Room Temperature Ionic Liquids as Replacements for Organic Solvents: Direct Preparation of Wholly Aromatic Polyamides Containing Phthalimide and S-valine Moieties

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Ionic liquids (IL)s are often considered as green solvents capable of replacing traditional organic solvents and have extensively studied in material chemistry and catalysis. In this work a new class of wholly aromatic and optically active polyamides (PAs) having phthalimide and S-valine pendent groups were prepared by the reaction of 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid as a diacid monomer with various aromatic diamines. ILs media in the presence of triphenyl phosphite was used as a condensing agent. The resulting novel optically active PAs with inherent viscosities ranging from 0.35–0.71 dLg^{-1}, were obtained in excellent yields. This method of polymerization was also compared with direct polyamidation using conventional phosphorylation reaction. Introduction of bulky and flexible clusters in these polymers pendent group, make them readily soluble in most organic solvents. The resulting polymers show optical rotation, therefore, are optically active.
KEY WORDS: Ionic Liquid / Polyamides / Green Chemistry / Optically Active Polymers / Direct Polycondensation /

Ionic liquids (IL)s may be sighted as a new and remarkable class of solvents, or as a type of materials that have useful history. ILs are either organic salts or mixtures of salts that are fluid at room or near-room temperature.[1] Research teams in industrial and academic are trying to redesign chemical processes to reduce or eliminate losses of solvents, particularly volatile organic solvents (VOS)s. Obviously, replacement of a VOS in a process with non-volatile solvent will reduce losses through evaporation. It is important that ILs are the chemicals that can be applied as solvents and catalysts in green chemistry processes. Non-volatility of ILs is an important property, but an interest in ILs arises also from other properties. ILs dissolve many organic but what is even more important many inorganic and metaloorganic compounds.[2] On the other hand, many organic reactions were performed in ILs with particular advantages. Several articles and reviews deals to the study and application of ILs as solvents, asymmetric synthesis, homogeneous catalysts, heterogeneous catalysts and bio catalysts media show the importance and growing role of the ILs in chemistry.[1–6]

The synthesis of polymers in ILs media is also of significant scientific interest.[7] Recently many kinds of polymerizations were performed in ILs, e.g., free radical,[8] atom transfer radical,[9,10] ring opening polymerization[11] and polycondensation.[12–14] ILs play the role of both catalyst and solvent for polycondensation. The polyamidation in ILs proceed as one pot path-way using the free dicarboxylic acid, diamines and have the advantages of direct polycondensation. Therefore, it seems reasonable that ILs may enhance polymer syntheses as well.

Wholly aromatic polyamides (PA)s are known for their excellent thermal and mechanical properties, which make them useful as high-performance materials. But, the poor solubility and high softening or melting temperatures caused by the high crystallinity and high stiffness of the PAs backbone lead to difficult processability of them. So, the applications of PAs are sometimes restricted because of difficulty in their fabrication.[15–17]

Much effort has been made to modify aromatic polymers having better characterization in terms of both solubility and processability with protection of their high thermal stability. Introduction of flexible chains into the polyamide backbone,[18] the use of meta-oriented or asymmetrically substituted monomers,[19,20] synthesis of cardo polymers,[21] synthesis of polyamides (PAs) with noncoplaner unit in the polymer chains,[22] preparation of copolymers such as poly(amide-imide)s,[23–25] poly(amide-ester)s,[26] and poly(amide-ester-imide)s[27] resulted in a number of modified polyamides. The other strategy is the introducing of bulky side groups. The solubility of polymers is often improved when flexible bonds, large pendent groups or polar substituents are included into the polymer backbone. If the pendent groups are carefully chosen, it is likely to increase solubility without affecting thermal and mechanical properties to any great extent. These modifications work by breaking the chain symmetry and regularity and by destroying hydrogen bonds and generally lead to lower transition temperatures and better solubility.[28–32] In many cases, the introduction of diverse heterocyclic rings into the chains of polyamides led to polymers with improved solubility and enhanced thermal stability.[32–35]

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513

In the history of polymer science, both naturally occurring and synthetic optically active polymers (**OAP**)s have received much attention in conjunction with their stereochemistry, and extensive studies have been conducted on their syntheses, conformations and functions.[36,37] Recent advances in asymmetric reactions and catalysis as well as in chiral separations have afforded a rapid increase in the number of optically active compounds and reagents.[38,39] This situation will influence new methodologies for the preparation of **OAP**s.

