Polym. Bull. (2009) 63:623–635
DOI 10.1007/s00289-009-0113-4

ORIGINAL PAPER

Preparation of thermally stable and optically active organosoluble aromatic polyamides containing L-leucine amino acid under green conditions

Shadpour Mallakpour · Mohammad Dinari

Received: 25 December 2008 / Revised: 10 April 2009 / Accepted: 4 June 2009 /

Abstract An optically active bulky dicarboxylic acid (2S)-4-[(4-methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid (**1**), was synthesized in five step starting from L-leucine and phthalic anhydride. A set of new aromatic polyamides containing (*N*-phthaloyl-L-leucine) units was synthesized by the direct one-pot phosphorylation polycondensation of diacid **1** with various aromatic diamines in the presence of different imidazolium salts and triphenyl phosphite (TPP) without adding extra compounds (Method I). This method was compared with a classical method in a medium consisting of TPP, *N*-methyl-2-pyrrolidinone, pyridine, and calcium chloride (Method II) and the results are comparable. The polymers were produced with high yields and from moderate to high inherent viscosities (0.43–0.81 dL g^{-1}). Amino acid existence in this backbone results in optically active polymers. The chemical structures of some of these polymers were characterized by ^{1}H-NMR and elemental analysis, and all of them with FT-IR and specific rotation tools. By introduction of bulky and flexible clusters in these new polyamides pendent group; make them soluble in most polar aprotic solvents.

Keywords Polyamides · Ionic liquid · Amino acid · Optically active polymers · Thermal gravimetric analysis (TGA) · Green chemistry

Introduction

Owing to their excellent balance of thermal and mechanical properties, aromatic polyamides (PA)s have received special importance as polymeric materials for advanced technologies [1]. They are extensively applied as high-temperature

---

S. Mallakpour (✉) · M. Dinari
Organic Polymer Chemistry Research Laboratory, Department of Chemistry,
Isfahan University of Technology, 84156-83111 Isfahan, Iran
e-mail: mallak@cc.iut.ac.ir; mallak777@yahoo.com; mallakpour84@alumni.ufl.edu

resistant polymers, while preserving their structural veracity, and an excellent grouping of chemical, physical and mechanical properties such as chemical resistance, and good tensile properties. On the other hand, generally they have the ordinary problem of being hard to process owing to their infusibility and poor solubility in organic solvents [2–5]. Therefore, much effort has been made to modify the structure of PAs in order to have better properties in terms of both solubility and processability with protection of their high thermal stability [6, 7]. Several approaches have been investigated in attempting to improve the solubility of PAs include the addition of pendant groups to the polymeric backbone, introduction of different heterocyclic rings into the macromolecular chains of PAs, preparation of copolymers such as poly(amide–imide)s, poly(amide–ester–imide)s, and incorporation of bulky substituents or flexible units within the parent chain [6–11].

The direct polycondensation between diacids and diamines is a recognized technique for the preparation of PAs with high molecular weight. In this technique many volatile aprotic organic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), activating agent such as triphenyl phosphite (TPP), $CaCl_2$, and pyridine (Py) have been used. When this technique is applied in industry, it will produce a large amount of toxic waste. Therefore, there is a need for the replacement of these solvents with eco-friendly, nonvolatile solvents for the preparation of PAs.

Several environmentally benign procedures have successfully been developed to avoid, or at least minimizing of using environmentally damaging solvents used on a large-scale, especially those that are volatile and difficult to handle. Ionic liquids (ILs) have recently gained recognition as possible environmentally friendly alternative solvents in various chemical processes. ILs are viewed as a novel class of green benign solvents, which promise to have widespread application in industry, possibly replacing currently used organic solvents, due to unique properties such as negligible vapor pressures, high thermal and chemical stability, broad liquid temperature ranges, an excellent ability to dissolve organic compounds, salts and metals, facile recyclabilities and high specific solvent abilities [12–14]. This unique set of properties has earned ILs recognition as environmentally benign alternatives to traditional organic solvents [15, 16]. On the other hand, the synthesis of polymers in ILs media is also of significant scientific interest. Direct polyamidation reaction in ILs is a recently developed method of polymerization. The polyamidations in ILs proceed as one-pot path-way reactions and have the advantages of direct polycondensation [17–22].

The growing knowledge of the importance of chirality in the framework of biological activity has stimulated an increasing demand for well-organized approaches for the synthesis of enantiomerically pure compounds such as pharmaceutical and agricultural chemicals. The existence of asymmetric centers along polymeric chains awards macromolecules special structural and physical properties. Recently, we have synthesized a variety of optically active polymers by insertion of optically active segments in polymer's backbone by diverse techniques [23–30].

In the work presented here, we wish to report a green, safe and fast method for preparation of thermostable and optically active aromatic PAs bearing amide–imidic linkage in the macromolecule backbone with the aim of removing the use of volatile organic compound. The solubility, physical and thermal properties of the polymers are presented in this article.

