Soluble New Optically Active Polyamides Derived from 5-(4-Methyl-2-phthalimidylpentanoylamino)isophthalic acid and Different Diisocyanates Under Microwave Irradiation in Molten Ionic Liquid

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ABSTRACT: Ionic liquids (IL)s have been generating increasing attention over the last decade. ILs were originally introduced as alternative green reaction media owing to their distinctive chemical and physical properties of nonvolatility, nonflammability, thermal stability, and controlled miscibility. In this investigation, 5-(4-methyl-2-phthalimidyl-pentanoylamino)isophthalic acid (**6**), as a bulky monomer, containing phthalimide and flexible chiral groups, has been synthesized. The direct polycondensation of this diacid monomer with several aromatic and aliphatic diisocyanates, such as 4,4′-methylenebis(phenyl isocyanate), toluylene-2,4-diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate, was carried out in tetrabutylammonium bromide as a molten IL in the presence of different catalysts under microwave irradiation as well as conventional heating. The resulting polyamides (PA)s were characterized by FTIR and ^{1}H NMR spectroscopy, inherent viscosity measurements, thermal and elemental analysis.

The obtained PAs showed high yields and moderate inherent viscosities in a range of 0.32–0.57 dL g^{-1}. The PAs were soluble in aprotic polar solvents. Thermogravimetric analysis showed that PAs are thermally stable, 10% weight loss temperatures in excess of 240 and 245°C, and char yields at 600°C in nitrogen higher than 14%. Since toxic and volatile solvent such as NMP was eliminated, this process was safe and green. It is very important to note that, because of high polarizability of ILs, they are very good solvents for absorbing microwaves. The combination of IL and microwave irradiation leads to large reductions in reaction times, very high heating rate with various benefits of the eco-friendly approach, named green chemistry. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 244–253, 2009

Key words: ionic liquid; polyamides; microwave irradiation; direct polycondensation; green chemistry; thermal properties; optically active polymers

INTRODUCTION

Ionic liquids (IL)s represent a category of neoteric solvents, having ionic structure. They can be introduced as low melting organic salts and consist of bulky organic cations in amalgamation with organic or inorganic anions. A main drive of these efforts with ILs in industry and fundamental research is the substitution of more environmentally benign technologies for conventional ones in which harmful and volatile organic solvents are generally used. ILs are considered as promising substitutes for organic solvents, not only because of their above properties,

but also because of their ability to act as catalysts.[1] ILs are differed in a number of unique properties, which are thermal and chemical stability, negligible vapor pressure, ability to dissolve organic, inorganic, organometallic, and high molecular weight compounds, which have led to their application in a variety of chemical reactions.[1–3] A number of exceptional publications are already presented in which the properties and various uses of these environmentally friendly media have been investigated such as coordinative, radical, cationic, group transfer, enzymatic, electrochemical, and step-growth polymerizations.[4–10] In some cases, the use of IL in place of conventional organic solvent was reported to lead to enhancement in reaction rate, higher molecular mass, and useful separation of polymer from catalyst residues.[11,12] However, the high cost of most conventional room temperature ILs and concern about their toxicity have led us to investigate the use of more benign and cheaper salts in the molten state as practical alternatives. Recently, molten tetrabutylammonium bromide (TBAB) was used as a low toxic

and cost-effective IL in a number of useful synthetic transformations.[5,13,14]

Lately, there has been increasing interest in the microwave synthesis of polymers. For monomers containing polar groups that favor the absorption of microwave energy, microwave polymerization has been proven to be more quick and well-organized than traditional polymerization. Microwave irradiation can heat reactants directly, selectively, without thermal inertia, and without the participation of a heat exchange medium.[15,16] In the field of macromolecules materials, especially, microwave heating has shown an enormous potential, still far from being extensively used as it could, for accelerated industrial processing of the complete selection of commercial (both commodity and high performance) plastics, rubbers, thermosetting resins, and related composites.[17–20]

Microwave-assisted polymer synthesis combined with ILs have attracted interest due to enhanced reaction rates, easier workup, and facilitated purification. The dipole characteristics of IL convert into rapid excitation by microwaves and therefore faster reactions.[21] However, the use of microwave chemistry to materials synthesis in conjunction with IL has hardly been exploited despite these advantages. By combining the benefits of both ILs and microwave heating, a new microwave-assisted IL method for the fast controlled synthesis has been developed.[22,23]

The manufacture of thermally stable organic polymers has been the topic of many research efforts for the past 30 years because of the growing use of thermally stable macromolecules in the fields of aerospace and electronics.[24,25] Most of the thermally stable polymers synthesized are aromatic, rigid-rod-type polymers that have difficulties in processing owing to their low solubility and high glass transition or melting temperatures. However, the poor solubility and high softening or melting temperature caused by high crystallinity and high stiffness of a polymer backbone lead to difficult processiblity of these aromatic polyamides. To improve solubility, numerous approaches for the chemical structure upgrading of aromatic polyamides, such as the incorporation of flexible or bulky aromatic units like naphthalene moiety, a nonsymmetric unit, a pendent group, or also heterocycle moiety into the polymer backbone or introduction of bent noncoplanar units in the polymer backbone, have been used to attain good solubility in typical solvents whereas maintaining their other distinctive properties. Many PAs with diverse pendent bulky groups have been synthesized and reported.[26–29]

We are certainly living in a chiral world. Most naturally occurring macromolecules such as proteins, polysaccharides, and nucleic acids are chiral and optically active. Optically active polymers including those bearing main or side chain amino acid units are used extensively in the pharmaceutical industry for enantio selective separation of drugs. This is achieved mainly via the application of chiral polymer membranes or chromatography and electrophoresis involving chiral polymers as the stationary phase. Despite of chiral separations, biocompatible amino acid-containing polymers are used in dentistry, drug delivery, gene therapy, tissue engineering, and etc.[30–36]

Given the extensive experience of our laboratory in the field of optically active and thermally stable polymers based on α-amino acid, herein, we wish to report a simple, fast, safe, and convenient method for the synthesis of novel PAs having phthalimide and L-leucine moieties using a green medium, TBAB under microwave irradiation, and compare with conventional heating by different catalysts. The introduction of thermally stable side chain may disrupt interchain hydrogen bonding and reduce packing effectiveness and crystallinity, so all of the polymers are expected to show good solubility in many organic solvents.

