Efficient and Rapid Synthesis of Optically Active Polyamides in the Presence of Tetrabutylammonium Bromide as Ionic Liquids Under Microwave Irradiation

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ABSTRACT: There is increasing interest in using ionic liquids (ILs) as solvents for polymerization processes. The use of an inexpensive and readily available IL such as tetrabutylammonium bromide (TBAB) as a solvent for clean synthesis and catalytic processes is becoming widely recognized and accepted. This article reports an extension of a microwave method, describing the synthesis of optically active polyamides (PAs) in TBAB. Polycondensation reactions of diacid 5-(3-methyl-2-phthalimidylpentanoylamino) isophthalic acid with different diisocyanates such as 4, 4′-methylenebis(phenyl isocyanate), toluylene-2,4-diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate were carried out in the presence of TBAB as a molten salt under microwave irradiation and with a conventional heating method, and they were compared with polymerizations in a traditional solvent such as 1-methyl-2-pyrrolidone. A series of optically active PAs with high yields and inherent viscosities ranging from 0.20 to 0.60 dL/g were obtained. These PAs were characterized with Fourier transform infrared spectroscopy, specific rotation measurements, ^{1}H-NMR, elemental analysis, thermogravimetric analysis, and differential scanning calorimetry. All data agreed with the proposed structures. Some physical properties and structural characterizations of these PAs are reported. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3603–3612, 2008

Key words: biodegradable; chiral; polyamides; polycondensation; thermogravimetric analysis (TGA)

INTRODUCTION

The use of microwave irradiation in organic chemistry started in 1969, and in 1991, it was reviewed by Abramovich.[1] As an alternative to classical heating techniques, microwave energy is an effective, selective, and fast synthetic means of heating molecules directly through the interaction between microwave energy and molecular dipole moments of monomers containing polar groups that favor the absorption of microwaves.[2–7] In the field of polymers, various types of processes and syntheses, such as the cross-linking of bisamides, synthesis of polyethers and polyurethanes, imidization of polyamic acids, and direct polycondensation of aromatic diamines, are derived from interesting efforts using microwave radiation.[8]

Ionic liquids (ILs), also called molten salts, are promising organic materials in modern chemical technologies.[9,10] ILs consist of a mixture of cations and anions heated above their melting points. To achieve ILs that have low melting points, bulky alkyl groups on the cations (*N*,*N*-dialkylimidazolium, quaternary ammoniums, phosphonium, and pyridinium) are used to prevent crystallization, which is typical with most ionic compounds.[11–16] Both academic and industrial research groups are trying to redesign chemical processes to reduce or eliminate losses of solvents, particularly volatile organic compounds. Noticeably, the replacement of a volatile organic compound solvent in a procedure with a nonvolatile solvent will diminish losses through evaporation, and it is noteworthy that ILs are chemicals that can be applied as solvents and catalysts in green chemistry processes.[17,18] Nevertheless, the high cost of most conventional room-temperature (RT) ILs and apprehension about their toxicity have led researchers to explore the use of more benign salts in the molten state as useful choices. Recently, molten tetrabutylammonium bromide (TBAB) has been used as a low-toxicity and cost-effective IL in a number of practical synthetic transformations.[19–22] Their unique physicochemical properties, such as a wide liquid range, low melting points, good solubility character-
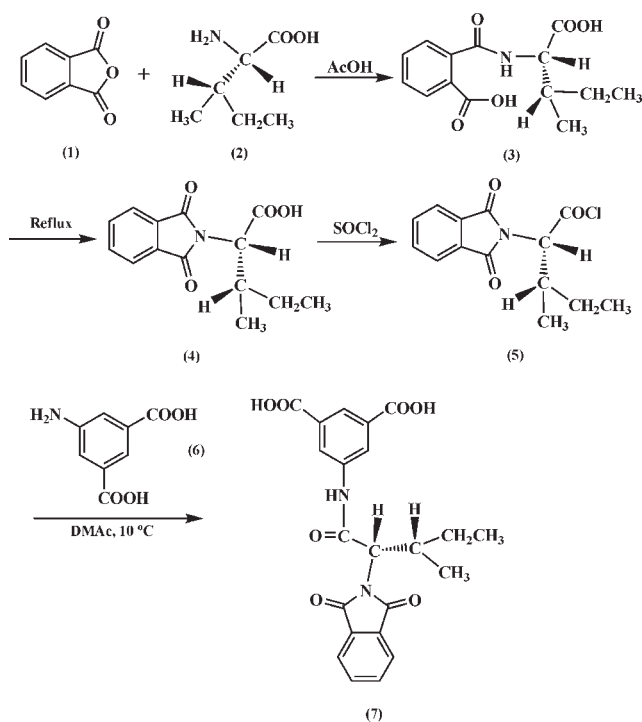
Scheme 1 Synthesis of monomer **7**.

istics, negligible vapor pressure, relatively low viscosities, high fluidity, nonflammability, a wide electrochemical window, tolerance to strong acids, and excellent thermal and chemical stability, are responsible for their rapid appearance as alternative solvents and the concomitant rapidly growing number of uses.[23,24] Furthermore, ILs show significant improvements in the reaction rate, yield, and selectivity. Recently, we have demonstrated a successful application of ILs to the synthesis of a wide variety of new polymers via step-growth polymerization.[25–28]

The application of ILs as aids for the microwave heating of nonpolar solvents has been studied, and this has allowed them to be used as media for microwave-assisted chemistry. With a suitable IL, heating can be carried out with no contamination of the solvent.[29]