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. DMAc and NMP were dried over BaO and then were distilled under reduced pressure. 1,5-Naphthalenediamine (**2e**), and 4,4′-diaminodiphenylmethane (**2b**) were purified by recrystallization from water. Benzidine (**2d**) was purified by recrystallization from ethanol. 4,4′-Diaminodiphenylether (**2c**), 2,5-diaminotoluene (**2f**), 1,4-phenylenediamine (**2h**), and 1,3-phenylenediamine (**2g**) were purified by sublimation. All room temperature ILs were prepared by reported procedure [19].

Equipments

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Germany) Avance 500 instrument. Proton resonances are designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). FT-IR spectra were recorded on Jasco-680 (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), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g dL^{-1} at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on a PerkinElmer (Pyris 1) instrument in a nitrogen atmosphere at a rate of 10 °C min^{-1}, and differential scanning calorimetry (DSC) data were recorded at a rate of 20 °C. 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 Iranian Polymer and Petrochemical Institute, Tehran, Iran.

Monomer synthesis

(2S)-4-[(4-Methyl-2-phthalimidylpentanoylamino)benzoylamino]isophthalic acid (**1**) was synthesizes according to our previous work [31].

Polymers synthesis

Polymerization under oil bath heating in RTIL as a reaction medium

The PAs were prepared by the following general procedure: as an example for the preparation of **PA5cI**, 0.100 g (0.244 mmol) of diacid **1** and 0.061 g (0.244 mmol) of diamine **2c** were dissolved in 0.150 g of 1,3-diisopropylimidazolium bromide (1,3-(isopr)$_2$im]Br), then 0.13 mL (0.488 mmol) of TPP was added. The whole solution was heated at 110 °C for 2.5 h. The solution becomes more viscous by progress of the polymerization reaction. The resulting product was dissolved in 1 mL of DMF and was poured into a beaker containing 30 mL of methanol (ethanol), or methanol (ethanol) was directly added to the reaction vessel without using DMF. The obtained solid was filtered off and dried under vacuum to give 0.146 g (94%) of **PA5cI**.

Polymerization under oil bath heating in NMP as a reaction medium

The PAs were prepared by the following general procedure. Taking **PA5cII** as an example, a mixture of 0.06 g (0.244 mmol) of diamine **2c**, 0.10 g (0.244 mmol) of diacid **1**, 0.060 g of $CaCl_2$, 0.15 mL of pyridine, 0.14 mL of TPP, and 0.5 mL of NMP was placed into the flask equipped with a mechanical stirrer and a condenser. The mixture blanketed by nitrogen was stirred and refluxed for 5 h. At the end of the reaction, the obtained polymer solution was trickled into 20 mL of stirred methanol or ethanol. The white-stringy polymer was washed thoroughly with hot water and methanol, collected by filtration and dried at 100 °C under reduced pressure to give 0.138 g (82%) of **PA5cII**.

PA5a FT-IR (KBr): 3369 (s), 3105 (w, sh), 2957 (w), 1774 (w), 1714 (s), 1668 (m), 1590 (s), 1525 (m), 1447 (w), 1404 (m), 1319 (m), 1249 (m), 1183 (m), 1015 (m), 962 (w, br), 879 (w), 857 (w), 822 (w), 757 (s), 692 (w) cm^{-1}.

PA5b FT-IR (KBr): 3299 (s, br), 3041 (w), 2958 (s), 2890 (m), 1775 (w), 1719 (s), 1668 (m), 1594 (s), 1468 (w), 1409 (m), 1384 (s), 1254 (m, sh), 1246 (m), 1187 (m), 954 (w), 876 (m), 757 (s), 691 (w), 530 (m) cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 0.89–0.94 (d, 6H, CH_3, $J = 7.21$ Hz), 1.36–1.38 (m, 1H, CH), 1.95–1.98 (m, 1H, CH_2), 2.10–2.12 (m, 1H, CH_2), 3.96 (s, 2H, CH_2), 4.87–4.89 (dd, 1H, CH, $J_1 = 6.64$, $J_2 = 6.92$ Hz), 6.90–7.20 (m, 4H, CH), 7.62–7.93 (m, 12H, CH), 8.01 (s, 1H, CH), 8.32 (s, 4H, CH), 10.21 (s, br, NH),10.35 (s, br, NH). ANAL. Calcd for $C_{42}H_{35}N_5O_6$: 69.36% C; 4.98% H; 9.92% N. Found: 68.14% C; 4.96% H; 9.62% N.

