

Preparation and Characterization of Thermostable Chiral Extended Polyamides Bearing *N*-Phthaloyl-*L*-leucine Pendent Architectures in Green Media

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Received 22 September 2007; accepted 7 July 2008

DOI 10.1002/app.28993

Published online 22 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ionic liquids (ILs) are often well-known benign solvents capable of replacing conventional organic solvents, and they have become attractive solvents for many chemical reactions. Aromatic polyamides (PAs) have received particular interest in past years because of their high thermal and chemical resistance and their potential as high-performance materials for different applications. In this investigation, the preparation of extended PAs derived from 5-aminoisophthalic acid containing chiral pendent linkage (*N*-phthaloyl-*L*-leucine) with various aromatic diamines was studied. The bulky monomer 5-(4-methyl-2-phthalimidylpentanoylamino)isophthalic acid was prepared in three steps. Direct polyamidation of this monomer with several commercially available diamines in the presence of IL (1,3-dipropylimidazolium bromide) and triphenyl phos-

phite gave novel PAs in good yields and inherent viscosities in the range of 0.38–0.55 dL g⁻¹. Because of the existence of amino acid in this architect, the resulting polymers are optically active. All of these PAs showed good solubility and readily dissolved in many organic solvents. Characterization of all the products was performed by FTIR, specific rotation, and representative ones by ¹H NMR, elemental analysis, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). TGA exhibited that two elite polymers were stable, with 10% weight loss recorded above 410 and 430°C in the nitrogen atmosphere. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1209–1215, 2009

Key words: chiral; green chemistry; polyamides; ionic liquids; thermal properties

INTRODUCTION

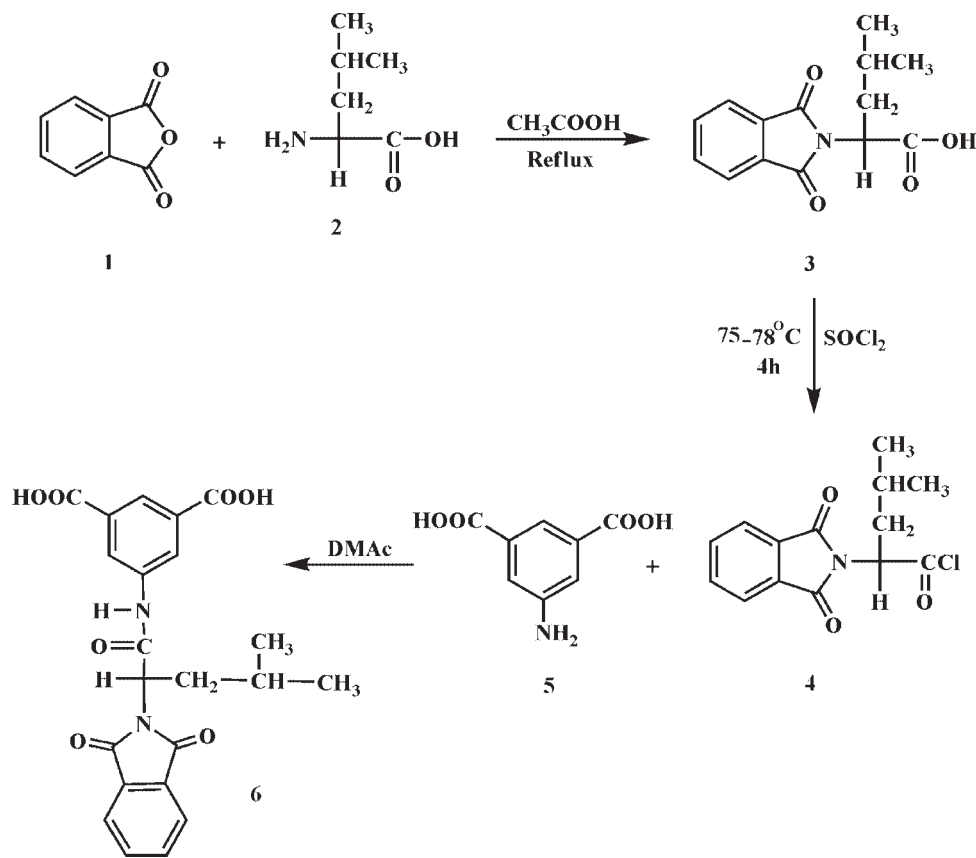
The development of neoteric solvents, i.e., ionic liquids (ILs) and supercritical fluids, for chemical synthesis grips great promise for green chemistry uses.¹ ILs are a recently developed category of materials that have roused a paradigm move in solvent chemistry because of the astonishing range of properties that they can offer. They have ionic character, yet are liquid at room temperature. ILs are finding uses in areas as diverse as electrochemistry, enzyme catalysis, and green chemistry because of their high stability and extraordinary solvency properties.² Recently, the innovative success of ILs has paved the way for convenient, efficient, and environmentally friendly methodologies for a wide variety of chemical reactions having remarkable synthetic