Aromatic polyamides (PAs) are well-known as high-performance polymeric materials because of their excellent thermal stability, electric insulation property, low flammability, and chemical resistance. However, their applications are limited because of their high softening or melting temperatures and their insolubility in most organic solvents. To overcome these drawbacks, modifications of the PA structure have often been made, such as the introduction of flexible linkages, a nonsymmetrical structure, or bulky substituents into the polymer backbone.[30–32] The synthesis and application of optically active polymers are newly considered topics that have been paid more attention recently because polymers with chiral structures are biologically very

important. Most natural polymers are optically active and have special chemical activities such as catalytic properties that exist in genes, proteins, and enzymes. Recently, we have synthesized optically active polymers by different methods.[28,33–37] Among the synthetic PAs, only those containing naturally occurring (L)-α-amino acids, being structurally close to natural polypeptides, possess potentially degradable linkages that make them appropriate as biomaterials.[38–40] With the aim of creating polymers containing naturally occurring (L)-α-amino acids, various approaches have been effectively attempted in the synthesis of new types of monomers.[41] This article describes a successful application of ILs to the green synthesis and characterization of optically active PAs via step-growth polymerization reactions of aromatic–aliphatic diacid 5-(3-methyl-2-phthalimidylpentanoylamino)isophthalic acid (**7**) with different diisocyanates. The use of dicarboxylic acids in direct polycondensation, instead of their significantly more toxic though more reactive derivatives, such as diacid chlorides, is one of the main and important prerequisites for the study of such polymer syntheses in ILs. This article also reports the microwave-assisted synthesis of optically active PAs, and this method is compared with conventional heating solution polymerization in ILs and in organic solvents.

EXPERIMENTAL

Materials and equipment

Reagents were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), and Riedel-de Haen AG (Seelze, Germany). N,N-Dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), pyridine (Py), and triethylamine (TEA) were dried over BaO and then were
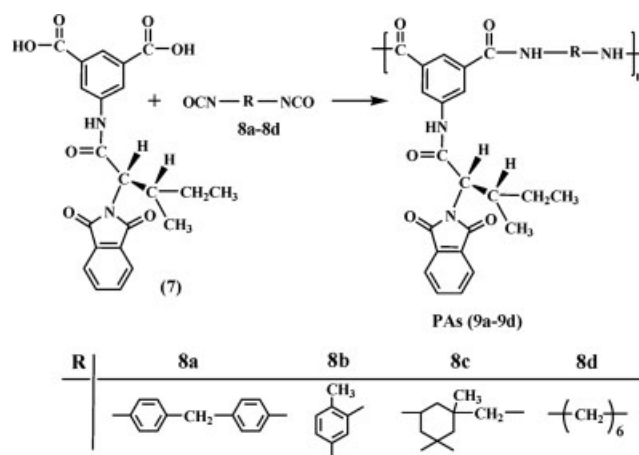
Scheme 2 Polycondensation reactions of monomer **7** with different diisocyanates.

TABLE I
Reaction Conditions for the Polymerization of Monomer 7 with Different Diisocyanates and Some Physical Properties of PAs 9aIA–9dIIIB Prepared by Methods I[a] and III[b]

Polymer	Diisocyanate	Catalyst	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	$[\alpha]_D^{25\ i}$
9aIA	**8a**	A	MeOH/water	80	0.46[c]	−24.72
9aIB	**8a**	B	MeOH/water	89	0.27[c]	−17.74
9aIC	**8a**	C	MeOH/water	86	0.26[c]	−34.96
9aID	**8a**	D	MeOH/water	86	0.28[c]	−16.62
9bIA	**8b**	A	Water	71	0.49[d]	−13.44
9bIB	**8b**	B	Water	66	0.23[c]	−45.24
9cIA	**8c**	A	Water	87	0.21[c]	−20.76
9cIB	**8c**	B	Water	91	0.31[c]	−20.70
9dIA	**8d**	A	MeOH/water	48	0.49[e]	−12.64
9dIB	**8d**	B	MeOH/water	77	0.38[e]	−13.82
9aIIIA	**8a**	A	MeOH/water	60	0.60[f]	−17.14
9aIIIB	**8a**	B	MeOH/water	57	0.48[f]	−13.02
9aIIIC	**8a**	C	MeOH/water	62	0.51[g]	−23.04
9aIIID	**8a**	D	MeOH/water	75	0.43[g]	−12.04
9bIIIA	**8b**	A	Water	54	0.24[c]	−14.64
9bIIIB	**8b**	B	Water	55	0.23[c]	−19.43
9cIIIA	**8c**	A	Water	85	0.20[c]	−19.50
9cIIIB	**8c**	B	Water	59	0.24[c]	−19.21
9dIIIA	**8d**	A	MeOH/water	53	0.32[h]	−13.26
9dIIIB	**8d**	B	MeOH/water	50	0.26[h]	−15.09

A = TEA; B = no catalyst; C = Py; D = DBTDL.
[a] Method I: Polymerization under conventional heating for 12 h at 120°C.
[b] Method III: Gradual heating at different temperatures: 1 h at RT, 3 h at 60°C, 8 h at 80–90°C, 2 h at 100°C, and 2 h at 120°C.
[c] Measured at a concentration of 0.5 g/dL in DMF at 25°C.
[d] Measured at a concentration of 0.5 g/dL in DMF containing 0.3% (w/w) LiCl (soluble fraction) at 25°C.
[e] Measured at a concentration of 0.5 g/dL in DMF containing 1% (w/w) LiCl (soluble fraction) at 25°C.
[f] Measured at a concentration of 0.5 g/dL in DMF containing 0.4% (w/w) LiCl (soluble fraction) at 25°C.
[g] Measured at a concentration of 0.5 g/dL in DMF containing 0.2% (w/w) LiCl (soluble fraction) at 25°C.
[h] Measured at a concentration of 0.5 g/dL in DMF containing 6% (w/w) LiCl (soluble fraction) at 25°C.
[i] Measured under the same conditions used for the inherent viscosity.