PA5c FT-IR (KBr): 3315 (m), 2957 (m), 2870 (w), 1774 (w), 1713 (s), 1662 (m), 1598 (m), 1522 (s), 1468 (w), 1385 (m), 1314 (w), 1246 (m), 1184 (w), 1077 (m), 958 (m), 853 (m), 759 (w), 721 (s), 529 (w) cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): δ 0.86–0.88 (d, 6H, CH_3, $J = 7.14$ Hz), 1.49–1.50 (m, CH), 2.01–2.08 (m, 1H, CH), 2.17–2.19 (m, 1H, CH), 4.93–4.96 (dd, 1H, CH, $J_1 = 6.57$, $J_2 = 6.85$ Hz), 7.01–7.12 (m, 4H, CH), 7.71–7.97 (m, 12H, CH), 8.10 (s, 1H, CH), 8.41 (s, 2H, CH), 10.01 (s, br, NH), 10.48 (s, br, NH).

PA5d FT-IR (KBr): 3413 (m), 3013 (w), 2957 (m), 2870 (w), 1774 (w), 1713 (s), 1662 (m), 1502 (s), 1462 (w), 1385 (s), 1314 (w), 1244 (m), 1184 (w), 1072 (m), 901 (w), 890 (w), 720 (m), 692 (w), 529 (m) cm^{-1}.

PA5e FT-IR (KBr): 3297 (m), 3095 (w), 2957 (m), 1775 (w), 1713 (s), 1660 (s), 1596 (m), 1513 (w), 1468 (m), 1403 (s), 1315 (s), 1248 (m), 1180 (w), 1108 (m), 880 (w), 759 (w), 721 (w), 614 (w), 530 (m) cm^{-1}. ANAL. Calcd for $C_{39}H_{31}N_5O_6$: 68.31% C; 5.03% H; 10.12% N. Found: 67.51% C; 5.16% H; 9.94% N.

PA5f FT-IR (KBr): 3248 (m), 2957 (m), 2870 (w), 1774 (w), 1714 (s), 1661 (m), 1597 (s), 1494 (w), 1384 (s), 1334 (w), 1246 (s), 1075 (m), 940 (w), 890 (w), 780 (m), 660 (w), 530 (m) cm^{-1}.

PA5g FT-IR (KBr): 3414 (m), 3034 (w), 2958 (m), 1774 (w), 1714 (s), 1661 (s), 1605 (s), 1536 (m), 1445 (w), 1384 (m), 1249 (m), 1185 (w), 1071 (w, br), 879 (w), 761 (w), 720 (w), 616 (w), 530 (m) cm^{-1}.

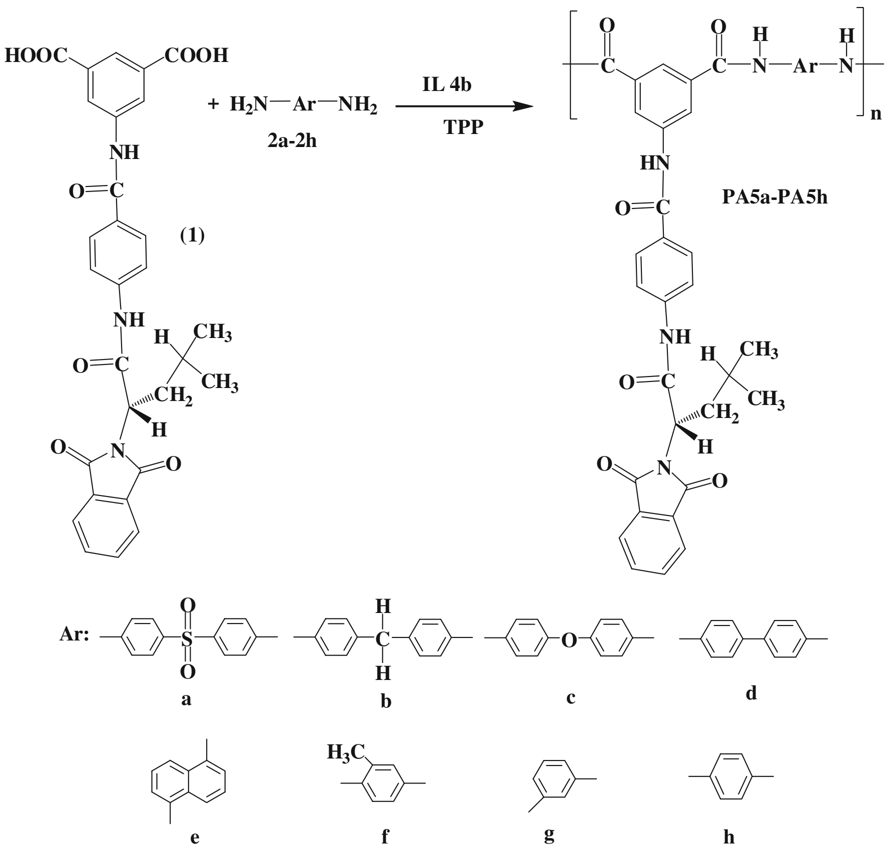
PA5h FT-IR (KBr): 3422 (s), 3140 (w), 2957 (m), 2924 (m), 1775 (w), 1714 (s), 1665 (m), 1596 (w), 1445 (m), 1387 (m), 1316 (m), 1248 (m), 1222 (s), 1186 (w), 1073 (m), 878 (w), 761 (w), 721 (w), 692 (m), 529 (m) cm^{-1}.