EXPERIMENTAL

Materials and equipments

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co (Darmstadt, Germany). Phthalic anhydride (**1**) was recrystallized from chloroform. 5-Aminoisophthalic acid (**5**) was recrystallized from water/N,N-dimethylformamide (DMF) (4 : 1) mixture. N,N-Dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were dried over BaO and then were distilled under reduced pressure. TBAB with M.P. = 100–103°C was purchased from Merck Co. (Darmstadt, Germany) and was used without further purification.

The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz, 900 W). All of the polymerization reactions were performed in a hood with strong ventilation. Proton Nuclear Magnetic Resonance (^{1}H NMR, 500 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Ettlingen, Germany) Avance 500 instrument and also Carbon Nuclear Magnetic Resonance (^{13}C NMR, 125 MHz) spectrum was recorded on a Bruker (Ettlingen, Germany) advance 500 instrument at Sharif University of Technology, Tehran, Iran. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd), and multiplet (m). FTIR spectra were recorded on Jasco-680 (Toyonaka, Osaka, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition
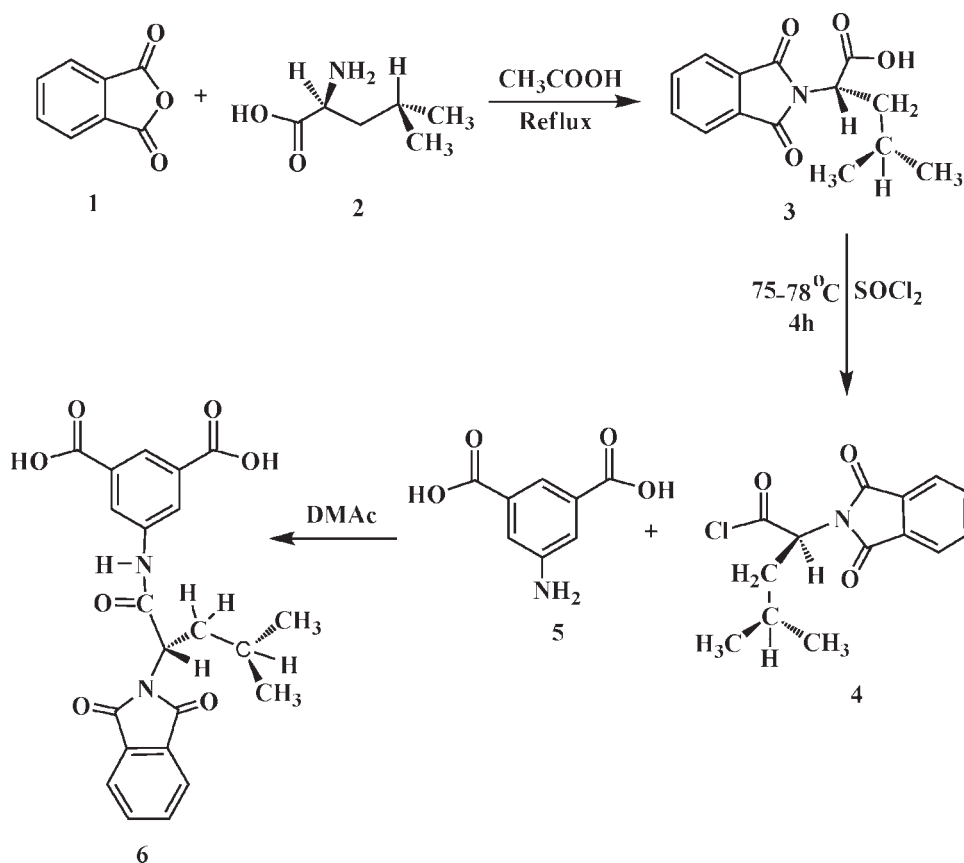
Scheme 1 Synthesis of monomer **6**.

frequencies are reported in wavenumbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Cannon, Mainz, Germany) at concentration of 0.5 g dL^{-1} at 25°C. Specific rotations were measured by a Jasco Polarimeter (Toyonaka, Osaka, Japan). Thermal Gravimetric Analysis (TGA) data for polymers were taken on Perkin-Elmer (Karlsruhe, Germany) in nitrogen atmosphere at a rate of 10°C min^{-1}. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran.

Monomer synthesis

(2S)-5-(4-Methyl-2-phthalimidylpentanoylamino)isophthalic acid (**6**), as an optically active diacid monomer, was synthesized according to our previous work.[37]

Polymer synthesis

Method I: Polymerization of diacid 6 with diisocyanates in TBAB under microwave irradiation

The PAs were prepared by the following general procedure: as an example for the preparation of

PA1, into a porcelain dish was placed 0.10 g (2.36 × 10^{-4} mol) of compound **6** and 0.23 g (6.98 × 10^{-4} mol) of TBAB. After the mixture was completely ground, 0.02 g (3.01 × 10^{-5} mol) of dibutyltin dilaurate (DBTDL) was added, and the mixture was ground for 5 min, then 0.06 g (2.36 × 10^{-4} mol) of 4,4′-methylenebis(phenyl isocyanate) MDI (**7**) was added, and the mixture was ground again for additional 2 min. The reaction mixture was irradiated in a microwave oven for 3 min at 100% of its power level (900 W). The resulting product was isolated by the addition of 30 mL of a mixture of methanol/water (50/50). It was then filtered off and dried at 80°C for 10 h in vacuum; this yielded 0.128 g (80%) of white **PA1**.