distilled under reduced pressure. TBAB (mp = 100–103°C) was purchased from Merck Co. (Darmstadt, Germany) and was used without further purification. ^{1}H-NMR (500 MHz) spectra were recorded on a Bruker (Ettlingen, Germany) Advance 500 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Impact 400$_D$ IR spectrophotometer (Thunderdome, Germany). Spectra of solids were carried out with KBr pellets. Vibrational transition frequencies are reported as wave numbers (cm^{-1}). Band intensities are designated as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure with a Cannon-Fenske (Mainz, Germany) routine viscometer. Specific rotations were measured with a Jasco (Osaka, Japan) P-1030 polarimeter. The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz, 900 W). All the polymerization reactions were carried out in a hood with strong ventilation. All melting points were taken with a melting-point apparatus (Gallenkamp, England). Quantitative solu-

bility was determined with 0.05 g of the polymer in 1 mL of the solvent. Elemental analyses were performed by the Research Institute of Polymers and Petrochemicals of Iran (Tehran, Iran). Thermogravimetric analysis (TGA) data for polymers were taken on a PerkinElmer thermogravimetric analyzer (Karlsruhe, Germany) under a nitrogen atmosphere at a heating rate of 10°C/min, and differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument (London, UK) under a nitrogen atmosphere by the Research Institute of Polymers and Petrochemicals of Iran. Glass-transition temperatures (T_g's) were read at the middle of the transition in the heat capacity taken from the DSC heating traces.

Monomer synthesis

7 was prepared according to our previous work.[42]

Polymer synthesis

The polymers were synthesized with four different methods.

Reaction Conditions for the Polymerization of Monomer 7 with Different Diisocyanates and Some Physical Properties of PAs 9aIIA–9dIVB Prepared by Methods II[a] and IV[b]

Polymer	Diisocyanate	Catalyst	Nonsolvent	Yield (%)	Inherent viscosity (dL/g)	$[\alpha]_D^{25}$ [h]
9aIIA	**8a**	A	MeOH/water	84	0.33[c]	−30.24
9aIIB	**8a**	B	MeOH/water	70	0.23[c]	−32.50
9aIIC	**8a**	C	MeOH/water	84	0.33[c]	−27.12
9aIID	**8a**	D	MeOH/water	96	0.35[c]	−20.30
9bIID	**8b**	D	Water	63	0.24[c]	−25.51
9bIIB	**8b**	B	Water	71	0.21[c]	−35.12
9cIID	**8c**	D	Water	69	0.20[c]	−12.60
9cIIB	**8c**	B	Water	78	0.26[c]	−25.92
9dIID	**8d**	D	MeOH/water	56	0.42[d]	−22.17
9dIIB	**8d**	B	—	—	—	—
9aIVA	**8a**	A	MeOH/water	42	0.30[e]	−13.06
9aIVB	**8a**	B	MeOH/water	73	0.36[f]	−18.32
9aIVC	**8a**	C	MeOH/water	53	0.47[f]	−11.26
9aIVD	**8a**	D	MeOH/water	62	0.51[e]	−13.66
9bIVD	**8b**	D	Water	78	0.22[c]	−19.22
9bIVB	**8b**	B	Water	67	0.28[c]	−17.18
9cIVD	**8c**	D	Water	58	0.21[c]	−12.40
9cIVB	**8c**	B	Water	64	0.20[c]	−22.52
9dIVD	**8d**	D	MeOH/water	66	0.41[g]	13.52
9dIVB	**8d**	B	MeOH/water	76	0.34[g]	−16.62

A = TEA; B = no catalyst; C = Py; D = DBTDL.

[a] Method II: The reaction mixture was irradiated in a microwave oven for 3 min and then cooled and irradiated for 1 min again at 100% (900 W) of its power level.

[b] Method IV: The reaction mixture was irradiated in a microwave oven for 2 min and then cooled and irradiated for 1 min again at 70% (630 W) of its power level.

[c] Measured at a concentration of 0.5 g/dL in DMF at 25°C.

[d] Measured at a concentration of 0.5 g/dL in DMF containing 1% (w/w) LiCl (soluble fraction) at 25°C.

[e] Measured at a concentration of 0.5 g/dL in DMF containing 0.4% (w/w) LiCl (soluble fraction) at 25°C.

[f] Measured at a concentration of 0.5 g/dL in DMF containing 0.6% (w/w) LiCl (soluble fraction) at 25°C.

[g] Measured at a concentration of 0.5 g/dL in DMF containing 3% (w/w) LiCl (soluble fraction) at 25°C.

[h] Measured under the same conditions used for the inherent viscosity.

Method I: Polymerization under conventional heating in TBAB as an IL medium

A mixture of aromatic diacid **7** (0.10 g, 2.36×10^{-4} mol) and TBAB (0.30 g, 9.42×10^{-4} mol) was ground until a powder was formed. After the mixture was completely ground, TEA (0.02 mL, 1.80×10^{-4} mol) was added; then, it was transferred into a 25-mL, round-bottom flask, and toluylene-2,4-diisocyanate (TDI or **8b**; 0.04 g, 2.36×10^{-4} mol) was added to the mixture, which was heated until a homogeneous solution was formed. Then, the solution was stirred for 12 h at 120°C, and the viscous solution was precipitated in 30 mL of water. The white solid was filtered off and dried to give 0.10 g (71%) of white **PA9bIA**. The aforementioned polymerization was repeated without a catalyst.