value. Recently, they have become striking solvents for reactions in organic, inorganic, and polymer chemistry as well as for separation processes. Insignificant vapor pressure, high thermal stability, and nonflammability differentiate them from ordinary solvents and make these molten salts interesting as substitutes for traditional solvents. There are countless combinations possible, which make ILs appropriate for tailor-made or designer solvents. Macroscopic properties such as melting behavior and viscosity of ILs are considered first when choosing them as solvents. However, efficiency of ILs in chemical reactions and extraction processes is strongly affected by the interactions between the ILs and the molecules dissolved.^{3–5} Furthermore, modern ILs are stable in contact with air and moisture.⁶ In recent times, ILs have also achieved increasing attention for application in polycondensation reactions.^{7–11} They can also be removed and recycled.^{12–14}

Wholly aromatic polyamides (PAs) (aramids) have been well recognized for their high mechanical properties, good chemical resistance, and excellent thermal stability, and functionalization of them is an attractive pathway to improve the properties of these macromolecules to expand their applications. Their relatively high stiffness favors high melting

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Contract grant sponsors: Research Affairs Division Isfahan University of Technology (IUT), Center of Excellency in Sensors and Green Chemistry Research (IUT).



Scheme 1 Synthesis of monomer 6.

temperatures and limited solubility, which restrict synthesis and uses especially of high molecular weight materials. It is difficult for aramids to be applied as thin films and coatings because they have low solubility in nearly all accessible solvents except for concentrated sulfuric acid. Thus, the interest was focused on the preparation of aramids with enhanced processability either by incorporation of flexible linkages or bulky groups in the main chain or by attachment of pendant alicyclic groups. These modifications lower the melting temperature and result in soluble and amorphous macromolecules without considerable decrease of their thermal properties. In general, amorphous PAs have lower softening temperature and improved solubility compared with crystalline analogues, thus they may open applications in the area of films, coatings, engineering plastics, polymer blends, and composites.¹⁵⁻²⁰

The increasing knowledge of the importance of chirality in the context of biological activity has moved a growing demand for well-organized approaches for the synthesis of enantiomerically pure compounds such as pharmaceutical and agricultural chemicals.³ Lately, we have synthesized a variety of optically active polymers by incorporation of optically active segments in polymer's backbone by different techniques.²¹⁻²³

As part of our continuing attempts in developing tractable high performance polymers containing pendent units, herein, we wish to demonstrate that the IL method is an efficient and environmentally benign green route for the production of chiral extended PAs containing pendent *N*-phthaloyl-*L*-leucine chiral groups via direct polyamidation.