Method II: Polymerization of diacid 6 with diisocyanates in TBAB under conventional heating

The PAs were prepared by the following general procedure: as an example for the preparation of **PA5**, a mixture of 0.10 g (2.36 × 10^{-4} mol) of diacid **6** and 0.30 g (9.42 × 10^{-4} mol) of TBAB was ground until a powder was formed. Then 0.02 mL (1.80 × 10^{-4} mol) of DBTDL was added, and it was transferred into a 25 mL round-bottom flask and 0.06 g (2.36 × 10^{-4} mol) of MDI was added to the mixture
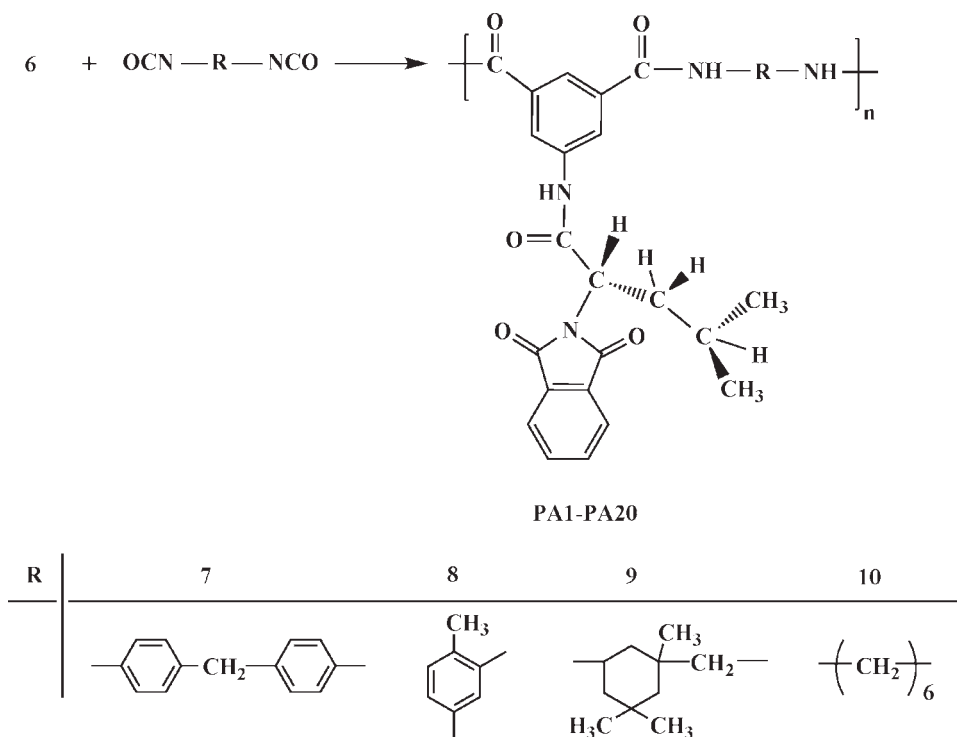
Scheme 2 Polycondensation reactions of monomer **6** with different diisocyanates.

and was heated until 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 methanol. The white solid was filtered off and dried to give 0.13 g (82%) of white **PA5**. The above polymerization was repeated with Py or TEA as a catalyst and without catalyst.

For each method the optimized reaction conditions according to reaction time and reaction catalysts were used for the polymerization of compound **6** with other diisocyanates such as toluylene-2,4-diiso-

cyanate (TDI) (**8**), isophorone diisocyanate (IPDI) (**9**), and hexamethylene diisocyanate (HMDI) (**10**).
PA1. FTIR (KBr, cm^{-1}): 3311 (s), 3125 (w, sh), 2957 (s), 1779 (s), 1720 (m), 1671 (m), 1644 (s), 1594 (w), 1555 (s), 1509 (m), 1466 (w), 1380 (s), 1361 (m), 1237 (m), 1161 (m), 1075 (w), 1018 (m), 961 (w, br), 879 (w), 832 (w), 779 (w), 753 (w), 717 (w), 472 (w). ^{1}H NMR (500 MHz) (ppm): 0.89 (d, 6H, CH$_3$, J = 7.21 Hz), 1.41–1.45 (m, 1H CH), 2.10–2.15 (m, 1H, CH$_2$), 2.21–2.27 (m, 1H, CH$_2$), 3.82–3.88 (m, 2H, CH$_2$), 4.93 (dd, 1H, CH, J_1 = 6.64, J_2 = 6.92 Hz), 7.30 (d, 4H,

TABLE I
Reaction Conditions for the Polymerization of Monomer 6 With MDI and Some Physical Properties of PA1-PA8 Under Microwave Irradiation and Conventional Heating in TBAB

Polymer	Diisocyanate	Method	Catalyst	Nonsolvent	Yield (%)	Inherent viscosity (dL g^{-1})	$[\alpha]_D^{25\ a}$
PA1	MDI	I[b]	DBTDL	MeOH	80	0.57[c]	−31.34
PA2	MDI	I[b]	Py	MeOH	76	0.46[c]	−30.56
PA3	MDI	I[b]	TEA	MeOH/water	74	0.46[d]	−28.32
PA4	MDI	I[b]	No Cat.	MeOH	79	0.54[c]	−27.32
PA5	MDI	II[e]	DBTDL	MeOH	82	0.56[c]	−27.30
PA6	MDI	II[e]	Py	MeOH/water	76	0.45[d]	−20.56
PA7	MDI	II[e]	TEA	MeOH	77	0.48[d]	−29.22
PA8	MDI	II[e]	No Cat.	MeOH/water	83	0.53[d]	−30.14

[a] Measured under the condition the same as inherent viscosity.
[b] Method I: The reaction mixture was irradiated in the microwave oven for 3 min at 100% of its power.
[c] Measured at a concentration of 0.5 g dL^{-1} in DMF at 25°C.
[d] Measured at a concentration of 0.5 g dL^{-1} in DMF containing 0.2% W/W LiCl (soluble fraction) at 25°C.
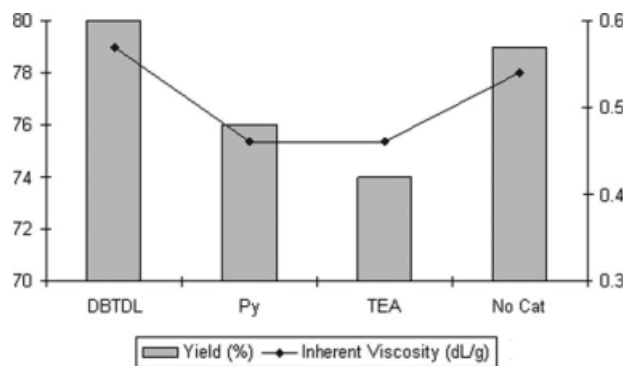[e] Method II: Conventional heating at 120°C for 12 h.

