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Microwave-assisted synthesis of optically active poly(amide–imide)s with benzophenone and L-alanine linkages

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Abstract

Rapid and highly efficient synthesis of poly(amide–imide)s was achieved under microwave irradiation by using a domestic microwave oven from the polycondensation reactions of 4,4′-carbonyl-bis(phthaloyl-L-alanine) diacid chloride [*N*,*N*′-(4,4′-carbonyldiphthaloyl)] bisalanine diacid chloride (**1**) with seven aromatic diamine (**2a**–**2g**) in the presence of a small amount of a nonpolar organic medium that acts as a primary microwave absorber. Suitable organic media was *o*-cresol. The polycondensation proceeded rapidly, compared with the conventional melt polycondensation and solution polycondensation and was almost completed within 10 min giving a series of poly(amide–imide)s with inherent viscosities about 0.36–0.85 dl g^{-1}. The resulting poly(amide–imide)s were obtained in high yield and were optically active and thermally stable. All of the above compounds were fully characterized by means of FTIR spectroscopy, elemental analyses, inherent viscosity (η_{inh}), solubility test and specific rotation. Thermal properties of the poly(amide–imide)s were investigated using TGA/DTG. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(amide–imide)s; Microwave oven; Polycondensation; Optically active polymers; L-alanine

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1. Introduction

Microwave irradiation has received growing application in organic synthesis for optimization and acceleration of chemical reactions [1–6]. In some cases, microwave heating is superior to thermal heating and has been shown to increase reaction rates, selectivity and yields of target products and reduce tarring [7]. Microwave energy is being investigated as a method to process resins, such as epoxides [8–10], polyesters [11,12], polyurethanes [13,14] and more recently polyimides [15–18] due to advantages of shorter processing time, improved energy utilization, and the potential for lower processing temperature and improved product uniformity. The microwave energy is absorbed by the molecules through the polarization or dipole reorientation of functional groups, and is consequently converted to thermal energy. As a result, heat is generated within each molecule thereby creating conditions for a homogeneous heating pattern in the material. In the conventional heating process, the heat is transferred from the outside to the inside of the material, resulting in very long processing times to achieve high product uniformity.

Monomers having carbonyl groups attract considerable attention because of the possibility of employing them in the preparation of polyimides with enhanced solubility, thermal stability and improved processibility. Furthermore, the use of monomers containing preformed imide rings is one method for the preventing of partial crosslinking in the course of reaction because it avoids high temperature curing cycles and handling unstable intermediates such as polyamic acids [19,20]. The synthesis and application of optically active polymers have gained more attention recently, as polymers with chiral structures are biologically very important. Most of the natural polymers are optically active and have special chemical activities such as catalytic

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properties that exist in genes, proteins and enzymes. Some other applications could be listed as (1) constructing chiral media for asymmetric synthesis, (2) chiral stationary phases for resolution of enantiomers in chromatographic techniques, (3) chiral liquid crystals in ferroelectrics and nonlinear optical devices [21–24]. These applications have resulted in attempts to improve different synthetic procedures of optically active polymers. Various optically active homopolymers as well as copolymers have been prepared and reported in the literature [25–35]. Recently, we have synthesized optically active polymers by different methods [36–39].

In a previous paper [40], we synthesized a series of optically active poly(amide–imide)s (PAIs) containing one group of hexafluoropropylidene as well as two groups of chiral L-leucine using microwave irradiation. In this article, we wish to report the synthesis and properties of novel optically active PAIs prepared by the polycondensation reactions of 4,4′-carbonyl-bis(phthaloyl-L-alanine) diacid chloride (**1**) with aromatic diamines using a domestic microwave oven.

2. Experimental

2.1. Materials

All chemicals were purchased from Fluka Chemical Co., Aldrich Chemical Co. and Riedel-deHaen AG. 3,3′,4,4′-benzophenonetetracarboxylic dianhydride was obtained from Fluka Chemical Co. as analytical grade material and was used as received. Benzidine (**2a**) and 4,4′-diaminodiphenyl methane (**2b**) were purified by recrystallization from ethanol and water, respectively. 2,6-diaminopyridine (**2d**) was purified by sublimation. The other diamines were used as obtained without further purification.