Results and discussion

Polymer synthesis

Optically active aromatic **PA5a–PA5h** containing bulky pendent group were synthesized from the reaction of optically active dicarboxylic diacid **1** with aromatic diamines **2a–2h** by the direct polycondensation procedure using two different methods (Scheme 1).

From a technological viewpoint, the use of an organic solvent in large-scale production is not very affable. So we carried out the polymerization reaction in imidazolium types ILs in order to description a safe, straightforward and efficient method for polymerization reaction. At first, in order to choose the best IL for the preparation of PAs, the reaction of monomer **1** with **2h** was carried out in different synthetic ILs such as: 1,3-dipropylimidazolium bromide, 1,3-diisopropylimidazolium bromide, 1,3-dibenzylimidazolium chloride, 1,3-dibenzylimidazolium bromide, 1,3-dibutylimidazolium bromide, 1,3-dipentylimidazolium bromide, 1,3-diheptylimidazolium bromide, 1,3-dialylimidazolium chloride and 1,3-dialylimidazolium bromide and in the absence of any IL under oil bath (Scheme 2) and the results are shown in Table 1. According to Table 1 the best inherent viscosity and yield was obtained when [1,3-$(isopr)_2$im]Br was used as IL for direct polycondensation. So [1,3-$(isopr)_2$im]Br was selected for other polymerization. It is interesting to mention that, the polymers were not obtained in the absence of either of ILs or TPP, so the presence of both components are necessary for polyamidation reactions, and consequently ILs play as a catalyst as well as solvent for these reactions. Since the amounts of ILs were used for each reaction is very low, we did not recycle them. Otherwise, these ILs could be easily separate from resulting polymers and reused.

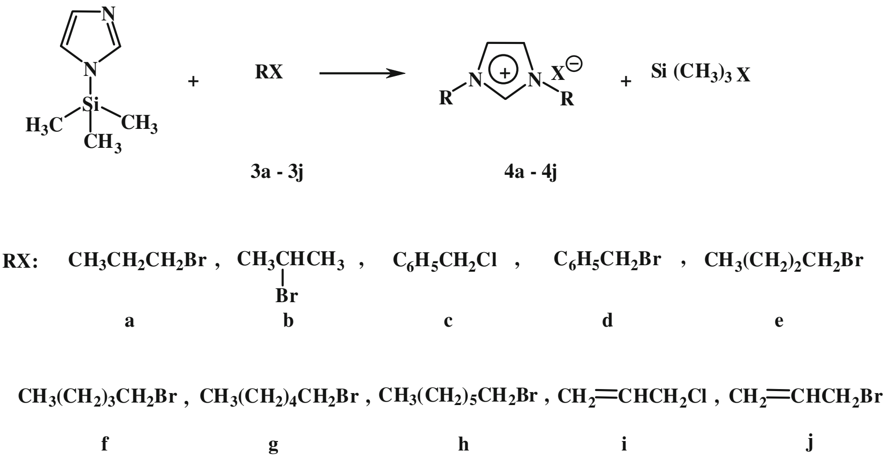


Scheme 1 Polycondensation reactions of monomer **1** with different diamines

Thus, an efficient, simplified and benign procedure for the preparation of PAs was carried out via direct polyamidation reaction of chiral diacid **1** with different aromatic diamines **2a–2h**.

The polymerization reaction was performed using oil bath heating by TPP and 1,3-(isopr)$_2$im]Br as a condensing agent (Method I) and also was carried out under same conditions via Yamazaki phosphorylation reaction, using TPP/Py/NMP/CaCl$_2$ as a condensing agent (Method II) and the results are shown in Tables 2 and 3.

At first polymerization reaction was carried out under oil bath in the presence of [1,3-(isopr)$_2$im]Br and TPP (Method I), and it took 2.5 h for the completion of the reaction. At the end of polymerization, the resulting viscous mixtures were precipitated in methanol (ethanol), which gave aromatic **PA5aI–PA5hI** in high yields and inherent viscosities and the result are shown in Table 2. The inherent viscosities of the resulting polymers under chosen conditions were in the range of 0.45–0.81 dL g^{-1} and the yields were 80–94%. In order to compare this method with Yamazaki phosphorylation reaction (Method II), we also performed the polymerization reactions under oil bath heating conditions using NMP as a solvent



Scheme 2 Synthesis of different ILs

Table 1 The effects of type of ILs on yield and inherent viscosity of the **PA5h** (*Reaction conditions*: 2.5 h, 120 °C)

Polymer	IL	Yield (%)	η_{inh}(dL g^{-1})
PA5h1	No IL	No polymer	–
PA5h1	4a	80	0.50
PA5h1	4b	80	0.74
PA5h1	4c	76	0.41
PA5h1	4d	78	0.45
PA5h1	4e	74	0.39
PA5h1	4f	68	0.35
PA5h1	4g	75	0.33
PA5h1	4h	65	0.41
PA5h1	4i	76	0.32
PA5h1	4j	70	0.41

and it took 5 h at 110 °C for the completion of the reaction. The reaction yields and viscosity of obtained PAs in this method were between 83–94% and 0.41–0.74 dL g^{-1}, respectively (Table 3).