Herein we wish to demonstrate the successful application of **IL**s for green synthesis of wholly aromatic optically active **PA**s containing S-valine amino acid and phthalimide groups in the side chain of the polymers. The bulky side chains disturb the interchain interaction and reduce packing efficiency and crystallinity. Therefore, these polymers may show good solubility. In this study we used **IL**s as a media for direct polyamidation.

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. 4,4′-Diaminodiphenylsulfone (**2a**) was used as obtained without further purification. Benzidine (**2d**) and 4,4′-diaminodiphenyl methane (**6c**) were purified by recrystallization from ethanol and water respectively. 4,4′-Diaminodiphenylether (**6b**), *p*-phenylenediamine (**6e**), *m*-phenylenediamine (**6f**) and 2,5-diaminotoluene (**6g**) were purified by sublimation. **IL**s were prepared according to the literature procedure.[14]

Apparatus

Proton nuclear magnetic resonance (^{1}H NMR, 500 MHz) spectra were recorded in dimethyl sulfoxide-d_6 (DMSO-d_6) solution using a Bruker (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. 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 wave numbers (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 (Germany) at concentration of 0.5 g/dL at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a rate of 10 °C/min. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran.

Monomer Synthesis

5-(2-Phthalimidyl-3-methylbutanoylamino)isophthalic acid (**1**) as a diacid monomer was prepared according to our pervious published paper.[40]

Polymer Syntheses

Method I: Direct Polycondensation in ILs. **PA**s were prepared by the following procedure. For example; for the synthesis of **PA1**, into a 25 mL round-bottom flask a mixture of 0.100 g (2.44×10^{-4} mol) of dicarboxylic acid **1** and 0.061 g (2.44×10^{-4} mol) of diamine **2a** were dissolved in 0.20 g of **IL** (1,3-dipropylimidazolium bromide) under heating. 0.13 mL (4.88×10^{-4} mol) of triphenyl phosphite (TPP) was added. The mixture was heated at 110 °C for 5 h. As the reaction proceeded, the solution became viscous. After cooling, the resulting polymer was isolated by the addition of 30 mL methanol followed by filtration. The product was dried under vacuum to give 0.151 g of **PA1** (94% yield). The inherent viscosity of the resulting polyamide in DMF was 0.71 dLg^{-1}, measured at a concentration of 0.5 gdL^{-1} at 25 °C.

Method II: Direct Polycondensation Phosphorylation Reaction. A mixture of 0.100 g (2.44×10^{-4} mol) of dicarboxylic acid **1**, 0.061 g (2.44×10^{-4} mol) of diamine **2a**, 0.128 mL of TPP, 0.1 mL of pyridine (Py), 0.08 g of calcium chloride and 0.5 mL of *N*-methyl-2-pyrrolidone (NMP) was refluxed for 5 h. After cooling, the reaction mixture was poured into 30 mL of methanol with constant stirring, and the precipitate was washed thoroughly with methanol and hot water, collected on a filter, and dried under vacuum to give 0.1478 g of **PA9** (92% yield). The inherent viscosity of the resulting polyamide in DMF was 0.45 dLg^{-1}, measured at a concentration of 0.5 gdL^{-1} at 25 °C.

PA1
FT-IR (KBr): 3316 (br), 2964 (w), 1764 (m), 1719 (s), 1665 (s), 1590 (s), 1528 (s), 1491 (m, sh), 1401 (m), 1385 (w), 1317 (m), 1250 (m), 1183 (w), 1152 (m), 1105 (m), 1072 (m), 1024 (w), 951 (m), 915 (m), 838 (m), 755 (m), 719 (m) cm^{-1}.

PA2
FT-IR (KBr): 3314 (br), 2965 (w), 1768 (m), 1714 (s), 1667 (s), 1598 (s), 1528 (m, sh), 1498 (s), 1405 (m), 1383 (m), 1331 (w), 1227 (s), 1167 (w), 1071 (m), 1013 (w), 880 (w), 832 (m), 719 (m) cm^{-1}.