2.2. Techniques

FTIR spectra were recorded using Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out 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 Cannon Fensk Routine Viscometer. Specific Rotations were measured using a Perkin Elmer-241 Polarimeter. Thermal gravimetric analysis (TGA) and deferential thermal gravimetric (DTG) data for polymers was obtained using a Mettler TA4000 System under air atmosphere at a rate of 10°C min^{-1}. Elemental analysis were performed by the Research Institute of Petroleum Industry, Tehran, Iran. As a source of microwave irradiation, we used a Samsung domestic microwave oven (2450 MHz, 900 W) device.

3. Monomer synthesis

4,4′-Carbonyl-bis(phthaloyl-L-alanine) and 4,4′-carbonyl-bis(phthaloyl-L-alanine) diacid chloride (**1**) were prepared according to our previous work [39].

4. Polymer synthesis

An equimolar mixture of diacid chloride (**1**) (0.2 g, 3.99×10^{-4} mol) and benzidine (**2a**) (0.073 g, 3.99×10^{-4} mol) were placed in a reaction vessel and the mixture was ground until a fine powder was formed. 0.45 ml of *o*-cresol was added to the mixture and the whole until homogeneous solution was formed. The reaction mixture was irradiated in a microwave oven at full power for 10 min. The reaction mixture was poured into 25 ml of methanol. The resulting polymer was filtered, and dried to yield 0.23 g (94%) of brown solid.

All other PAIs (**3a**–**3g**) were synthesized by the above method.

4.1. Polymer 3a

FTIR (KBr): 3300–3400 (s,br), 2800–3000 (w), 2360 (m), 1790 (m), 1720 (s), 1690 (m), 1508 (m), 1384 (m), 1248 (w), 1150 (w), 820–800 (w), 720 (w) cm^{-1}.

4.2. Polymer 3b

FTIR (KBr): 3370 (s,br), 2360 (m), 2180 (w,br), 1803 (m), 1716 (s), 1680–1700 (m), 1508 (m), 1384 (m), 1248 (w), 1151 (w), 727 (w) cm^{-1}.

4.3. Polymer 3c

FTIR (KBr): 3300–3400 (s,br), 3000–2900 (w), 1790 (m), 1740 (s), 1700 (s), 1640 (w), 1620 (w), 1590 (m), 1520 (w), 1380 (w), 1250 (m), 1180 (w), 1070 (w), 1040 (w), 880 (w), 720–700 (w) cm^{-1}.

4.4. Polymer 3d

FTIR (KBr): 3340 (s,br), 1776 (s), 1712 (s), 1664 (s), 1452 (m), 1383 (s), 1221 (m), 1170 (m), 1109 (m), 727 (w) cm^{-1}.

4.5. Polymer 3e

FTIR (KBr): 3369 (s,br), 3111 (w), 1795 (w), 1716 (s), 1710 (m), 1589 (m), 1518 (m), 1246 (m), 1149 (m), 1103 (m), 720 (w) cm^{-1}.

4.6. Polymer 3f

FTIR (KBr): 3321 (s,br), 2380 (w), 1778 (m), 1718 (s), 1700 (m), (s), 1516 (m), 1377 (s), 1246 (m), 1149 (m), 1093 (m), 727 (w) cm^{-1}.

4.7. Polymer 3g

FTIR (KBr): 3350 (s,br), 2380 (m), 1774 (m,s), 1716 (s), 1521 (m), 1384 (s), 1248 (w), 1151 (w), 727 (w) cm^{-1}.

5. Results and discussion

5.1. Polymer synthesis

The PAIs (**3a**–**3g**) were synthesized by microwave assisted polycondensation reactions of an equimolar mixture of monomer (**1**) with seven different aromatic diamines (**2a**–**2g**) in *o*-cresol as organic solvent by using a domestic microwave oven as shown in Scheme 1. *o*-Cresol was used as the polar organic medium since it acts as a primary microwave absorber and as a solvent for both of the starting monomers and the resulting polymers.