Method II: Polymerization under microwave irradiation in TBAB as an IL medium

The PAs were prepared with the following general procedure (e.g., **PA9dIID**). Into a porcelain dish was placed diacid **7** (0.10 g, 2.36×10^{-4} mol), and TBAB (0.23 g, 6.98×10^{-4} mol) was added. After the mix-

ture was completely ground, dibutyltin dilaurate (DBTDL; 0.02 g, 3.01×10^{-5} mol) was added, and the mixture was ground for 5 min; then, hexamethylene diisocyanate (HDI or **8d**; 0.04 g, 2.36×10^{-4} mol) was added, and the mixture was ground again for an additional 2 min. The reaction mixture was irradiated in the microwave oven for 3 min, and
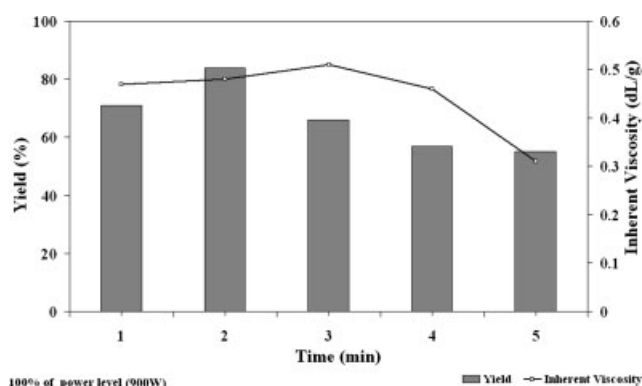

Figure 1 Effect of the reaction time on the inherent viscosities and yields of PAs based on MDI by method IV in the presence of Py as a catalyst.
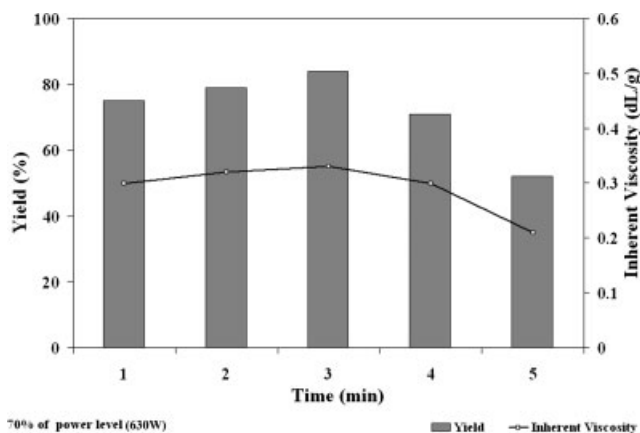
Figure 2 Effect of the reaction time on the inherent viscosities and yields of PAs based on MDI by method II in the presence of Py as a catalyst.

then it was cooled and irradiated for 1 min more at 100% of its power level (900 W). The resulting product was isolated by the addition of 30 mL of a methanol/water (50/50) mixture solution. It was then filtered and dried at 80°C for 10 h *in vacuo*; this yielded 0.08 g (56%) of yellow **PA9dIID**. The aforementioned polymerization was repeated, but the reaction mixture was irradiated in a microwave oven with TBAB without a catalyst.

Method III: Polymerization under gradual heating in NMP as a solvent

In a 25-mL, round-bottom flask, a solution of diacid **7** (0.09 g, 2.16×10^{-4} mol) in 0.18 mL of NMP was added to a solution of 4,4′-methylenebis(phenyl isocyanate) (MDI or **8a**; 0.05 g, 2.16×10^{-4} mol) and TEA (0.02 mL, 1.80×10^{-4} mol) in 0.20 mL of dry NMP. The mixture was stirred for 1 h at RT, 3 h at 60°C, and 8 h at 80°C and then was heated gradually from 100 to 120°C for 4 h. During this period, 0.20 mL of NMP was added. The reaction mixture was poured into 30 mL of methanol to precipitate the polymer. The solid was filtered off and dried to give 0.09 g (60%) of yellow **PA9aIIIA**. This polymerization was also repeated with Py and DBTDL as catalysts and without any catalyst.

### Method IV: Polymerization under microwave irradiation in NMP as a solvent

The PAs were prepared by the following general procedure (**PA9aIVD** is used as an example). Into a porcelain dish, monomer **7** (0.09 g, 2.16×10^{-4} mol) and 0.18 mL of NMP were placed. After the mixture was completely ground, DBTDL (0.02 g, 3.01×10^{-5} mol) was added, and the mixture was ground for 5 min. A solution of MDI (**8a**; 0.05 g, 2.16×10^{-4} mol)
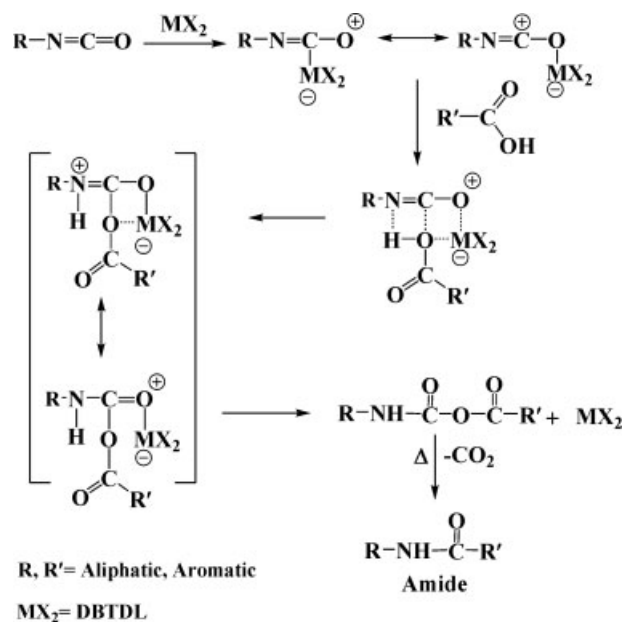
Scheme 3 Mechanism of the reaction of carboxylic acid with isocyanate activated by organometallic compounds.