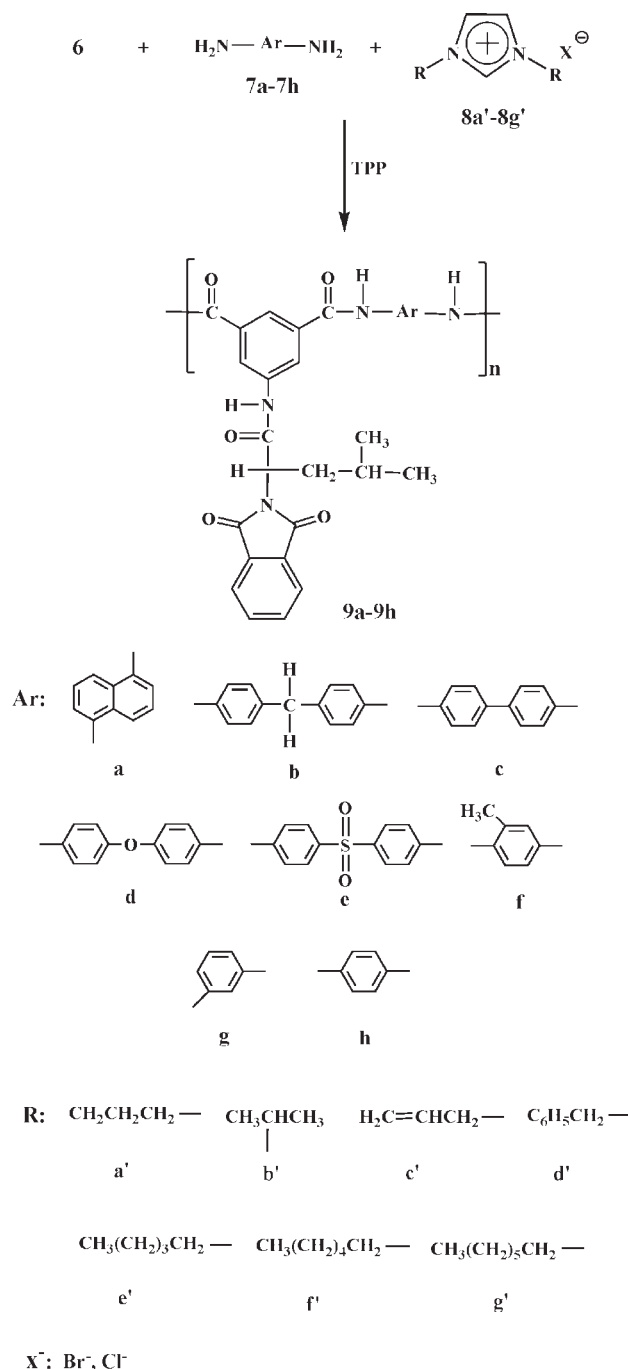
EXPERIMENTAL

Materials

1,5-Naphthalenediamine (**7a**) and 4,4'-diaminodiphenylmethane (**7b**) were purified by recrystallization from water. Benzidine (**7c**) was purified by recrystallization from ethanol. 4,4'-Diaminodiphenylether (**7d**), 2,5-diaminotoluene (**7f**), 1,3-phenylenediamine (**7g**), and 1,4-phenylenediamine (**7h**) were purified by sublimation. *N*-(Trimethylsilyl)-imidazole and all the alkyl halides were purchased from Merck Chemical (Darmstadt, Germany).

Techniques

Proton nuclear magnetic resonance (¹H NMR, 500 MHz) spectra were recorded in DMSO-*d*₆ solution using a Bruker (Ettlingen, Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran.



Scheme 2 Polyamidation reactions of monomer **6** with different aromatic diamines.

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 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 a 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 $10^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) data were recorded on a Setaram instrument (Caluire, France) under nitrogen atmosphere. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. 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**) was prepared according to our previous work.²⁴

Preparation of symmetrical ILs **8a'–8g'**

ILs **8a'–8g'** were prepared according to the previous work.^{7,10}

Polymer synthesis

The **PA9a–PA9h** were prepared by the following general procedure: For synthesis of polymer **PA9a** as an example, 0.10 g (0.23 mmol) of diacid **6** and 0.037 g (0.23 mmol) of diamine **7a** were dissolved in 0.40 g of 1,3-dipropylimidazolium bromide (**8a'**) under heating, and then 0.136 mL (0.52 mmol) of triphenyl phosphite (TPP) was added. The whole solution was heated at 110°C for 3 h. As the reaction proceeded, the solution became viscous. Then, the resulting product was isolated by the addition of 30 mL of methanol and trituration, followed by filtration, and was dried at 120°C for 7 h in vacuum to yield 0.139 g (88%) of polymer **PA9a**.

FTIR (KBr): 3317 (m), 2957 (m), 1774 (w), 1713 (s), 1669 (s), 1599 (m), 1532 (s), 1494 (m), 1444 (m), 1384 (s), 1333 (m), 1268 (m), 1075 (w), 877 (w), 783 (w), 720 (w) cm^{-1} .

The other **PA9b–PA9h** were prepared following an analogous procedure.