The optimum period of reaction time (irradiation time) was found to be 10 min and below this time polymers with low inherent viscosities were produced and above this time the materials will be degraded.

5.2. Polymer characterization

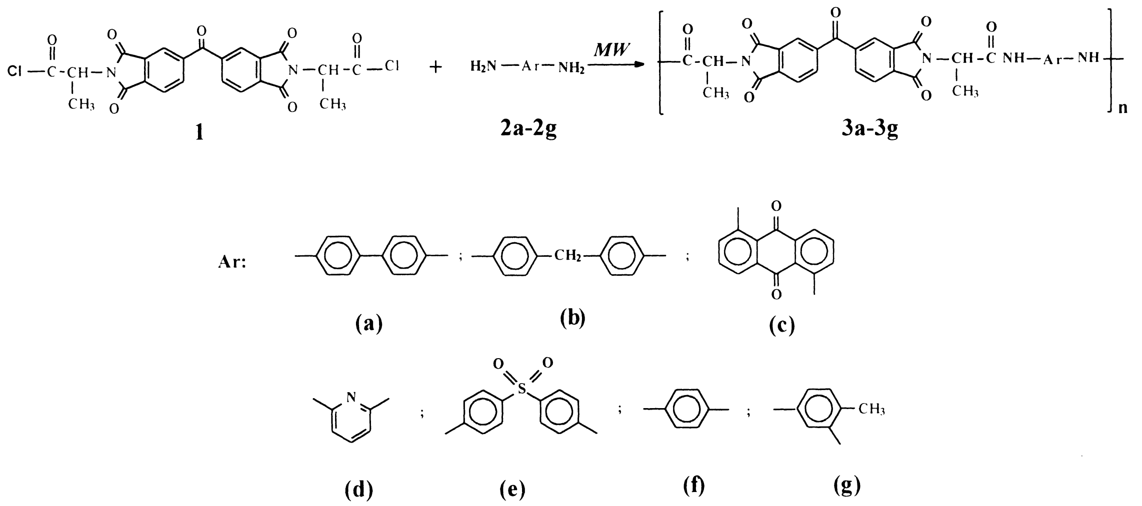
Synthesis and some physical properties of PAIs (**3a**–**3g**) are summarized in Table 1. These polymers have inherent viscosities in a range of 0.36–0.85 dl g^{-1}. PAIs derived from monomer (**1**) may range in color from cream or off-white to pale-yellow, except polymers (**3c**) and (**3d**) which have an intense, orange and pale-orange color, respectively. Because of the intensive of this color, polarized light could not be transmitted through the polymer solution and therefore their optical rotation were undefined (Table 1). The other resulting polymers show optical rotation and are optically active.

Table 1
Synthesis and some physical properties of PAIs (**3a**–**3g**)

Diamine	Polymer	Yield (%)	η_{inh} (dl g^{-1})$^{\text{a}}$	$[\alpha]_{\text{D}}^{25\text{b}}$
2a	**3a**	94	0.60	−34.00
2b	**3b**	96	0.78	−14.00
2c	**3c**	91	0.65	–$^{\text{c}}$
2d	**3d**	95	0.36	–$^{\text{c}}$
2e	**3e**	96	0.85	−36.00
2f	**3f**	98	0.45	−18.00
2g	**3g**	95	0.55	−35.00

$^{\text{a}}$ Measured at a concentration of 0.5 g dl^{-1} in DMF at 25°C.
$^{\text{b}}$ Measured at a concentration of 0.5 g dl^{-1} in DMF at 25°C.
$^{\text{c}}$ Specific rotation was undefined.

The structures of these polymers were confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The FTIR spectra of all polymers showed absorptions around 3300 cm^{-1} (N–H) and two overlapped carbonyl (amide and imide C = O) absorptions at 1720 and 1780 cm^{-1}. All of these PAIs exhibited strong absorption at 1370–1380 and 710–720 cm^{-1} that show the presence of the imide heterocycle in these polymers. The polymer (**3e**) showed characteristic absorptions at 1246 and 1149 cm^{-1} due to the sulfone moiety (SO_2 stretching). The elemental analysis values of



Scheme 1.

the resulting polymers are in good agreement with the calculated values for the proposed structures (Table 2).