in 0.20 mL of dry NMP was added, and the mixture was ground again for an additional 2 min. The reaction mixture was irradiated in the microwave oven for 2 min and then was cooled and irradiated for 1 more min at 70% (630 W) of its power level. The resulting product was precipitated by the addition of 20 mL of methanol. It was then filtered and dried at 80°C for 10 h *in vacuo*; this yielded 0.09 g (62%) of yellow **PA9aIVD**. The aforementioned polymerization was repeated, but the reaction mixture was irradiated in a microwave oven with Py and TEA as catalysts and without catalyst.

For each method, reaction conditions optimized according to the reaction time and reaction catalysts were used for the polymerization of diacid **7** with
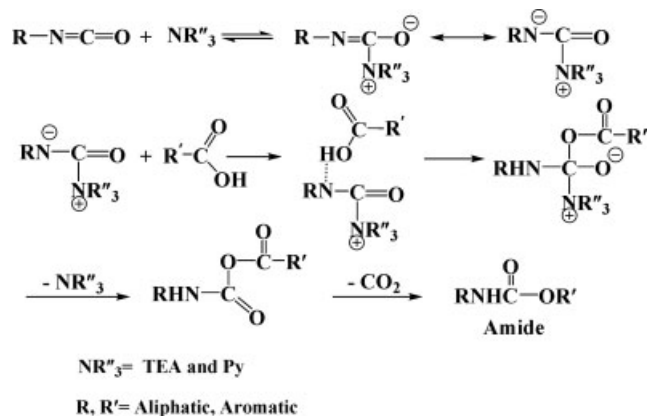
Scheme 4 Mechanism of the reaction of carboxylic acid with isocyanate activated by tertiary amines.

TABLE III
¹H-NMR and FTIR Characterization of the PAs

Polymer	Spectral data
9aIIIA	¹H-NMR (ppm): 0.85 (t, CH_3, J = 7.21 Hz), 1.06 (d, CH_3, J = 6.20 Hz), 0.96 (m, 1H, CH_2), 1.55 (m, 1H, CH_2), 3.85 (s, CH_2), 4.67 (s, CH), 7.09 (d, 4H, CH, J = 8.23 Hz), 7.36 (distorted dd, 4H, CH), 7.67 (d, 2H, CH, J = 7.50 Hz), 7.90 (distorted dd, 2H, CH), 8.24 (s, br, 3H, CH), 8.40 (s, br, NH), 10.23 (s, br, NH). FTIR (cm^{-1}): 3310 (s), 3120 (w, sh), 2961 (m), 2926 (m), 1776 (w), 1719 (s), 1644 (s), 1595 (s), 1553 (s), 1509 (s), 1465 (w), 1427 (w), 1411 (m), 1383 (m), 1304 (m), 1236 (m), 1201 (m), 1108 (w), 1070 (w), 1018 (w), 961 (w, br), 904 (w), 878 (w), 856 (w), 815 (w), 779 (w), 753 (w), 717 (w).
9dIIIA	¹H-NMR (ppm): 0.83 (distorted t, CH_3), 1.03 (distorted d, CH_3), 1.22–1.49 (m, 10H, CH_2), 2.65 (m, 1H, CH), 3.60 (distorted t, CH_2), 4.65 (d, CH, J = 8.81 Hz), 7.86–7.96 (distorted dd, 2H, CH), 8.1 (m, 3H, CH), 8.27 (s, 2H, CH, br), 8.46 (s, br, NH), 10.18 (s, br, NH). FTIR (cm^{-1}): 3331 (s, br), 3088 (w), 2932 (s), 2857 (m), 1776 (w), 1719 (s), 1622 (s), 1570 (s), 1460 (m), 1382 (s, br), 1254 (m), 1213 (m), 1071 (m), 1017 (w), 903 (w), 878 (w), 832 (w), 777 (w), 740 (w), 718 (m).
9bIID	FTIR (cm^{-1}): 3318 (m, br), 3102 (w), 2962 (m), 2930 (w), 2873 (m), 1774 (w), 1715 (s), 1669 (s, br), 1599 (s), 1531 (s), 1468 (m), 1450 (s), 1422 (m), 1383 (s), 1322 (m), 1332 (m), 1243 (s), 1121 (w), 1070 (w), 1003 (w, br), 963 (w), 899 (w), 878 (w), 778 (w), 752 (w), 719 (m).
9cIA	FTIR (cm^{-1}): 3347 (m, br), 3101 (w, sh), 2960 (s), 2931 (w), 2873 (w), 1775 (w), 1720 (s), 1611 (m), 1558 (m), 1456 (m),1385 (s), 1333 (m), 1240 (m), 1193 (m), 1121 (w), 1070 (w), 1019 (w), 965 (w), 904 (w), 879 (w), 761 (w), 719 (m).
9bIVD	FTIR (cm^{-1}): 3316 (m, br), 3120 (w), 2963 (w), 2927 (w), 2874 (m), 1776 (w), 1719 (s), 1674 (s, br), 1599 (s), 1544 (s), 1447 (m), 1421 (s), 1383 (s), 1322 (m), 1303 (m), 1266 (m), 1222 (s), 1119 (w), 1071 (w, br), 1001 (w), 901 (w), 878 (w), 778 (w), 753 (w), 718 (m).
9cIVD	FTIR (cm^{-1}): 3318 (m, br), 3100 (m, sh), 2957 (s), 2925 (s), 1776 (m), 1719 (s), 1557 (s), 1461 (m), 1384 (s), 1249 (m), 1124 (w), 1070 (m), 1001 (w), 961 (w), 906 (w), 877 (w), 832 (w), 777 (w), 754 (w), 718 (m).