Figure 1 The effect of different catalyst on yield and inherent viscosity in Method I.

Figure 2 The effect of different catalyst on yield and inherent viscosity in Method II.

CH, J = 8.23 Hz), 7.62 (d, 4H, CH, J = 8.23 Hz), 8.21–8.28 (distorted dd, 4H, CH), 8.32–8.34 (m, br, 1H, CH), 8.55–8.59 (m, br, 2H, CH), 10.21 (s, br, NH), 10.35 (s, br, NH); elemental analysis calculated for $(C_{35}H_{30}N_4O_5)_n$: C, 68.22; H, 5.13; N, 10.97; Found: C, 67.97; H, 5.45; N, 10.43.

PA10. FTIR (KBr, cm^{-1}): 3339 (s, br), 3028 (w), 2931 (s), 1775 (m), 1719 (s), 1670 (s), 1523 (s), 1467 (w), 1384 (s), 1254 (m), 1210 (m), 1094 (m), 916 (m), 876 (w), 768 (w), 720 (m), 661 (w), 530 (w), 476 (w). ^{1}H NMR (500 MHz) (ppm): 0.86 (d, 6H, CH$_3$, J = 7.14 Hz), 1.49–1.52 (m, CH), 2.01–2.06 (m, 1H, CH$_2$) 2.17–2.19 (m, 1H, CH$_2$) 2.24 (s, 3H, CH$_3$), 4.93 (dd, 1H, CH, J_1 = 5.68, J_2 = 6.81 Hz), 7.43 (d, 2H, CH, J = 8.23 Hz), 7.57 (s, 1H, CH), 7.68 (d, 4H, CH, J = 7.50 Hz) 8.25 (s, 1H, CH), 8.41 (s, br, 2H, CH), 10.01 (s, br, NH), 10.48 (s, br, NH); elemental analysis calculated for $(C_{29}H_{26}N_4O_5)_n$: C, 71.65; H, 5.15; N, 9.55; Found: C, 70.85; H, 4.98; N, 9.17.

PA14. FTIR (KBr, cm^{-1}): 3369 (m, sh), 3109 (m, sh), 2957 (s), 1776 (w), 1715 (s), 1527 (m), 1467 (w), 1384 (m), 1309 (w), 1254 (m), 1214 (w), 1096 (m), 876 (m), 769 (m), 720 (w), 611 (m), 531 (w), 476 (w).

PA20. FTIR (KBr, cm^{-1}): 3339 (s, br), 3068 (w), 2931 (s), 2857 (m), 1776 (w), 1719 (s), 1674 (s, br), 1599 (s), 1544 (s), 1477 (m), 1421 (s), 1383 (m), 1322 (m), 1266
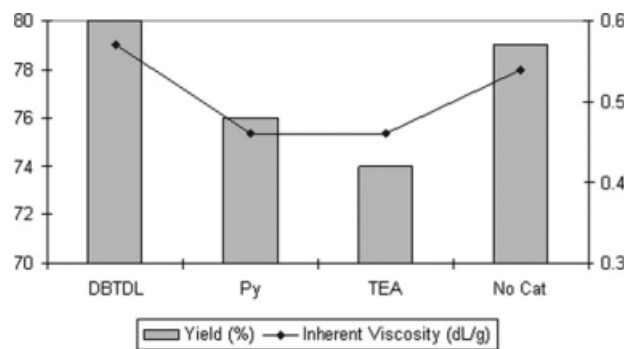
(m), 1222 (s), 1119 (w), 1002 (m), 901 (w), 871 (w), 778 (m), 753 (w), 718 (m), 661 (w), 530 (m).

RESULTS AND DISCUSSION

Monomer synthesis

The bulky diacid **6** with chiral structure was synthesized in three steps, as shown in Scheme 1. The chemical structures and purities of compounds **3**, **4**, and **6** were proved with thin layer chromatography, elemental analyses, FTIR, specific rotation measurements, and ^{1}H NMR and ^{13}C NMR spectroscopy techniques.[37]

Polymer synthesis

The direct polycondensation of a dicarboxylic acid and diisocyanate is one of the well-known methods for PA synthesis. Solution polymerization reactions as well as microwave-assisted polycondensation reaction of an equimolar mixture of monomer **6**, with different aromatic and aliphatic diisocyanates in the presence of molten TBAB, with different catalysts and without catalyst were used to furnish **PA1-PA20**, as shown in Scheme 2. In the first step, we

TABLE II
Reaction Conditions for the Polymerization of Monomer 6 with TDI and Some Physical Properties of PA9-PA12 under Microwave Irradiation and Conventional Heating in TBAB

Polymer	Diisocyanate	Method	Catalyst	Nonsolvent	Yield (%)	Inherent viscosity (dL g^{-1})[a]	$[\alpha]_D^{25}$ [b]
PA9	TDI	I[c]	DBTDL	MeOH	85	0.49	−21.45
PA10	TDI	I[c]	No Cat.	MeOH	79	0.47	−28.31
PA11	TDI	II[d]	DBTDL	MeOH	91	0.36	−43.24
PA12	TDI	II[d]	No Cat.	MeOH	82	0.33	−48.51

[a] Measured at a concentration of 0.5 g/dL in DMF at 25 °C.
[b] Measured under the condition the same as inherent viscosity.
[c] Method I: The reaction mixture was irradiated in the microwave oven for 3 min at 100% of its power.
[d] Method II: Conventional heating at 120 °C for 12 h.