The abovementioned results demonstrate that in Method I by 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 as well as polymers to provide homogeneity and easily separate from resulting polymers, are some other advantages of using IL systems. The yields and inherent viscosities of the resulting polymers obtained by both methods are comparable. The optimum conditions which were obtained in these methods have been applied for the preparation of other PAs. All of the PAs show optical rotations

Table 2 Physical properties of PAs synthesized using ILs as a reaction medium (Method I)

Diamine	Polymer				
	Polymer	Yield (%)	η_{inh} (dL g^{-1})^a	$[\alpha]_D^{25a}$	$[\alpha]_{Hg}^{25\,a}$
2a	**PA5aI**	93	0.48	+56.2	+72.1
2b	**PA5bI**	85	0.64	−48.6	−49.9
2c	**PA5cI**	94	0.52	−54.2	−53.6
2d	**PA5dI**	80	0.45	−41.3	−42.3
2e	**PA5eI**	83	0.66	−53.7	−42.2
2f	**PA5fI**	85	0.72	+50.6	+53.6
2g	**PA5gI**	84	0.81	−52.8	−71.9
2h	**PA5hI**	80	0.74	−62.4	−66.5

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

Table 3 Physical properties of PAs synthesized in NMP as a reaction medium (Method II)

Diamine	Polymer				
	Polymer	Yield (%)	η_{inh} (dL g^{-1})^a	$[\alpha]_D^{25a}$	$[\alpha]_{Hg}^{25\,a}$
2a	**PA5aII**	94	0.46	−32.3	−31.3
2b	**PA5bII**	84	0.57	−40.7	−32.2
2c	**PA5cII**	86	0.43	−47.6	−53.6
2d	**PA5dII**	89	0.53	+29.8	+40.9
2e	**PA5eII**	88	0.54	−70.4	−85.5
2f	**PA5fII**	83	0.67	−44.2	−35.9
2g	**PA5gII**	85	0.72	+38.6	−25.9
2h	**PA5hII**	90	0.74	−72.4	−57.2

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

therefore are optically active. The incorporation of chiral unit into the polymer structure was confirmed by measuring their specific rotations. The quantity and the sign of specific rotation of PAs are not predictable because optical rotation is highly dependent on the chemical structure of the resulting polymeric materials and any small changes in the structure has substantial random effect on the optical rotation.

Polymer characterization

FT-IR study

The structures of these polymers were confirmed as PAs by means of FT-IR spectroscopy. All of the polymers were characterized by absorption peak for the amide N–H groups around 3,300 cm^{-1}. Absorption of amide N–H bonds appeared around 3,310–3,331 cm^{-1} (hydrogen band) and the peaks at 1,765 and 1,710 cm^{-1} (C = O asymmetric and symmetric, respectively, imide group), 1,670 cm^{-1} (C = O, amide) confirm the presence of different carbonyl groups in the polymer

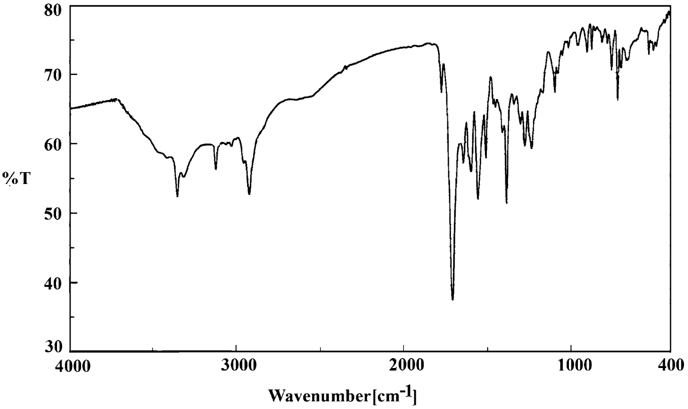


Fig. 1 FT-IR (KBr) spectrum of **PA5cI**

chain. The absorption bands appeared around 3,013–3,100 and 2,850–2,930 cm^{-1} are related to the corresponding aromatic and aliphatic C–H stretching vibration, respectively. All of them exhibited strong absorptions at 1,384 and 718–720 cm^{-1} that show the presence of the imide heterocycle ring in these polymers. For example the FT-IR spectrum of **PA11cI** is shown in Fig. 1.