PA3
FT-IR (KBr): 3299 (br), 2965 (w), 1768 (m), 1715 (s), 1662 (s), 1595 (s), 1512 (s, sh), 1467 (w), 1444 (w), 1408 (m), 1383 (m), 1318 (m), 1247 (m, sh), 1071 (m, sh), 1019 (w), 888 (m, sh), 814 (w), 720 (m) cm^{-1}.
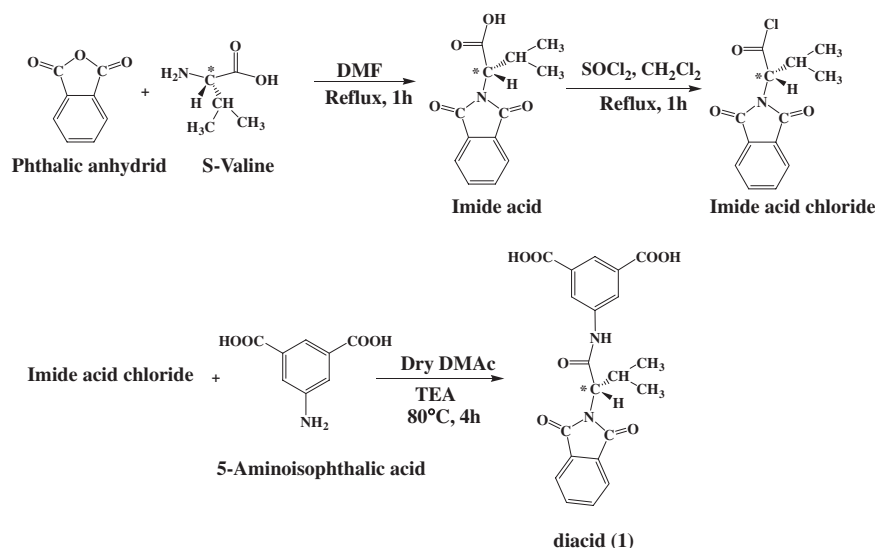
PA4
FT-IR (KBr): 3305 (br), 2965 (w), 1768 (m), 1714 (s), 1666 (s), 1593 (s), 1501 (s, sh), 1468 (w), 1413 (w), 1384 (m), 1322 (m), 1241 (m), 1114 (w), 1069 (m), 1004 (m, sh), 959 (w), 887 (m), 820 (m), 719 (m) cm^{-1}.

PA5
FT-IR (KBr): 3303 (br), 2965 (w), 1767 (m), 1713 (s), 1667 (s), 1597 (s), 1513 (s, sh), 1467 (w), 1445 (w), 1384 (m, sh), 1313 (m), 1240 (m), 1075 (m, sh), 1019 (w), 890 (m), 834 (m), 720 (m) cm^{-1}.

PA6
FT-IR (KBr): 3303 (br), 2965 (w), 1766 (m), 1714 (s), 1669 (s), 1605 (s), 1541 (s), 1487 (m), 1443 (w), 1384 (m), 1328 (m), 1242 (m), 1078 (s), 1024 (w, sh), 889 (s), 720 (m) cm^{-1}.

Scheme 1. Synthesis of 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid (**1**).

PA7

FT-IR (KBr): 3298 (br), 2964 (w), 1768 (w), 1711 (s), 1669 (s), 1594 (s), 1529 (s, sh), 1444 (m), 1384 (m), 1325 (m), 1242 (m, sh), 1078 (m, sh), 892 (m), 821 (w), 749 (m), 721 (m) cm^{-1}.

PA8

FT-IR (KBr): 3289 (br), 2965 (w), 1769 (m), 1715 (s), 1661 (s), 1595 (s), 1531 (s), 1492 (m), 1444 (w), 1412 (w), 1384 (m), 1334 (m), 1269 (w, sh), 1236 (m), 1069 (m), 1010 (w), 959 (w), 887 (m), 783 (m), 754 (m), 719 (m) cm^{-1}.

RESULTS AND DISCUSSION

Syntheses of Monomer

The 5-(2-phthalimidyl-3-methylbutanoylamino)isophthalic acid (**1**) as a diacid monomer was synthesized in three steps as reported previously (Scheme 1).[40]

Syntheses of Polyamides

In order to prepare **PA**s in **IL**s, first the reaction of monomer **1** with diamine **2a** was carried out in different **IL**s bearing different alkyl groups (Table I). The best inherent viscosity and yield was obtained when 1,3-dipropylimidazolium bromide used as **IL** for direct polycondensation (Table I, **PA1**a). So 1,3-dipropylimidazolium bromide was used for other polymerization reactions. Table II shows the selected conditions for polyamidation reactions in **IL**s.