other diisocyanates such as TDI (**8b**), isophorone diisocyanate (IPDI or **8c**), and HDI (**8d**).

RESULTS AND DISCUSSION

Monomer synthesis

Diacid **7** was prepared by the three-step process shown in Scheme 1.[42] The chemical structures and purities of compounds **4**, **5**, and **7** were proved with thin-layer chromatography, elemental analyses, FTIR, specific rotation measurements, and ¹H-NMR and ¹³C-NMR spectroscopy techniques.

Polymer synthesis

The direct polycondensation of a dicarboxylic acid and diisocyanate is one of the well-known methods for PA synthesis. Solution polymerization reactions and microwave-assisted polycondensation reactions of an equimolar mixture of monomer **7** with different aromatic and aliphatic diisocyanates (**8a–8d**) were used to produce **PA9a–PA9d**, as shown in Scheme 2. At first, polycondensation was performed under conventional heating (method I), and this was compared with microwave irradiation (method II) in TBAB. Then, the polymerization was carried out under gradual heating (method III), and this was also compared with the microwave irradiation technique (method IV) in an NMP solution. Different catalytic conditions were applied for these polycondensation reactions, and after modification of the system, the optimum conditions were used for other

polymerization reactions and were compared with no catalytic conditions. In the classical heating method, gradual heating was necessary to prevent decomposition of the resulting products. The reaction yields and some physical data for the solution polycondensations are listed in Tables I and II. The aforementioned results demonstrate that microwave-assisted polymerization reactions (methods II and IV)
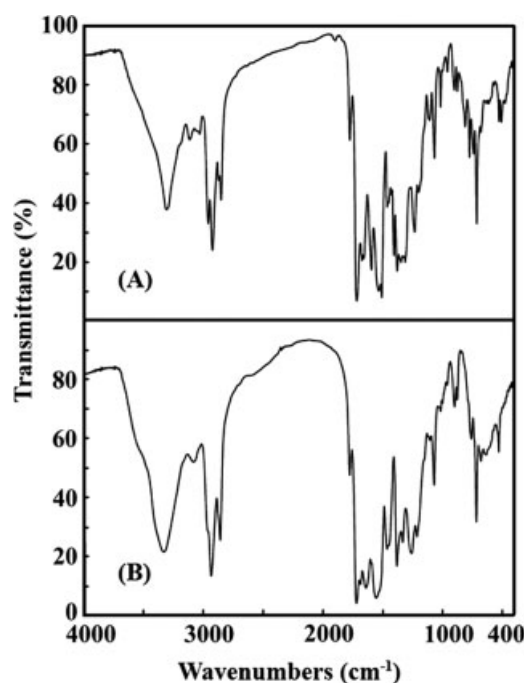

Figure 3 FTIR spectra of (A) **PA9aIB** and (B) **PA9dIIC**.

TABLE IV
Elemental Analysis of the PAs

Polymer	Formula		C (%)	H (%)	N (%)
9bIIIA	$(C_{29}H_{26}N_4O_5)_n$ [(510.54)$_n$ g/mol]	Calcd	68.22	5.13	10.97
		Found	68.11	5.25	10.83
9aIVD	$(C_{35}H_{30}N_4O_5)_n$ [(586.64)$_n$ g/mol]	Calcd	71.65	5.15	9.55
		Found	70.65	5.75	9.37

are efficient processes (shorter reaction times and high energy efficiency) for polycondensation reactions. In another investigation, we compared method II with method IV. The replacement of a volatile and toxic organic solvent in the polymerization with a nonvolatile solvent will reduce losses through evaporation, and it is important that ILs are chemicals that can be used as solvents in green chemistry processes. The ability of ILs to dissolve monomers and polymers to provide homogeneity and their great tendency to absorb microwave energy because of their highly polar character are some other advantages of using IL systems in method II. In method IV, direct polycondensation is carried out in volatile organic and more toxic media such as NMP, which is not suitable, so using nonvolatile TBAB instead of NMP will be preferred.

Under microwave irradiation conditions, the polymerization reactions were also performed in NMP and TBAB in the presence of DBTDL as a catalyst. The resulting polymers were obtained with moderate yields and inherent viscosities (Table II). To determine the best irradiation time at 100 and 70% power levels, the effect of the reaction time on the

viscosity and yields of the resulting polymers by methods II and IV in the presence of Py as a catalyst and TBAB or NMP as a solvent was studied, and the results are shown in Figures 1 and 2. The best results under microwave irradiation methods II and IV were obtained after 180 + 60 s and 120 + 60 s at 100 and 70% power levels, respectively. After the first irradiation for 180 or 120 s, the reaction mixture was taken out, mixed again for 10 s, and heated at the same power level for an additional 60 s. With higher radiation times, dark products were obtained, but with low radiation times or the low power level, the reactions produced low yields. The polymerization reactions of monomer **7** with TDI, HDI, and IPDI were also carried out by the same procedure with four different methods according to the optimized conditions and are listed in Tables I and II. From these tables, it is clear that PAs obtained with MDI had higher inherent viscosities than PAs based on TDI, HDI, or IPDI.