The inherent viscosities of the resulting PAIs obtained by this new method were compared with those obtained with solution polymerization method [39] and are shown in Table 3. These data indicate that the internal heat generation of both the solvent and the monomers under the microwave irradiation was much more effective for the progress of polycondensation, producing PAIs with high viscosity values in a shorter polymerization time, than the conventional external heating did.

The solubility of PAIs are given in Table 4. Most of the polymers are soluble in organic solvents, such as DMF, DMAc and DMSO at room temperature, and are insoluble in solvents, such as chloroform, methylene chloride and so on.

Table 2
Elemental analysis of PAIs

Polymer	Formula		C (%)	H (%)	N (%)
3b	$C_{36}H_{26}O_7N_4$	Calculated	69.01	4.15	8.94
		Found	69.50	4.40	7.80
3e	$C_{35}H_{24}O_9N_4S$	Calculated	62.13	3.58	8.25
		Found	63.60	4.20	6.90
3g	$C_{30}H_{22}O_7N_4$	Calculated	65.45	4.00	10.18
		Found	65.50	4.10	9.10

Table 3
Inherent viscosity differences between solution and microwave methods

Method	Polymer				
	3a	**3b**	**3c**	**3d**	**3e**
Solution	0.20	0.20	0.32	0.23	0.18
Microwave	0.60	0.78	0.65	0.36	0.85

Table 4
Solubility of PAIs (**3a–3g**)

Solvents	3a	3b	3c	3d	3e	3f	3g
DMAc	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+
THF	–	–	–	–	–	–	–
DMSO	+	+	+	+	+	+	+
MeOH	–	–	–	–	–	–	–
EtOH	–	–	–	–	–	–	–
$CHCl_3$	–	–	–	–	–	–	–
CH_2Cl_2	–	–	–	–	–	–	–
H_2O	–	–	–	–	–	–	–

+; Soluble at room temperature, –; Insoluble.

5.3. Thermal properties

The thermal properties of PAIs (**3b**, **3e**, **3g**) were evaluated by means of TGA/DTG in air atmosphere. All of these polymers show similar decomposition behavior (Figs. 1–3), they show three different decomposition maxima. The first two which are slower decomposition occur at lower temperatures and the third one occurs at higher rates and higher temperatures. Table 5 summarizes the thermal properties of PAIs (**3b**, **3e**, **3g**). These PAIs exhibited good resistance to thermal decomposition up to 233–275°C in air atmosphere and began to decompose gradually above that temperature. The temperature of 5% weight loss for the polymers (**3b**, **3e**, **3g**) ranged from 227°C to 251°C and the residual weight for these polymers at 600°C ranged from 60.00% to 74.28% in air atmosphere.

6. Summary and conclusions

The present work has shown that 4,4′-carbonyl-bis(phthaloyl-L-alanine) diacid chloride (**1**) is an interesting monomer which contains both the benzophenoneimide group as well as chiral L-alanine groups.

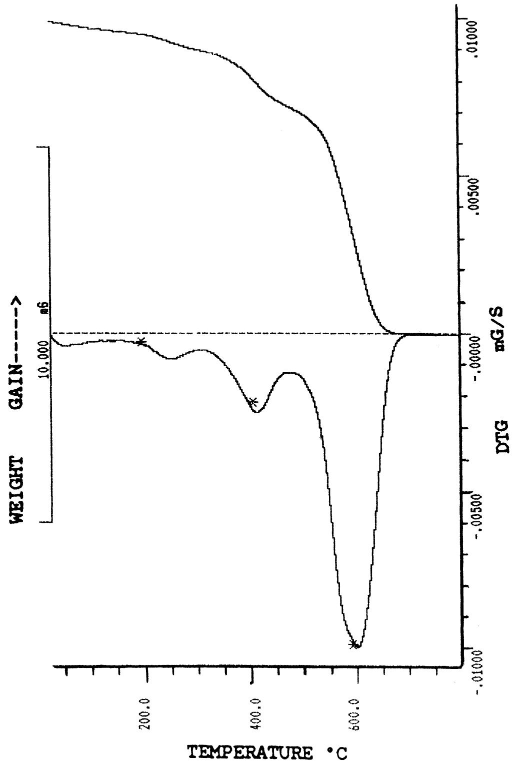


Fig. 1. TGA/DTG thermograms of PAI (**3b**) in air atmosphere.