TABLE I
Influence of the Reaction Medium on the Inherent Viscosity and Yield of Optically Active **PA9a**

ILs	η_{inh} (dL g^{-1}) ^a	Yield (%)
8a'	0.55	85
8b'	0.37	85
8c'	0.33	71
8d'	0.32	70
8e'	0.41	70
8f'	0.36	73
8g'	0.36	73

^a Measured at a concentration of 0.5 g dL^{-1} in DMF at 25°C .

TABLE II
Physical Properties of PA9a–PA9h

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh} (dL g ⁻¹) ^a	$[\alpha]_D^{25,b}$	$[\alpha]_{Hg}^{25,b}$	Color ^c
7a	PA9a	88	0.55	-9.86	-17.32	W
7b	PA9b	86	0.49	-38.80	-61.20	W
7c	PA9c	84	0.42	-31.50	-64.04	W
7d	PA9d	86	0.44	-29.46	-55.08	W
7e	PA9e	88	0.51	-24.50	-26.12	W
7f	PA9f	83	0.38	-25.42	-49.02	OW
7g	PA9g	83	0.31	-29.70	-47.30	G
7h	PA9h	81	0.33	-42.10	-69.30	OW

^a Measured at a concentration of 0.5 g dL⁻¹ in DMF at 25°C.

^b Measured at a concentration of 0.5 g dL⁻¹ in DMF at 25°C.

^c W, white; OW, off white; G, gray.

PA9d: ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.90–0.91 (d, 3H, CH₃, *J* = 6.48 Hz), 0.94–0.95 (d, 3H, CH₃, *J* = 6.38 Hz), 1.47 (m, 1H, CH), 2.05–2.07 (m, 1H, CH), 2.24–2.26 (m, 1H, CH), 4.97–5.00 (dd, 1H, CH, *J*₁ = 11.12 Hz, *J*₂ = 4.25 Hz), 7.03–7.05 (d, 4H, Ar–H, *J* = 8.79 Hz), 7.71–7.79 (d, 4H, Ar–H, *J* = 8.81 Hz), 7.90–7.91 (m, 2H, Ar–H), 7.94–7.95 (m, 2H, Ar–H), 8.24 (s, 1H, Ar–H), 8.31 (s, 2H, Ar–H), 10.30 (s, 1H, N–H), 10.44 (s, 2H, N–H).

PA9e: ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.89–0.90 (d, 3H, CH₃, *J* = 5.73 Hz), 0.93–0.94 (d, 3H, CH₃, *J* = 5.84 Hz), 1.48 (m, 1H, CH), 2.05–2.10 (m, 1H, CH), 2.23–2.27 (m, 1H, CH), 4.96–4.97 (m, 1H, CH), 7.88–7.94 (m, 8H, Ar–H), 8.00–8.01 (m, 4H, Ar–H), 8.23 (s, 1H, Ar–H), 8.33 (s, 2H, Ar–H), 10.28 (s, 1H, N–H), 10.78 (s, 2H, N–H).

PA9f: ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.89–0.90 (d, 3H, CH₃, *J* = 4.99 Hz), 0.92–0.93 (d, 3H, CH₃, *J* = 5.17 Hz), 1.45 (dd, 1H, CH, *J*₁ = 14.44 Hz, *J*₂ = 7.25 Hz), 2.04 (m, 1H, CH), 2.22 (s, 3H, CH₃), 4.96–4.98 (m, 1H, CH), 7.25–7.26 (d, 1H, Ar–H, *J* = 8.20 Hz), 7.56–7.57 (d, 1H, Ar–H, *J* = 7.61 Hz), 7.80–7.81 (d, 1H, Ar–H, *J* = 1.20 Hz), 7.88 (m, 2H, Ar–H), 7.93

(m, 2H, Ar–H), 8.30 (s, 1H, Ar–H), 8.34 (s, 2H, Ar–H), 10.15 (s, 1H, N–H), 10.31 (s, 1H, N–H), 10.46 (s, 1H, N–H).

RESULTS AND DISCUSSION

In the following discussion, two aspects are taken into consideration. First, in contrast to traditional solvents, the use of ILs as safe and polar reaction media for the polyamidation reactions was investigated. Following this, the presence of thermostable phthalimide heterorings as pendent group may compensate any loss of thermal properties that can be caused by incorporation of aliphatic spacers was studied. These properties, associated with an easy processibility, make these polymers potential candidates for practical applications such as in the area of films, coatings, engineering plastics, polymer blends, and composites.