TABLE III
Reaction Conditions for the Polymerization of Monomer 6 with IPDI and Some Physical Properties of PA13-PA16 Under Conventional Heating and Microwave Irradiation in TBAB

Polymer	Diisocyanate	Method	Catalyst	Non-solvent	Yield (%)	Inherent viscosity (dL g^{-1})[a]	$[\alpha]_D^{25}$ [b]
PA13	IPDI	I[c]	DBTDL	MeOH	79	0.48	−27.86
PA14	IPDI	I[c]	No Cat.	MeOH	83	0.36	−37.16
PA15	IPDI	II[d]	DBTDL	MeOH	76	0.49	−29.06
PA16	IPDI	II[d]	No Cat.	MeOH	74	0.46	−29.32

[a] Measured at a concentration of 0.5 g/dL in DMF at 25 °C.
[b] Measured under the condition the same as inherent viscosity.
[c] Method I: The reaction mixture was irradiated in the microwave oven for 3 min at 100% of its power.
[d] Method II: Conventional heating at 120 °C for 12 h.

examined the formation of PAs via polycondensation of diacid **6** with MDI **7** under microwave irradiation (Method I). The effect of microwave power levels and duration of heating was examined to provide the optimum reaction conditions. A series of experiments, which were performed with different reaction times and power levels under microwave irradiations, revealed that the optimal results were obtained after 3 min at 100% of power level. At higher radiation times, dark products were obtained, and on the other hand, under low radiation times or power level, low yields were achieved. To find the best catalyst in these methods (Method I and Method II) and effect of these catalysts on the viscosity and yield of the resulting polymers, the reaction of **6** with MDI **7** in the presence of DBTDL, Py, TEA, and without catalyst has been performed and the result are shown in Table I, Figures 1, and 2. To compare the microwave-assisted method with conventional heating, the polycondensations were also carried out under conventional heating in TBAB (Method II). When the same experiment was conducted by conventional heating in the presence of TBAB as a solvent, it took much longer time (12 h of heating at 120°C) for the completion of the polymerization reactions. Under these conditions, yields and inherent viscosities of the polymers were ranging

from 73 to 91% and 0.32–0.56 dL g^{-1}, respectively. On the other hand, a more homogeneous heating and exceptional rate acceleration were observed under microwave irradiation. This demonstrated the advantageous effect of microwave as the energy source. The yields and inherent viscosities of the resulting polymers obtained by microwave irradiation verses thermal heating are comparable. The optimum conditions, which were obtained under microwave and conventional heating, have been applied for the preparation of other PAs by the reaction of compound **6** with other diisocyanates (Scheme 2) and the results are demonstrated in Tables II–IV. Most of the polymers precipitated in a fiber-like form when the resulting polymer solutions were slowly poured into methanol. The inherent viscosities of the resulting polymers under microwave irradiation were in the range of 0.36–0.57 dL g^{-1} and the yields were 68–85%, respectively.

To compare the efficiency of these novel methods of polymerization with conventional polymerization method, the above reactions were performed in polar organic solvent such as NMP in the presence and in the absence of different catalysts with graduate heating and the results had been reported in our previous work.[37] We obtained better yields and viscosities by using of molten TBAB. It is interesting to

TABLE IV
Reaction Conditions for the Polymerization of Monomer 6 with HDI and Some Physical Properties of PA17-PA20 under Conventional Heating and Microwave Irradiation in TBAB

| Polymer	Diisocyanate	Method	Catalyst	Non-solvent	Yield (%)	Inherent viscosity (dL g^{-1})	$[\alpha]_D^{25}$ [a]
PA17	HDI	I[b]	DBTDL	MeOH	80	0.45[c]	−38.66
PA18	HDI	I[b]	No Cat.	MeOH	68	0.39[d]	−41.26
PA19	HDI	II[e]	DBTDL	MeOH	79	0.36[d]	+16.05
PA20	HDI	II[e]	No Cat.	MeOH	73	0.32[c]	−34.25

[a] Measured under the condition the same as inherent viscosity.
[b] Method I: The reaction mixture was irradiated in the microwave oven for 3 min at 100% of its power.
[c] Measured at a concentration of 0.5 g dL^{-1} in DMF at 25°C.
[d] Measured at a concentration of 0.5 g dL^{-1} in DMF containing 0.2% W/W LiCl (soluble fraction) at 25°C.
[e] Method II: Conventional heating at 120°C for 12 h.

R, R'= Aliphatic, Aromatic

MX$_2$= DBTDL
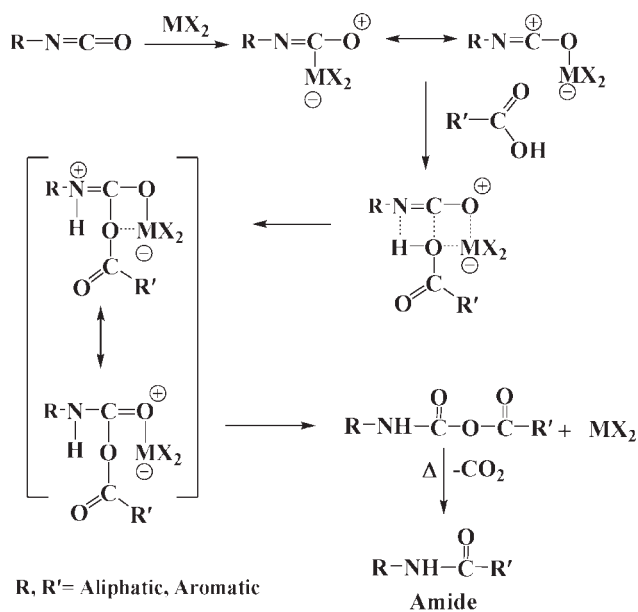
Scheme 3 Mechanism of reaction of carboxylic acid with isocyanate activated by organometallic compounds.

mention that when NMP was used as a solvent, which is volatile, and will cause a change in the concentration of reaction mixture during polymerization process and lead to the formation of polymers with lower yields and inherent viscosity. In this study, molten TBAB was used as a solvent which is green, safe, and cost effective. Thus, TBAB acts both as effective solvent and catalyst to mediate clean poly-

NR''$_3$= TEA and Py

R, R'= Aliphatic, Aromatic
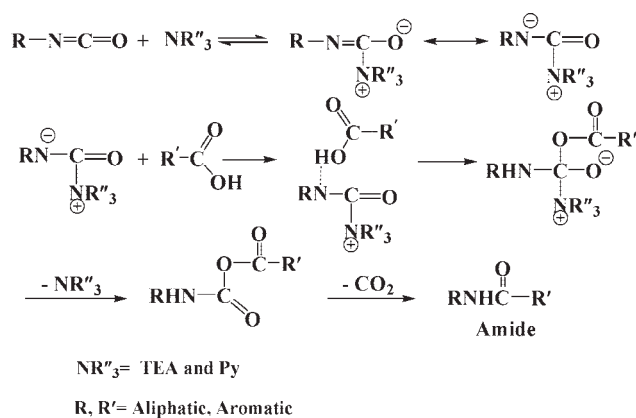
Scheme 4 Mechanism of reaction of carboxylic acid with isocyanate activated by tertiary amines.

merization reactions to yield the desired PAs. When polymerization reaction was performed in molten TBAB, viscous solutions were formed and the resulting polymers were never precipitated, whereas precipitation was observed during of conventional method in NMP as a solvent.