Two different methods (method I and II) were used for the direct polycondensation of dicarboxylic acid **1** with various diamines. In the method **I**, the **IL**s in the presence of TPP promotes polyamidation reaction, and in method **II** direct polycondensations of selected diamines were carried out by phosphorylation reaction using NMP/TPP/Py as a condensing agent (Scheme 2). In method **II**, CaCl$_2$ was also added to the reaction mixture and the polymerization proceeded homogenously.

**Table I.** The effects of type of **IL**s on yeild and inherent viscosity of the **PA1**[a]

Polymer code	IL	Yield (%)	η_{inh}(dL/g)
PA1a		94	0.71
PA1b		90	0.57
PA1c		80	0.42
PA1d		78	0.48
PA1e		82	0.35
PA1f		76	0.38

[a]Reaction time 5 h and reaction temperature 110 °C.

Table II. Reaction conditions for polymerization in **IL**s

IL	
TPP/monomer (mmol/mmol)	2
Reacion time (h)	5
Reaction temperature (°C)	110

PAs from method **I** were obtained in excellent yields (yields were above 90%), had inherent viscosity values ranging between 0.35–0.71 dLg^{-1} and had bright color (Table III). In method **II**, **PA9** and **PA10** were obtained with almost lower yields in compare to **PA1** and **PA4** which were prepared by method **I** with same diamines, respectively. Table III also

R: Different alkyl groups as identified in Table I
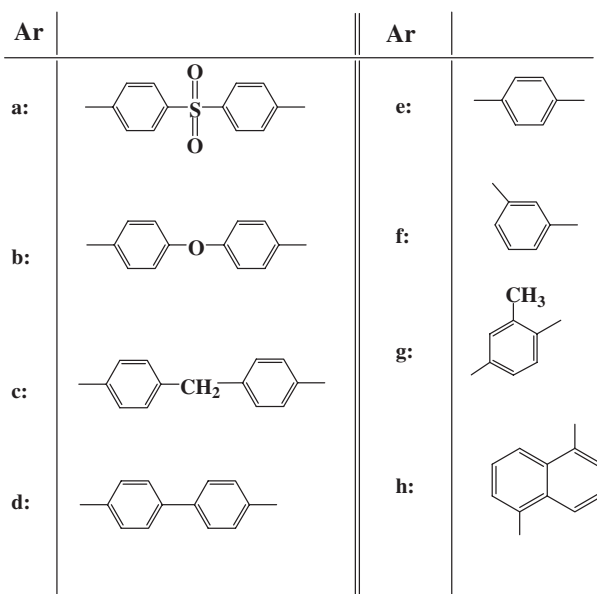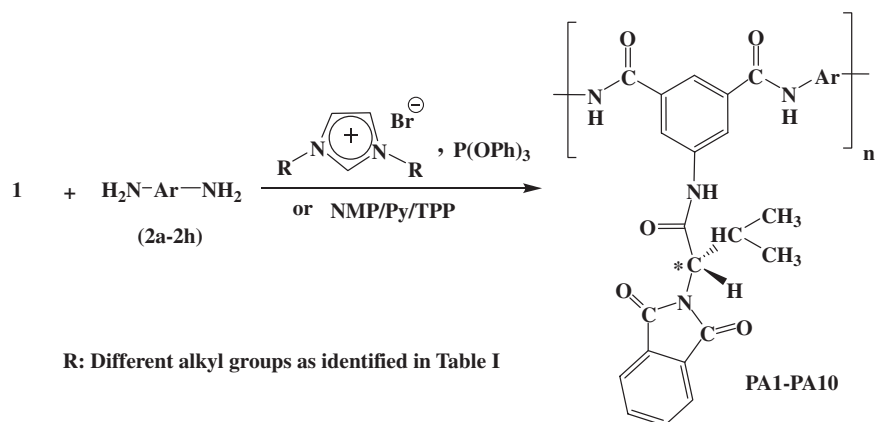
PA1-PA10

Scheme 2. Direct polyamidation reactions of monomer **1** with various aromatic diamines in **IL**s and phosphorylation reaction.