Monomer synthesis

Dicarboxylic acid **6** was prepared according to our previous work (Scheme 1).²⁴

TABLE III
FTIR Spectra of PA9a–PA9h

Polymer	Wavenumber (cm ⁻¹)
PA9a	3317 (m), 2957 (m), 1774 (w), 1713 (s), 1669 (s), 1599 (m), 1532 (s), 1494 (m), 1444 (m), 1384 (s), 1333 (m), 1268 (m), 1075 (w), 877 (w), 783 (w), 720 (w).
PA9b	3328 (m), 2957 (m), 1774 (w), 1714 (s), 1665 (s), 1595 (m), 1512 (s), 1444 (w), 1408 (w), 1384 (s), 1318 (w), 1247 (w), 1076 (w), 916 (w), 815 (w), 720 (w).
PA9c	3352 (m), 2957 (m), 1774 (w), 1714 (s), 1665 (s), 1593 (m), 1501 (s), 1445 (w), 1384 (s), 1321 (w), 1243 (w), 1078 (w), 821 (w), 721 (w).
PA9d	3422 (m), 2958 (m), 1713 (s), 1663 (m), 1599 (m), 1498 (s), 1384 (s), 1229 (m), 876 (w), 720 (w).
PA9e	3329 (s, br), 3100 (w), 2958 (w), 1775 (w), 1713 (w), 1675 (s, sh), 1590 (s), 1526 (s), 1446 (w), 1399 (m, sh), 1384 (s), 1319 (s), 1248 (m), 1150 (s), 837 (m), 720 (s).
PA9f	3244 (m), 2957 (m), 1775 (w), 1716 (s), 1664 (s), 1596 (m), 1445 (m), 1384 (s), 1303 (w), 1200 (s), 1137 (s), 1093 (m), 1064 (m), 917 (s), 752 (w), 721 (w), 662 (w).
PA9g	3317 (m), 2958 (m), 1774 (w), 1714 (s), 1666 (s), 1606 (s), 1541 (s), 1488 (s), 1445 (m), 1384 (s), 1332 (m), 1243 (s), 1080 (m), 909 (w), 721 (w), 690 (w).
PA9h	3317 (m), 2957 (m), 1774 (w), 1714 (s), 1666 (s), 1606 (s), 1541 (s), 1488 (s), 1445 (m), 1384 (s), 1332 (m), 1243 (s), 1080 (m), 909 (w), 721 (w), 690 (w).

Polymer synthesis

In this investigation, the direct polyamidation of chiral monomer **6** with different aromatic diamines **7a–7h** was carried out applying TPP/IL as condensing agent to prepare new **PA9a–PA9h** (Scheme 2).^{7,10}

The direct polycondensation of a dicarboxylic acid and a diamine is one of the famous methods for PAs synthesis. ILs bearing different alkyl groups and ions were synthesized **8a'–8g'**, and their applications as solvents and also catalysts were examined for the direct polymerization reaction of bulky diacid **6** with 1,5-naphthalenediamine (**7a**). According to the yields and viscosities, in the presence of 1,3-dipropylimidazolium bromide (**8a'**), a better result was achieved (Table I).

The synthesis and some physical properties of these novel optically active PAs are listed in Table II. The inherent viscosities of the resulting polymers under chosen conditions were in the range of 0.31–0.55 dL g⁻¹ and the yields were 81–88%. All of the PAs are optically active.

Polymer characterization

FTIR data

The formation of **PA9a–PA9h** was confirmed by means of FTIR spectroscopic analyses. The FTIR spectrum data of these polymers are reported in Table III. All of these PAs exhibited absorption at 1661–1678 cm⁻¹ peculiar to carbonyls stretching of amide. The presence of the imide heterocycle in these polymers was confirmed by absorption of 1370–1380 and 715–725 cm⁻¹ that belong to carbonyls bendings of imide, and the characteristic absorptions of imide group occurred around 1780 cm⁻¹ that concerned to carbonyls stretching of imide. Bands of amide N–H groups appeared around