Reaction of diisocyanates with diacids originally forms anhydrides linkages, which are not stable under the reaction conditions, and CO_2 was evolved to give stable amide linkages. The polymerization reactions can be speed up by using organotin or tertiary amines compounds. The organotin catalysts are used primarily to accelerate the reaction of isocyanate with hydroxyl and carboxylic acid groups. These catalysts are more active than the amine type
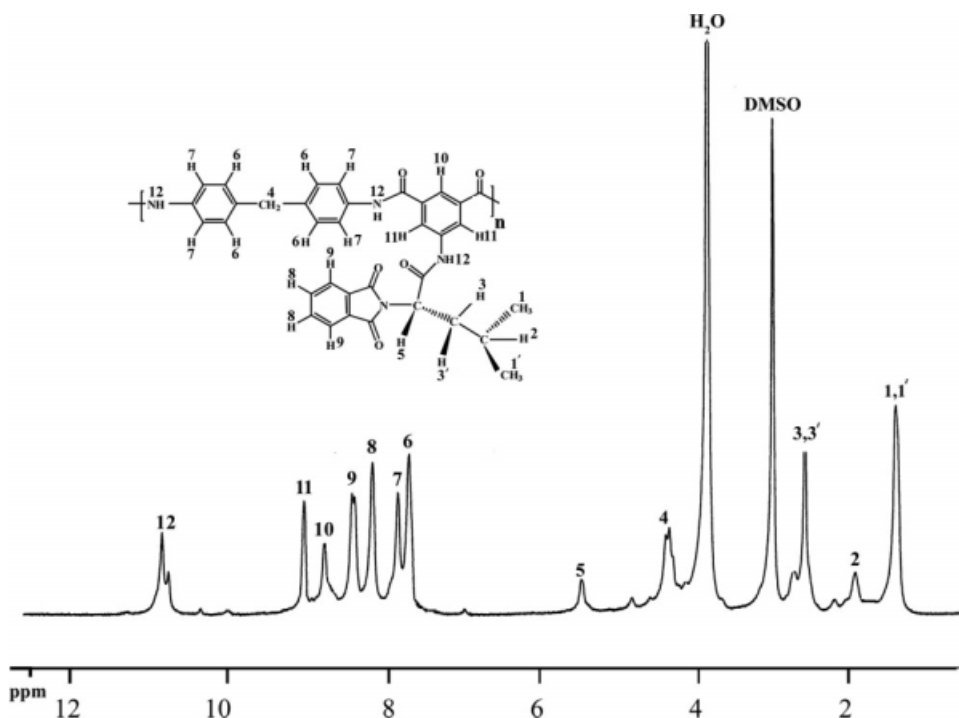

Figure 3 ^{1}H NMR (500 MHz) spectrum of **PA1** in DMSO-d_6 at RT.

TABLE V
Thermal Properties of PA1 and PA13

Polymer	Decomposition Temperature (°C)		Char Yield (%)[a]
	T_5 (°C)[b]	T_{10} (°C)[c]	
PA1	223	245	28
PA13	210	240	12

[a] Percentages weight of material left undecomposed after TGA analysis at a temperature of 600°C in a nitrogen atmosphere.
[b] Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min. in a nitrogen atmosphere.
[c] Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min. in a nitrogen atmosphere.

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 gradual, faster, or slower volatilization. Both di and tetravalent tin compounds act as catalysts. A general mechanism of the reaction of carboxylic acid with isocyanates activated by organometallic compounds is proposed and is shown in Scheme 3, where M is a metal or alkylmetal and X is an acid residue.[38]

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

A mechanism of activation for the reaction of carboxylic acid with isocyanates in the presence of terti-

ary amines has been proposed and is shown in Scheme 4.[38]

Polymer characterization

The resulting polymers were characterized by FTIR, and two of the representative polymers by ^{1}H NMR spectroscopy techniques and elemental analyses. The FTIR spectra of resulting PAs showed the presence of the characteristic peaks for amide and imide functions and the absence of the original peaks arising from the COOH and NCO groups in the corresponding diacid and diisocyanates precursors. Absorption of amide N—H bonds appeared around 3310–3331 cm^{-1} (hydrogen band) and the peak at 1650–1675 cm^{-1} confirms the presence of amide group. All of these PAs exhibited absorption at 1370–1380 and 715–725 cm^{-1}, which show the presence of the imide heterocycle in these polymers.

In the ^{1}H NMR spectra of **PA1** and **PA10**, appearances of the N—H protons of amides groups around 10.30 and 10.45 ppm as two peaks indicate the presence of amide group in the polymers side chain, as well as main chain. The resonance of aromatic protons appeared in the range of 7.03–8.31 ppm. The proton of the chiral center appeared as multiplets in the range of 4.97–5.00 ppm. The resonance of the diastereotopic hydrogens bonded to neighbor carbon of chiral center appeared in the range of 2.05–2.07 and 2.24–2.26 ppm as two discrete multiplets peaks. The resonance of the diastereotopic CH$_3$ protons groups of L-leucine appeared as a broad multiplet peak at 0.89–0.94 ppm. For example, ^{1}H NMR spectrum of **PA1** is shown in Figure 3. Elemental analysis values of the resulting polymers are also in good