The reaction of diisocyanates with diacids initially forms anhydride linkages that are not stable under the reaction conditions, and CO_2 evolves, producing stable amide linkages. The polymerization reactions can be accelerated with organotin or tertiary amine

TABLE V
Solubility Properties of the PAs

Solvent	PA9aIC	PA9aIIIC	PA9bIB	PA9bIIIB	PA9cIIB	PA9cIVB	PA9dIID	PA9dIVD
DMF	+++	++	+++	+++	+++	+++	+	+
4% LiCl–DMF	+++	+++	+++	+++	+++	+++	+++	+++
NMP	+++	+++	+++	+++	+++	+++	++	+
DMAc	+++	+	+++	+++	+++	+++	+	±
CH_2Cl_2	−	−	−	−	−	−	−	−
$CHCl_3$	−	−	−	−	−	−	−	−
H_2O	−	−	−	−	−	−	−	−
Acetone	−	−	−	−	−	−	−	−
Dimethyl sulfoxide	+++	+	+++	+++	+++	+++	±	±
CH_3CN	−	−	−	−	±	−	−	−
HOAc	±	±	±	±	±	±	−	−
EtOAc	−	−	−	−	±	−	−	−
MeOH	±	±	±	+++	+++	+++	±	±
EtOH	±	±	±	+++	+++	+++	±	±
n-Hexane	−	−	−	−	−	−	−	−
Cyclohexane	−	−	−	−	−	−	−	−
Tetrahydrofuran	−	−	−	−	−	−	−	−
H_2SO_4	+++	+++	+++	+++	+++	+++	+++	+++

+ = soluble at the boiling temperature of the solvent; ++ = soluble at the boiling temperature of water; +++ = soluble at RT; ± = partially soluble; − = insoluble.

TABLE VI
Thermal Properties of PA9aIIIB, PA9aIB, PA9BIIB, PA9cIIB, PA9dIVD, and PA9dIID

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char yield (%)[c]	T_g (°C)[d]	LOI
9aIIIB	250	299	28	—	29
9aIB	302	361	28	195	29
9bIIB	—	—	—	166	—
9cIIB	—	—	—	128	—
9dIVD	230	282	6	—	20
9dIID	276	293	12	135	22

[a] T_5 was recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere.
[b] T_{10} was recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere.
[c] Weight percentage of material left undecomposed after TGA at a temperature of 800°C in a nitrogen atmosphere.
[d] T_g was recorded at a heating rate of 20°C/min in a nitrogen atmosphere.

compounds. The organotin catalysts are used primarily to speed up the reaction of isocyanates with hydroxyl and carboxylic acid groups. These catalysts are more active than amine-type catalysts, and for this reaction, they are used in smaller amounts. A disadvantage of organotin catalysts is that they remain in the macromolecule end product, whereas the amines are detached from it by a gradually faster or slower volatilization. Both divalent and tetravalent tin compounds act as catalysts. A general mechanism for the reaction of carboxylic acid with isocyanates activated by organometallic compounds is proposed in Scheme 3, where M is a metal or alkyl metal and X is an acid residue.[43]

Tertiary amines also catalyze reactions of isocyanates with hydroxyl and carboxylic acid groups. Their activity increases with basicity and decreases if steric hindrance is involved.

A mechanism for the reaction of carboxylic acid with isocyanates activated with tertiary amines has been proposed and is shown in Scheme 4.[43]
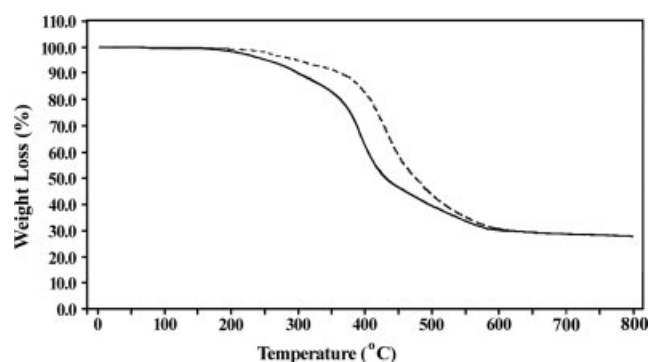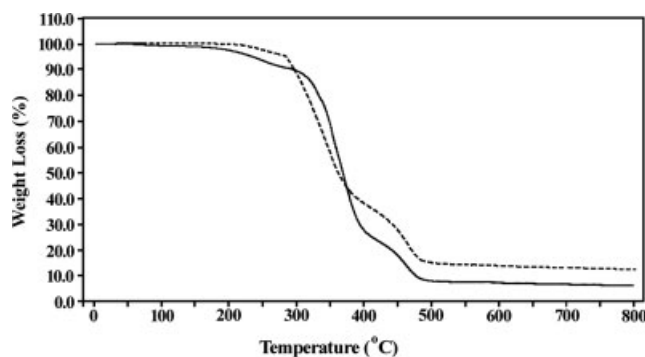

Figure 5 TGA thermograms of **PA9dIID** and **PA9dIVD** under a nitrogen atmosphere at a heating rate of 10°C/min.

