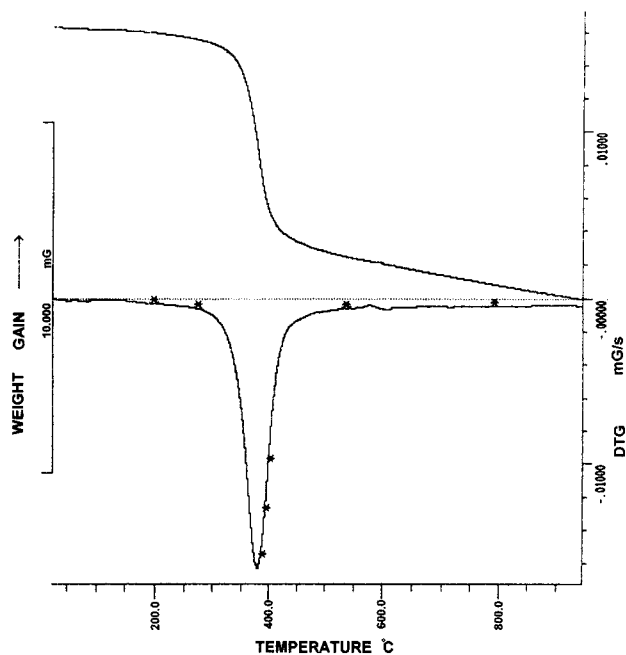


Figure 2. TGA and DTG thermogram of PAIs 3a.

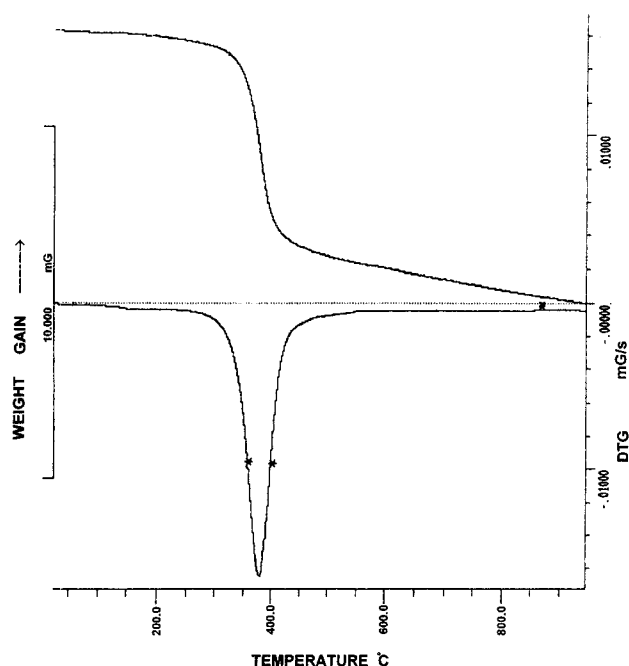


Figure 3. TGA and DTG thermogram of PAIs 3d.

nitrogen.

Conclusion

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 heterocycles unit. 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 the separation of the 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.

Acknowledgment. We wish to express our gratitude to the Research Affairs Division of University of Arak for financial support.

Appendix A. The PAIs 3a-h analyses using FT-IR

Polymer 3a

FT-IR(KBr): 1774 (m, sh), 1722 (s, br), 1490(w), 1465(w), 1383 (s), 1370(s), 1240 (m), 1221(s, br), 1170 (s), 1109 (m), 1100 (m), 750 (m), 725 (m) cm^{-1} .

Polymer 3b

FT-IR(KBr): 1776 (m, sh), 1724 (s, br), 1491(w), 1465(w), 1383 (s), 1369(s), 1240 (w), 1221(s, br), 1170 (s, br), 1109 (m), 1098 (m), 752 (m), 725 (m) cm^{-1} .

Polymer 3c

FT-IR(KBr): 1772 (m, sh), 1720 (s, br), 1490(w), 1464(w), 1381 (s), 1370(s), 1240 (m), 1221(s, br), 1170 (s), 1108 (m), 1100 (m), 750 (m), 722 (m) cm^{-1} .

Polymer 3d

FT-IR(KBr): 1764 (m, sh), 1720 (s, br), 1674(w), 1491(w), 1384 (s), 1296(w), 1246 (m), 1221(s, br), 1170 (s), 1145(m), 1109 (m), 1070 (w), 750 (m), 725 (m) cm^{-1} .

Polymer 3e

FT-IR(KBr): 1764 (m, sh), 1724 (s, br), 1491(m), 1467(w), 1383 (s), 1370(s), 1242 (s), 1221(s, br), 1170 (s, br), 1109 (m), 1085 (m), 754 (m), 725 (m) cm^{-1} .

Polymer 3f

FT-IR(KBr): 1776 (m, sh), 1724 (s, br), 1491(w), 1465(w), 1383 (s), 1370(s), 1240 (m), 1221(s, br), 1170 (s), 1109 (m), 1086 (m), 750 (m), 725 (m) cm^{-1} .

Polymer 3g

FT-IR(KBr): 1764 (m, sh), 1724 (s, br), 1491(w), 1465(w), 1383 (s), 1369(s), 1242 (m), 1221(s, br), 1170 (s), 1109 (m), 1087(m), 750 (m), 725 (m) cm^{-1} .

Polymer 3h

FT-IR(KBr): 1772 (m, sh), 1724 (s, br), 1491(w), 1465(w), 1383 (s), 1369(s), 1240 (m), 1221(s, br), 1170 (s), 1109 (m), 1087(m), 750 (m), 734 (m) cm^{-1} .

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