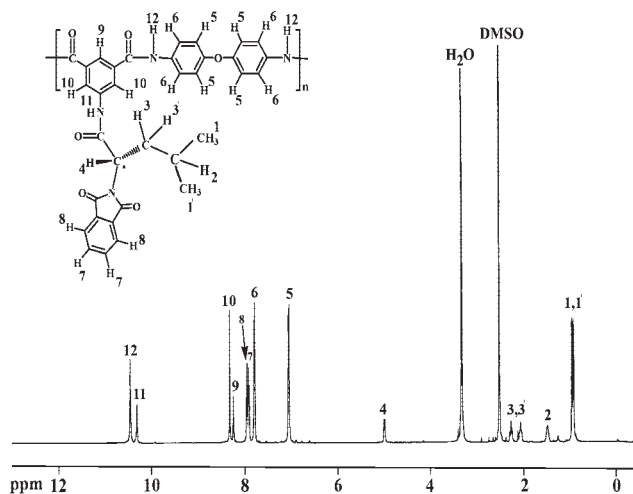


Figure 1 ¹H NMR (500 MHz) spectrum of **PA9d** in DMSO-d₆ at R.T.

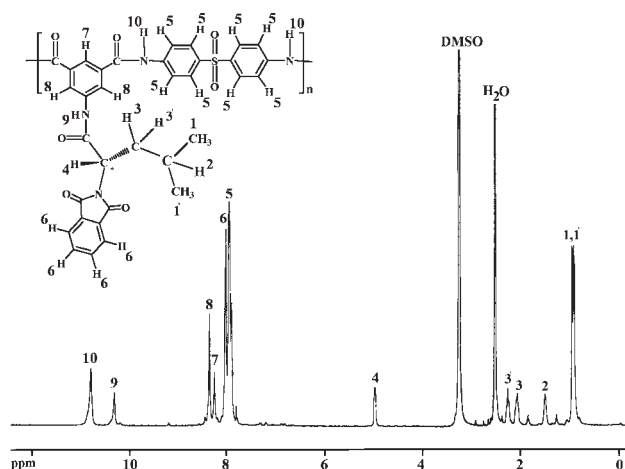


Figure 2 ¹H NMR (500 MHz) spectrum of **PA9e** in DMSO-d₆ at R.T.

3300–3400 cm⁻¹. The **PA9e** showed characteristic absorptions at 1320 and 1152 cm⁻¹ because of the sulfone group of diamine **7e** moiety.

¹H NMR data

Figures 1 and 2 show the ¹H NMR (500 MHz) spectra of polymers **PA9d** and **PA9e**. In the ¹H NMR spectrum of these two polymers, appearances of the N–H protons of amides groups at 10.30 and 10.45 ppm as two singlet peaks, respectively, indicate the amide group in the polymer's side chain and main chain. The absorption 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 absorption of the diastrotopic hydrogens bonded to neighbor carbon of chiral center appeared in the range of 2.05–2.07, 2.24–2.26 ppm as two discrete multiplet peaks. The absorption of the diastrotopic CH₃ protons group of L-leucine appeared as a multiplet peak at 0.90–0.94 ppm.

Elemental analysis, solubility study, and thermal properties

Elemental analysis values of the resulting polymers are listed in Table IV.

Because of flexible group and amide and imide groups in polymer's side chain, these polymers are

TABLE IV
Elemental Analysis of Typical PAs

Polymer	Formula		Elemental analysis (%)		
			C	H	N
PA9a	(C ₃₂ H ₂₆ N ₄ O ₅) _n	Calc.	70.32	4.79	10.25
		Found	68.52	4.65	8.95
PA9c	(C ₃₄ H ₂₈ N ₄ O ₅) _n	Calc.	71.32	4.93	9.78
		Found	70.97	4.38	9.99

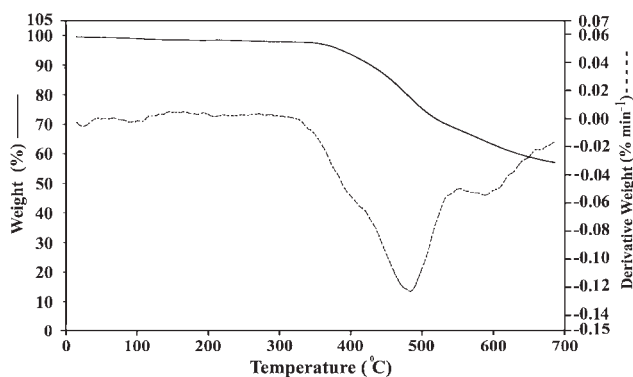


Figure 3 TGA/DTG of PA9c with a heating rate of $10^{\circ}\text{C min}^{-1}$.

expected to have higher solubility. The solubility of PAs was tested quantitatively in various solvents. For solubility test, 5 mg of polymer in 1 mL of solvent was used. All of the PAs are soluble in organic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), tetrahydrofuran, dimethyl sulfoxide, *N*-methyl-2-pyrrolidinone, and in sulfuric acid at room temperature and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water.