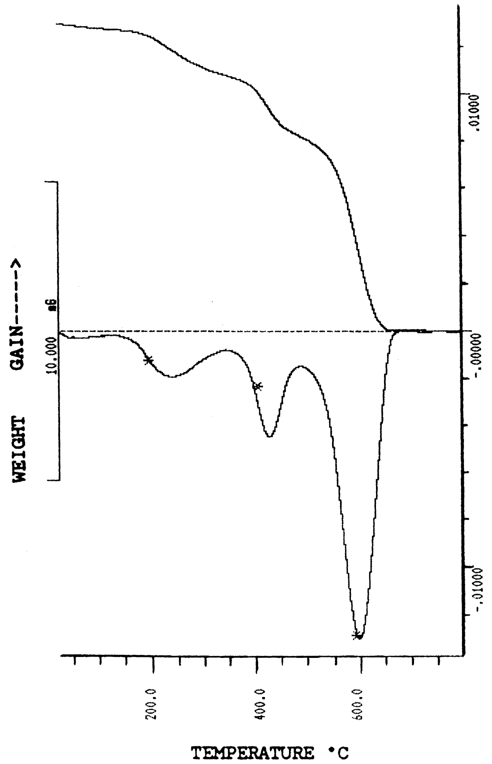


Fig. 2. TGA/DTG thermograms of PAI (**3e**) in air atmosphere.

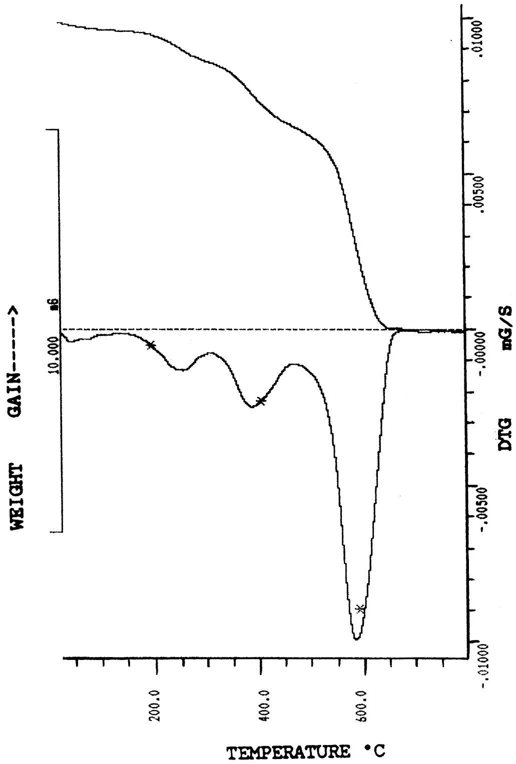


Fig. 3. TGA/DTG thermograms of PAI (**3g**) in air atmosphere.

Thus, a series of new optically active PAIs having inherent viscosities of 0.36–0.85 dl g^{-1} were synthesized by microwave assisted polycondensation reaction of the optically active monomer 4,4′-carbonyl-bis(phthaloyl-L-alanine) diacid chloride (**1**) with seven aromatic diamines (**3a**–**3g**). These aromatic poly(amide–imides) are optically active and are readily soluble in various organic solvents and have good thermal stability. The inherent viscosities obtained from microwave assisted polycondensation reactions are much higher than those polymers obtained from solution polymerization. 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.

Table 5
Thermal behavior of PAIs

Polymer	Decomposition temperature (°C) T_5[a]	Char yield (%)[b]
3b	275	21.00
3e	251	8.50
3g	233	5.50

[a] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C min^{-1} in air atmosphere.

[b] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600°C in air atmosphere.

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