^{1}H-NMR study

The ^{1}H-NMR spectra of soluble **PA5cI** is shown in Fig. 2. In the ^{1}H-NMR spectra of these polymers, the resonance of the diastereotopic CH_3 protons groups of L-leucine appeared as a broad multiplet peak at 0.90–0.94 ppm. The resonance of the diastereotopic 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 multiplets peaks. The proton of the chiral center appeared as multiplets in the range of 4.97–5.00 ppm. The resonance of aromatic protons appeared in the range of 6.93–8.45 ppm. Appearances of the N–H protons of amides groups at 10.30 and 10.45–10.51 ppm as three peaks indicate the presence of amide group in the polymers side chain, as well as main chain. The aforementioned results show that PAs were synthesized successfully.

Thermal properties

DSC and TGA were used to evaluate the thermal properties of the resulting PAs. The thermal behavior data of some of the PAs such as: **PA5cI**, **PA5cII**, **PA5hI** and **PA5hI** are given in Table 4. The glass transition temperature (T_g) values of the **PA5cI**, **PA5hI** were obtained from DSC measurements. **PA5cI** and **PA5hI** showed T_g values in the ranges of 155 and 168 °C, respectively. The thermal stabilities of these PAs were evaluated by TGA under nitrogen with a 10% weight loss temperature ($T_{10\%}$) for comparison. These are summarized in Table 4. The decomposition temperatures at a 10% weight loss of **PA5cI**, **PA5cII**, **PA5hI** and

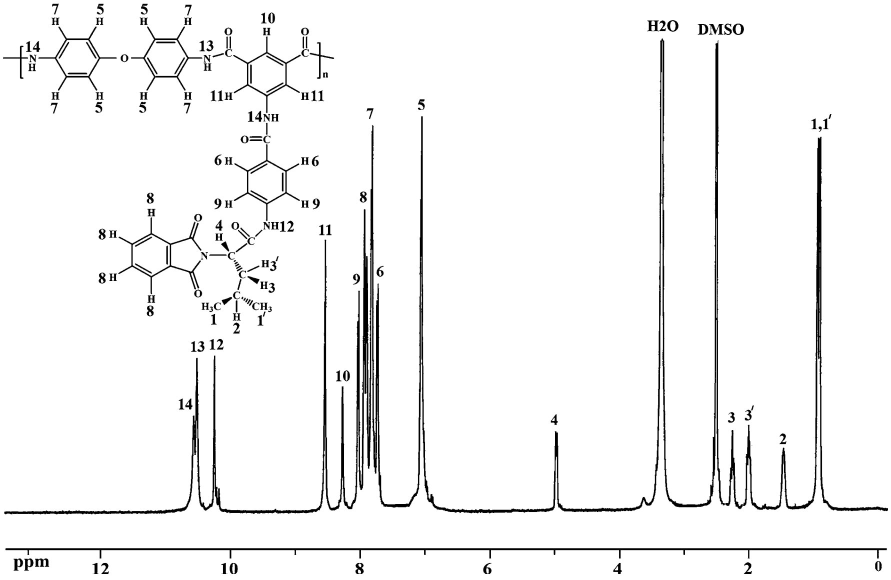


Fig. 2 ^{1}H-NMR (500 MHz) spectrum of **PA5cI** in DMSO-d_6 at RT

PA5hI were recorded in the range of 385–453 °C in nitrogen. **PA5hI** and **PA5hII** exhibited higher T_{10} values than their analogous **PA5hI** and **PA5hII** counterparts and this increase may be a result of relatively higher rigidity of the molecular chains. According to Table 4, it is clear that the **PA5hI** and **PA5hII** (based on 1,4-phenylenediamine) have higher thermal stability than the other PAs. It could be pertained to aromatic, rigid structure of diamines for **PA5hI** and **PA5hII** compare to flexible structure of 4,4′-diaminodiphenylether for **PA5cI** and **PA5cII**. Figure 3 shows the TGA thermograms of **PA5cI**, **PA5hI**, which indicate two steps thermal degradation. The results reveal that PAs are thermally stable up to 350 °C.

Table 4 Thermal properties of PAs

Polymer	Decomposition temperature (°C)		Char yield (%)[b]	T_g^c (°C)
	T_5 [a]	T_{10} [a]		
PA5cI	348	385	56	156
PA5cII	351	386	59	–
PA5hI	400	451	68	168
PA5hII	403	454	66	–

[a] Temperature at which 5 and 10% weight loss were recorded by TGA at heating rate of 10 °C min^{-1} in a N_2 atmosphere

[b] Weight percent of the material left undecomposed after TGA at maximum temperature 800 °C in a N_2 atmosphere

[c] Glass transition temperature was recorded at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere

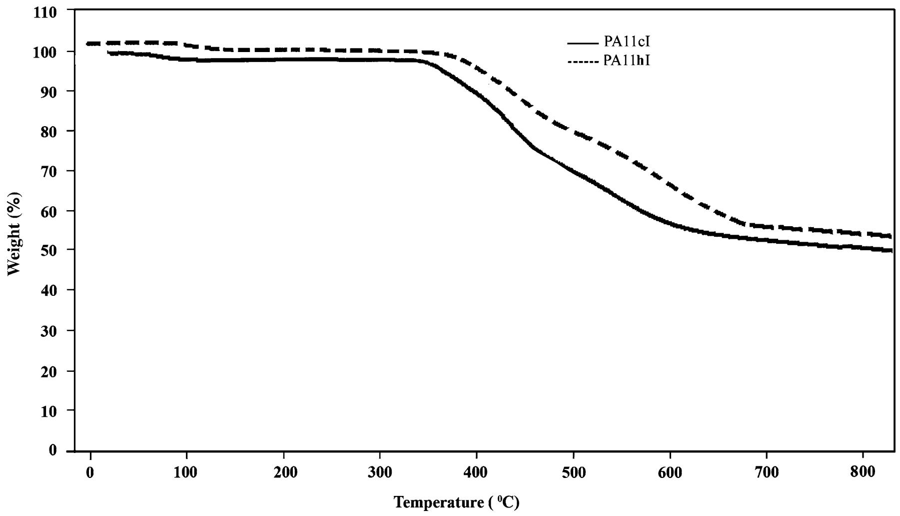


Fig. 3 TGA thermograms of **PA5cI** and **PA5hI** under N_2 atmosphere

Solubility of PAs

One of the purposes of this study was producing modified PAs with enhanced solubility. The incorporation of bulky side groups into the polymer structure, reduces molecular packing, and restricts the formation of interchain hydrogen bonds, which are responsible of the PAs intractability. Because of flexible bulky groups in polymer's pendent, these polymers are expected to have higher solubility. The solubility of PAs (polymer synthesis using both methods) was tested at a concentration of 0.5 g dL^{-1} and at ambient temperature in various solvents. Almost all of the PAs are soluble in organic polar aprotic solvents such as DMF, DMAc, dimethyl sulfoxide, NMP and polar protic solvent such as H_2SO_4 at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Conclusions

Ultimate goals of this investigation were the synthesis of a series of organosoluble and optically active aromatic PAs that possess several advanced characteristics such as optical activity, possession of wholly aromatic backbone and organosolubility under green condition using imidazolium type ILs. This environmentally friendly green technique is a safe, fast, high yielding, economical and simple manipulation route, which avoids the usage of volatile organic solvents and catalyst. Optical activity of resulting PAs, make them the potentially useful candidates as the new chiral stationary phases in HPLC techniques. Wholly aromatic backbones of PAs provide some superior properties such as stability toward thermal shocks, chemical resistances and mechanical strength and at last, organosolubility of PAs removes the processing difficulties which regularly are associated with handing out of the wholly aromatic PAs. Potential applications of amino acid-based polymers include drug delivery agent, chiral stationary phases for resolution of enantiomers in chromatographic techniques and biomaterials.

Acknowledgments We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged.

References

1. Yamashita M, Kakimoto M, Imai YJ (1993) Preparation and properties of new aromatic polyamides from bis (4-aminophenyl) phenylphosphine and aromatic dicarboxylic acids. J Polym Sci Part A Polym Chem 31:1513–1518
2. Calderon V, Garcia F, de la Pena JL, Maya EM, Lozano AE, de la Campa JG, de Abajo J, Garcia JM (2006) Synthesis and characterization of new aromatic polyamides bearing crown ethers or their dipodal counterparts in the pendant structure. J Polym Sci Part A Polym Chem 44:4063–4075
3. Zhu X, Jian X (2004) Soluble aromatic poly(ether amide)s containing aryl-, alkyl-, and chloro-substituted phthalazinone segments. J Polym Sci Part A Polym Chem 42:2026–2030
4. Mallakpour S, Kowsari E (2005) Synthesis and characterization of new optically active poly(amide–imide)s containing epiclon and L-methionine moieties in the main chain. Polym Adv Technol 16:732–737
5. Garcia JM, Garcia F, Sanz R, de la Campa JG, Lozano AE, de Abajo J (2001) Synthesis and characterization of new soluble polyamides derived from 2,6-bis(4-aminophenyl)-3,5-dimethyltetrahydro-4H-pyran-4-one. J Polym Sci Part A Polym Chem 39:1825–1832
6. Mallakpour S, Kolahdoozan M (2007) Preparation of new poly(amide–imide)s with chiral architectures via direct polyamidation reaction. J Appl Polym Sci 104:1248–1254
7. Sava I, Bruma M (2006) Aromatic polyamides containing pendent acetoxybenzamide groups. Macromol Symp 239:36–42
8. Hamciuc E, Hamciuc C, Sava I, Bruma M (2001) Fluorinated heterocyclic polyamides. Eur Polym J 37:287–293
9. Kim JH, Kim YH, Kim YJ, Won JC, Choi KY (2004) Synthesis and characterization of novel aromatic condensation polymers containing rigid benzoxazole pendent groups. J Appl Polym Sci 92:178–185
10. Hsiao SH, Chang YH (2004) New soluble aromatic polyamides containing ether linkages and laterally attached *p*-terphenyls. Eur Polym J 40:1749–1757
11. Liu YL, Li SH, Lee HC, Hsu KY (2006) Selective reactivity of aromatic amines toward 5-maleimidoisophthalic acid for preparation of polyamides bearing *N*-phenylmaleimide moieties. React Funct Polym 66:924–930
12. Wu W, Li W, Han B, Zhang Z, Jiang T, Liu Z (2005) A green and effective method to synthesize ionic liquids: supercritical CO_2 route. Green Chem 7:701–704
13. Ding K, Miao Z, Liu Z, Zhang Z, Han B, An G, Miao S, Xie Y (2007) Facile synthesis of high quality TiO2 nanocrystals in ionic liquid via a microwave-assisted process. J Am Chem Soc 129:6362–6363
14. Wasserscheid P, Keim W (2000) Ionic liquids—new solutions for transition metal catalysis. Angew Chem Int Ed Engl 39:3773–3789
15. Mallakpour S, Rafiee Z (2008) Use of ionic liquid and microwave irradiation as a convenient, rapid and eco-friendly method for synthesis of novel optically active and thermally stable aromatic polyamides containing *N*-phthaloyl-L-alanine pendent group. Polym Degrad Stab 93:753–759
16. Alvarez JC, Campa JG, Lozano AE, Abajo JD (2001) Thermal and mechanical properties of halogen containing aromatic polyamides. Macromol Chem Phys 202:3142–3148
17. Vlad-Bubulac T, Hamciuc C, Petreus O, Bruma M (2006) Synthesis and properties of new phosphorus-containing poly(ester–imide)s. Polym Adv Technol 17:647–652