TABLE VI
Solubility Properties of PAs

Solvent	PA3	PA5	PA9	PA11	PA13	PA15	PA17	PA19
DMF	+	++	+++	+++	+++	+++	++	+
NMP	+	+++	+++	+++	+++	++	++	+
DMAc	+	++	+++	+++	++	++	+	+
CH2Cl2	−	−	−	−	−	−	−	−
CHCl3	−	−	−	−	−	−	−	−
H2O	−	−	−	−	−	−	−	−
Acetone	−	−	−	−	−	−	−	−
DMSO	±	+	+++	+++	++	±	±	±
CH3CN	−	−	−	−	−	−	−	−
HOAc	−	±	±	±	−	−	−	−
EtOAc	−	−	−	−	−	−	−	−
MeOH	±	±	++	++	±	±	±	±
EtOH	±	±	++	++	±	++	±	±
n-Hexane	−	−	−	−	−	−	−	−
Cyclohexane	−	−	−	−	−	−	−	−
THF	−	−	±	±	±	±	−	−
H2SO4	+++	+++	+++	+++	+++	+++	+++	+++

+++, Soluble at RT; ++, Soluble at boiling water bath temperature; +, Soluble at boiling temperature; ±, Partially soluble; −, Insoluble.
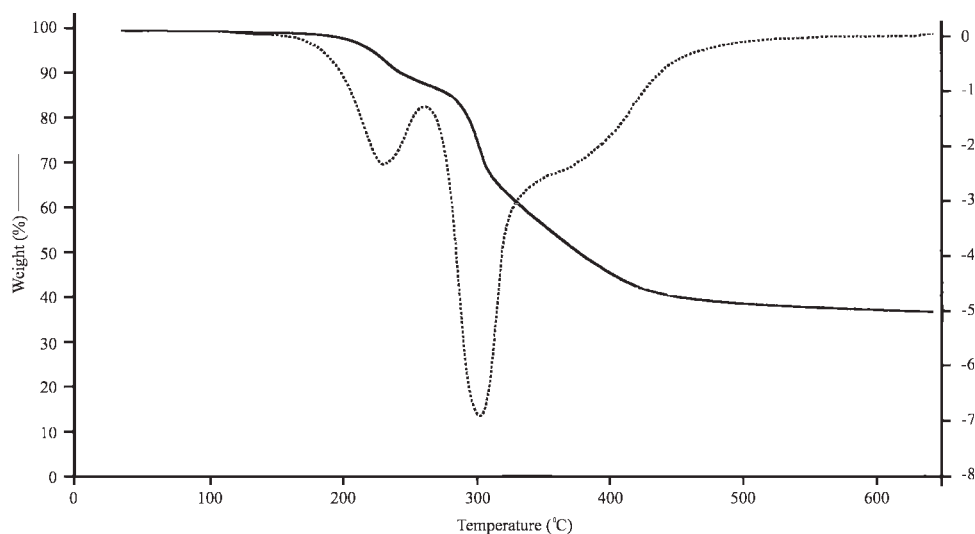
Figure 4   TGA/DTG thermogram of **PA1** under a nitrogen atmosphere at a heating rate of 10°C/min.

agreement with calculated values of carbon, hydrogen, and nitrogen in the polymers.

Solubility of PAs

The solubility properties of PAs were studied in different solvents (Table V). Polymers are soluble in organic polar solvents, such as DMAc, DMF, NMP, and in sulfuric acid, and are insoluble in solvents, such as chloroform, methylene chloride, acetone, cyclohexane, tetrahyrofuran, and water. Because of the presence of bulky side chain, these polymers show good solubility.

Thermal properties

The thermal properties of **PA1** and **PA13** were evaluated by means of TGA/DTG in a nitrogen atmos-

phere at a heating rate of 10°C/min. Thermal stability of the polymers were studied based on 5 and 10% weight loss (T_5, T_{10}) of the polymers and residue at 600°C (char yield). In addition, TGA data reveals that PAs are thermally stable up to 216°C. The thermoanalysis data of these polymers are summarized in Table VI. The temperature of 5%, 10% weight loss and the residual weight for this polymer at 600°C for **PA1** were 223, 245°C and 28% under nitrogen atmosphere. According to Table VI, it is clear that the **PA1** (based on MDI) has higher thermal stability than **PA13** (based on IPDI). It could be pertained to aromatic, rigid structure of diisocyanate for **PA1** compare to aliphatic, flexible structure of diisocyanate for **PA13**. According to these data, it can be concluded that the resulting polymers are rather thermally stable. Figures 4 and 5 show the TGA/DTG thermograms of these PAs.
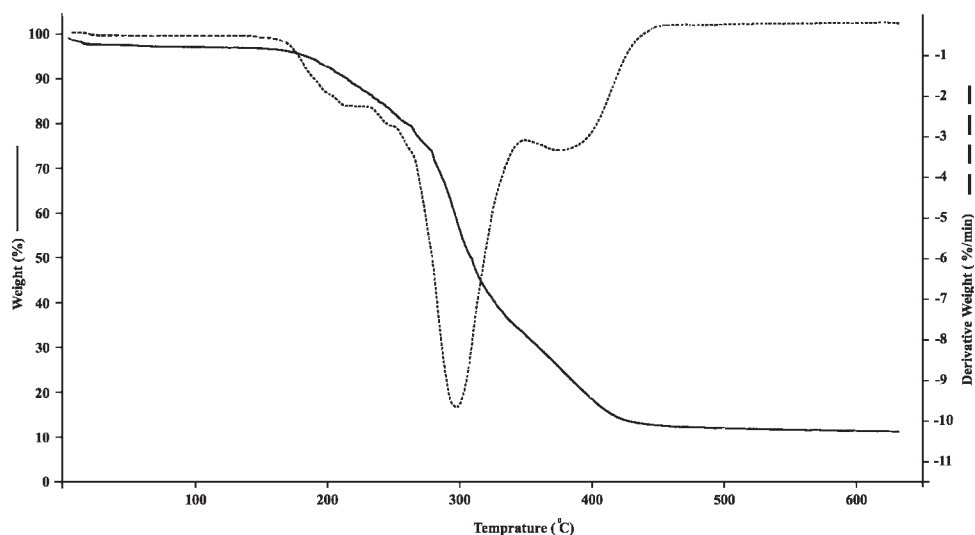

Figure 5   TGA/DTG thermogram of **PA13** under a nitrogen atmosphere at a heating rate of 10°C/min.