Polymer characterization

FTIR and ^{1}H-NMR data

FTIR spectra of all the polymers showed the characteristic absorption peaks for the imide ring at 1719 and 1776 cm^{-1} due to the symmetrical and asymmetrical carbonyl stretching vibrations. Bands of amide NH groups appeared around 3310–3331 cm^{-1} (hydrogen band). All of them exhibited strong absorptions near 1382 and 638–753 cm^{-1} that showed the presence of the imide heterocycle ring in these polymers (Table III). The FTIR spectra of **PA9aIB** and **PA9dIIC** are shown in Figure 3. The structures of these polymers were also confirmed with ^{1}H-NMR spectroscopy and elemental analysis. ^{1}H-NMR and elemental analysis data of the resulting polymers are listed in Tables III and IV.

Solubility of the PAs

The solubility properties of PAs were studied in different solvents (Table V). The polymers were soluble in organic polar solvents such as DMAc, DMF,
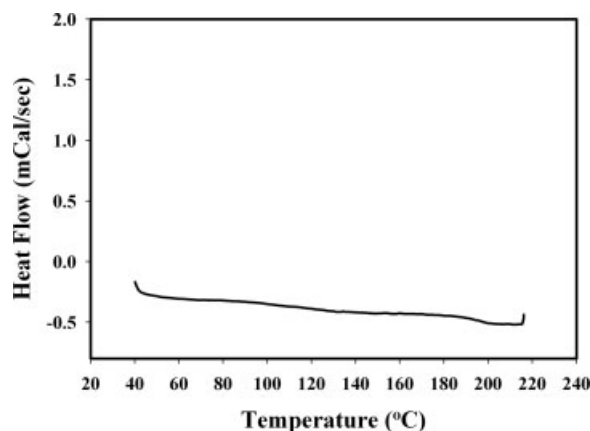

Figure 4 TGA thermograms of **PA9aIB** and **PA9aIIIB** under a nitrogen atmosphere at a heating rate of 10°C/min.

Figure 6 DSC thermogram of **PA9aIB** under a nitrogen atmosphere at a heating rate of 20°C/min.
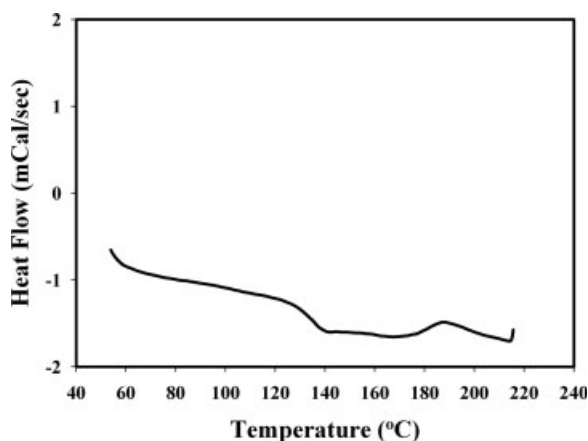
Figure 7 DSC thermogram of **PA9dIID** under a nitrogen atmosphere at a heating rate of 20°C/min.

NMP, and sulfuric acid at RT, partially soluble in methanol and ethanol, and insoluble in solvents such as chloroform, methylene chloride, acetone, cyclohexane, tetrahydrofuran, and water. Because of the presence of bulky side chains, these polymers showed good solubility.

Thermal properties

The thermal stability of some PAs were investigated by TGA techniques under a nitrogen atmosphere (Table VI). Figures 4 and 5 show the TGA curves for **PA9aIIIB**, **PA9aIB**, **PA9dIVD**, and **PA9dIID**. The thermal stability of the polymers was studied on the basis of 5 and 10% weight losses (T_5 and T_{10}, respectively) of the polymers and the residue at 800°C (char yield). The results revealed that the PAs were thermally stable up to 230°C. According to Table VI, **PA9aIB** (based on MDI) had higher thermal stability than the other PAs. This could pertain to the aromatic, rigid structure of diisocyanates for **PA9aIB** and **PA9aIIIB** versus the aliphatic, flexible structure of diisocyanates for **PA9dIID** and **PA9dIVD**. TGA data showed that the resulting polymers were moderately thermally stable. The DSC analyses for PAs showed T_g around 128–195°C (Table VI). Figures 6 and 7 show the DSC curves for **PA9aIB** and **PA9dIID**.

The char yield can be applied as a decisive factor for estimated the limiting oxygen index (LOI) of polymers according to the equation of Van Krevelen and Hoftyzer:[44]

$$LOI = 17.5 + 0.4CR$$

where CR is the char yield.

PA9aIB and **PA9aIIIB** had LOI values around 29, which were calculated from their char yield. On the basis of the LOI values, such macromolecules can be classified as self-extinguishing polymers. On the other hand, **PA9dIID** and **PA9dIVD** showed LOIs around 20 and were less thermally stable (Table VI).

CONCLUSIONS

In this investigation, optically active PAs were synthesized by direct polycondensation reactions in TBAB and NMP as reaction media. Microwave irradiation and conventional heating were used as sources of heating for these polymerization reactions. The nature and amount of the solvent had a great influence on the polymerization process and the inherent viscosity of the resultant polymers. TBAB as a green solvent is harmless, economical, and environmentally friendly. Furthermore, the results demonstrate that microwave heating is a more efficient method (shorter reaction time and high energy efficiency) for the polycondensation reactions. Because the resulting polymers contained optically pure L-isoleucine moiety, they showed optical rotations and were optically active. The high degree of flexibility of this amino acid functionality and bulky pendent groups existing in the side chains of these polymers could lead to the formation of macromolecules with good solubility. Potential applications of amino acid based polymers include drug delivery agents, chiral stationary phases for the resolution of enantiomers in chromatographic techniques, and biomaterials.

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