18. Hamciuc C, Ronova IA, Hamciuc E, Bruma M (1998) The effect of the rotation hindrance on physical properties of some heterocyclic polyamides containing pendent imide groups. Die Angewandte Makromolekulare Chemie 254:67–74
19. Mallakpour S, Kowsari E (2005) Ionic liquids as novel solvents and catalysts for the direct polycondensation of *N*,*N*-(4,4-oxydiphthaloyl)-bis-L-phenylalanine diacid with various aromatic diamines. J Polym Sci Part A Polym Chem 43:6545–6553
20. Kubisa P (2004) Application of ionic liquids as solvents for polymerization processes. Prog Polym Sci 29:3–12
21. Mallakpour S, Rafiee Z (2008) Safe and fast polyamidation of 5-[4-(2-phthalimidiylpropanoylamino) benzoylamino]isophthalic acid with aromatic diamines in ionic liquid under microwave irradiation. Polymer 48:3007–3013
22. Mallakpour S, Yousefian H (2008) Direct polyamidation in molten tetrabutylammonium bromide: novel and efficient green media. Polym Bull 60:191–198
23. Wen-Yong L, Min-Hua Z (2006) Efficient kinetic resolution of (R, S)-1-trimethylsilylethanol via lipase-mediated enantioselective acylation in ionic liquids. Chirality 18:814–821
24. Vandermeulen GWM, Klok HA (2004) Peptide/protein hybrid materials: enhanced control of structure and improved performance through conjugation of biological and synthetic polymers. Macromol Biosci 4:383–398
25. Mallakpour S, Moghaddam E (2006) Direct polyamidation of *N*,*N*′-(4,4′-hexafluoroisopropylidendiphthaloyl)-bis-L-isoleucine with different aromatic diamines via vilsmeier adduct derived from tosyl chloride and *N*,*N*-dimethylformamide. Polym Bull 56:339–347
26. Mallakpour S, Khani M (2007) Novel optically active poly(amide–imide)s derived from *N*-trimellitylimido-L-isoleucine and different diisocyanates. Polym Bull 59:587–596
27. Feng L, Hu J, Liu Z, Zhao F, Liu G (2007) Preparation and properties of optically active poly (*N*-methacryloyl L-leucine methyl ester). Polymer 48:3616–3623
28. Kakizawa Y, Harada A, Kataoka K (2001) Glutathione-sensitive stabilization of block copolymer micelles composed of antisense DNA and thiolated poly(ethylene glycol)-block-poly(L-lysine): a potential carrier for systemic delivery of antisense DNA. Biomacromolecules 2:491–497
29. Mallakpour S, Rafiee Z (2008) Step-growth polymerization of 5-(3-acetoxynaphthoylamino) isophthalic acid with different aromatic diols. Iran Polym J 17(3):217–226
30. Mallakpour S, Kowsari E (2006) Microwave heating in conjunction with ionic liquid as a novel method for the fast synthesis of optically active poly(amideimide)s. Iran Polym J 15:239–247
31. Mallakpour S, Sepehri S (2008) Synthesis and characterization of new optically active polyesters by step-growth polymerization of novel aromatic (2*s*)-4-[(4-methyl-2-phthalimidylpentanoylamino) benzoylamino]isophthalic acid with aromatic diols. J Appl Polym Sci 55:51–58