CONCLUSIONS

In this investigation, we have successfully synthesized a chiral aromatic dicarboxylic acid **6**, containing a rigid phthalimide and flexible L-leucine pendent group using microwave irradiation in conjunction with a green solvent, TBAB. A new series of **PA1-PA20** containing imide pendent group were prepared by two methods such as microwave-assisted polycondensation and solution polycondensation reactions in the presence of TBAB and several catalysts. The best results were obtained from the reaction of monomer **6** with MDI by both methods in the presence of DBTDL and no catalyst conditions. The resulting polymers have inherent viscosities in the range of 0.32–0.57 dL g^{-1}. Good yields and very short reaction times are the main aspects of using microwave for polymerization. This environmentally friendly green technique is a fast, high yielding, and simple management route, which avoids the usage of volatile organic solvents and catalyst. Moreover, the use of any organic solvent was not needed throughout the whole process of polymerization; in fact, organic solvent removal is of importance to minimize economic cost and environmental impact of chemical processes.

On the other hands, the introduction of bulky side chains should disturb interchain hydrogen bonding, inherent macromolecular rigidity, and diminish packing efficiency and crystallinity. The outcome offered herein also express obviously that the phthalimide linkage in the polymer side chain outstandingly enhanced the solubility and thermal stability of the polymers. Since, these optically active polymers have amino acids in the polymer architecture; they are expected to be used as biomaterials. In addition, they have potential to be used as chiral stationary phase in GC for the separation of racemic mixtures.

References

1. Wasserscheid, P.; Welton, T. Ionic Liquids in Synthesis; Wiley-VCH: Verlag, 2003.
2. Kubisa, P. J Polym Sci Part A: Polym Chem 2005, 43, 4675.
3. Lopez, M. S.; Mecerreyes, D.; Lopez, C. E.; Lopez, R. B. Biosens Bioelectron 2006, 21, 2320.
4. Welton, T. Chem Rev 1999, 99, 2071, 2084.
5. Mallakpour, S.; Rafiee, Z. Eur Polym J 2007, 48, 5017.
6. Pringle, J. M.; Ngamnac, O.; Chenc, J.; Wallace, G. G.; Forsyth, M.; MacFarlane, M. R. Synth Met 2006, 156, 979.
7. Mallakpour, S.; Kowsari, E. J Polym Sci Part A: Polym Chem 2005, 43, 6545.
8. Rangits, G.; Kollar, L. J Mol Catal A: Chem 2006, 246, 59.
9. Kubisa, P. Prog Polym Sci 2004, 29, 3.
10. Ranu, B. C.; Dey, S. S.; Hajra, A. Tetrahedron 2003, 59, 2417.
11. Mori, H.; Iwata, M.; Ito, S.; Endo, T. Polymer 2007, 48, 5867.
12. Harrisson, S.; Mackenzie, S. R.; Haddleton, D. M. Macromolecules 2003, 36, 5072.
13. Mallakpour, S.; Dinari, M. e-Polymer 2007, 035.
14. Mallakpour, S.; Rafiee, Z. Eur Polym J 2007, 43, 1510.
15. Yu, Z. J.; Liu, L. J.; Zhuo, R. X. J Polym Sci Part A: Polym Chem 2003, 41, 13.
16. Huang, J. L.; Zhang, Y. L.; Cheng, Z. H.; Tao, H. C. J Appl Polym Sci 2007, 103, 358.
17. Pourjavadi, A.; Zamanlu, M. R.; Zohuriaan-Mehr, M. J. Die Angew Makromol Chem 1999, 269, 54.
18. Bezdushna, E.; Ritter, H. Macromol Rapid Commun 2005, 26, 1087.
19. Celik, G. B.; Kysakurek, D. J Appl Polym Sci 2006, 102, 5427.
20. Lidstrom, P.; Tierney, J.; Wathey, B.; Westman, J. Tetrahedron 2001, 57, 9225.
21. Peng, Y.; Song, G. Catal Commun 2007, 8, 111.
22. Mallakpour, S.; Rafiee, Z. Polymer 2007, 43, 5017.
23. Mallakpour, S.; Kowsari, E. Ir Polym J 2006, 15, 239.
24. Luise, R. R. Applications of High Temperature Polymers; CRC Press: Boca Raton, 1997.
25. Kim, J. H.; Kim, Y. H.; Kim, Y. J.; Won, C.; Choi, K. Y. J Appl Polym Sci 2004, 92, 178.
26. Zhu, X.; Jian, X. J Polym Sci Part A: Polym Chem 2004, 42, 2026.
27. Ubale, V. P.; Sager, A. D.; Maldar, N.; Birajdar, M. V. J Appl Polym Sci 2001, 79, 566.
28. Haio, S. H.; Chang, Y. M.; Chen, H. W.; Liou, J. S. J Polym Sci Part A: Polym Chem 2006, 44, 4579.
29. Mallakpour, S.; Rafiemanzelat, F. Ir Polym J 2005, 14, 909.
30. Vandermeulen, G. M.; Klok, H. A. Macromol Biosci 2004, 4, 383.
31. Feng, L.; Hu, J.; Liu, Z.; Zhao, F.; Liu, G. Polymer 2007, 48, 3616.
32. Soai, K.; Niwa, S. Chem Rev 1992, 92, 833.
33. Mallakpour, S.; Taghavi, M. Eur Polym J 2008, 44, 87.
34. Mallakpour, S.; Kolahdoozan, M. React Funct Polym 2008, 68, 91.
35. Mallakpour, S.; Kolahdoozan, M. Eur Polym J 2007, 43, 3344.
36. Kakizawa, Y.; Harada, A.; Kataoka, K. Biomacromolecules 2001, 2, 491.
37. Mallakpour, S.; Dinari, M. Polym Adv Technol 2008, 19, 1334.
38. Wirpsza, Z. In Polyurethanes: Chemistry, Technology and Applications; Ellis Horwood Ltd.: New York, 1993; Chapter 3.