The thermal properties of PA9c and PA9d were evaluated by means of TGA/DTG and DSC in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$. Several thermal regions are selected on TGA curves for comparison of the relative thermal stabilities of PAs, which have been calculated by means of thermograms in Figures 3 and 4. They showed good resistance to thermal decomposition up to 350°C in nitrogen and began to decompose gradually above that temperature. The thermoanalysis data of these polymers are summarized in Table V. The temperature of 5% weight loss for PA9c was 385°C , the temperature of 10% weight loss ranged from 430°C , and the residual weight for this polymer at 600°C was 63% under nitrogen atmosphere. These new polymers exhibited good thermal stability because of the existence of the aromatic main chain compared with

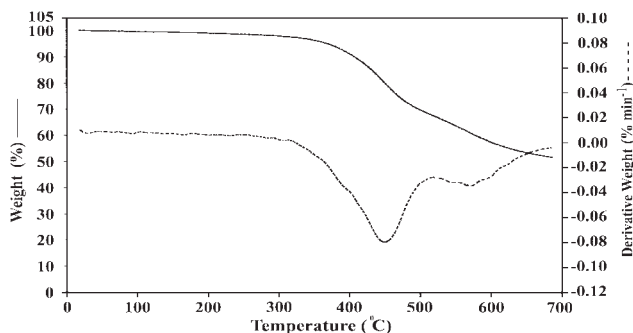


Figure 4 TGA/DTG of PA9d with a heating rate of $10^{\circ}\text{C min}^{-1}$.

TABLE V
Thermal Properties of Some PAs Prepared Using TPP/IL as a Condensing Agent

Polymer	T_5^a ($^{\circ}\text{C}$)	T_{10}^b ($^{\circ}\text{C}$)	T_g^c ($^{\circ}\text{C}$)	Char yield ^d (%)
PA9c	385	430	253	63
A9d	365	410	197	58

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of $10^{\circ}\text{C min}^{-1}$ in a N_2 atmosphere.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of $10^{\circ}\text{C min}^{-1}$ in a N_2 atmosphere.

^c Glass transition temperature was recorded at a heating rate of $20^{\circ}\text{C min}^{-1}$ in a nitrogen atmosphere.

^d Weight percent of the material left undecomposed after TGA at maximum temperature 600°C in a N_2 atmosphere.

other PAs. The DSC analyses for PAs show T_g around $197\text{--}253^{\circ}\text{C}$ (Table V).

CONCLUSIONS

In summary, several novel PAs containing chiral side chain were synthesized by direct polyamidation of chiral monomer **6** with various aromatic diamines under green conditions. ILs hold potential as green and safe solvents, because of their insignificant vapor pressure, and they are opening up a growing new field of organic and polymer synthesis. It is extremely important to mention that in these polyamidation reactions volatile, toxic solvents such as NMP and pyridine are avoided and extra materials such as CaCl_2 is not required. Significantly, the IL not only acts as a solvating medium but also as a promoter for this polycondensation reaction. On the other hand, the introduction of bulky side chains should perturb interchain hydrogen bonding, inherent macromolecular rigidity, and diminish packing efficiency and crystallinity. The results offered herein also express obviously that the phthalimide linkage in the polymer side chain significantly improved the solubility and thermal stability of the polymers. Because these optically active polymers have amino acids in the polymer architecture, they are expected to be biodegradable, and therefore are classified under environmentally friendly polymers. In addition, they have potential to be used as chiral stationary phase in gas chromatography for the separation of racemic mixtures.

Kindly help of Dr. M. Kolahdoozan, Miss. Z. Rafiee, and Mr. H. Yousefian is gratefully acknowledged.

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