Table III. Synthesis and some physical properties of **PA1-PA10**

Diamine	Polymer	Method of Polymerization[a]	Yield (%)	η_{inh} (dL/g)[b]	$[\alpha]^{25,c}_{Na,589}$	$[\alpha]^{25,c}_{Hg}$	Color	Film Properties[e]
2a	**PA1a**	I	94	0.71	−52.44	−82.70	White	Flexible
2b	**PA2**	I	90	0.43	−17.44	−24.82	Pale yellow	Brittle
2c	**PA3**	I	99	0.40	−12.88	−20.16	Yellow	Brittle
2d	**PA4**	I	98	0.67	−14.86	−29.02	Yellow	Flexible
2e	**PA5**	I	97	0.53	−16.40	−21.82	White	Brittle
2f	**PA6**	I	94	0.35	−14.42	−15.86	Yellow	Brittle
2g	**PA7**	I	92	0.44	−11.36	−32.58	Pale yellow	Flexible
2h	**PA8**	I	97	0.41	−7.50	−30.56	White	Brittle
2a	**PA9**	II	92	0.45	—[d]	−13.92	Off white	Brittle
2d	**PA10**	II	94	0.74	−34.10	−60.18	Off white	Brittle

[a]Method **I**: TPP in ionic liquid as a condensing agent; Method **II**: NMP/TPP/Py as a condensing agent. [b]Measured at a concentration of 0.5 g/dL in DMF at 25 °C. [c]Measured at a concentration of 0.5 g/dL in DMF at 25 °C. [d]not observed. [e]Film formed by evaporation of solvent from polymer solution in DMF.

Table IV. Elemental Analysis of typical **PA1**, **PA2**

Polymer code	Formula		Elemental Analysis (%)			Moisture Intake(%)[a]
			C	H	N	
PA1	$C_{33}H_{26}N_4O_7S$	Calcd	63.66	4.21	9.00	3.4
	$(622.15)_n$	Found	61.25	4.44	8.33	
		Corr[b]	63.34	4.28	8.61	
PA2	$C_{33}H_{26}N_4O_6$	Calcd	68.98	4.56	9.75	2.3
	$(574.18)_n$	Found	67.18	4.69	9.30	
		Corr[b]	68.72	4.58	9.52	

[a]Moisture Intake(%) = $(W − W_0)/W_0 \times 100$, W = weight of polymer sample after standing at room and W_0 = weight of polymer sample after dried in vacuum at $100\,°C$ for 10 h. [b]Corrected value for C, N and S = Found value $\times (100 + $ moisture intake$)/100$, and Corrected value for H = Found value $\times (100 − $ moisture intake$)/100$.

shows that **PA1** has higher inherent viscosity than **PA9**, but the inherent viscosities of **PA4** and **PA10** are comparable. The main advantage of the method **I** is that, in this procedure, the volatile and toxic solvents such as NMP, Py and extra material such as $CaCl_2$ are not required to be used and the reaction is eco-friendly and green. In addition high temperature polymerization reaction which was used in phosphorylation reaction (reflux condition) may slightly decompose the resulting polymers or even cause to break the chains, but this problem in **IL**s method is lower, since polymerization temperature in **IL**s is much lower ($110\,°C$). It is very interesting to mention that, in method **I**, the polymers were not obtained in the absence of either **IL**s or TPP, so the presence of both components are necessary for polyamidation reactions, and consequently **IL**s play as a catalyst as well as solvent for these reactions.

The structure of **PA**s was confirmed by elemental analysis, FT-IR and ^1H NMR spectroscopy techniques. Films were formed by evaporation of solvent from polymer solutions in *N,N*-dimethylformamide (DMF). The incorporation of chiral unit into polymer backbone was confirmed by measuring their specific rotation (Table III). The specific rotations of polymers based different diamines showed random changes. These observations are the result of different polymers' structure and inherent viscosity. All of the **PA**s show optical rotation and therefore are optically active.

Elemental analysis data of two typical **PA**s are listed in the Table IV. The chemical structures of these newly synthesized polymers were confirmed by the good agreement of the elemental analysis values with those of the calculated values.

Polymer Characterizations

FT-IR Study. The structures of these polymers were confirmed as **PA**s by means of FT-IR spectroscopy. The FT-IR spectral data of polymer **PA1-PA8** are listed in the experimental section. The FT-IR spectra of all polymers showed absorptions around $3300\,cm^{-1}$ (υN-H), $1765\,cm^{-1}$ (υC=O asymmetric, imide), $1710\,cm^{-1}$ (υC=O symmetric, imide), $1670\,cm^{-1}$ (υC=O, amide). All of these **PA**s exhibited absorption at $1380–1385\,cm^{-1}$ (υC-N, imide) and $715–725\,cm^{-1}$ that show the presence of the imide heterocycle in these polymers. The **PA1** showed characteristic absorptions at $1250, 1152\,cm^{-1}$ due to the sulfone moiety (SO_2 stretching).
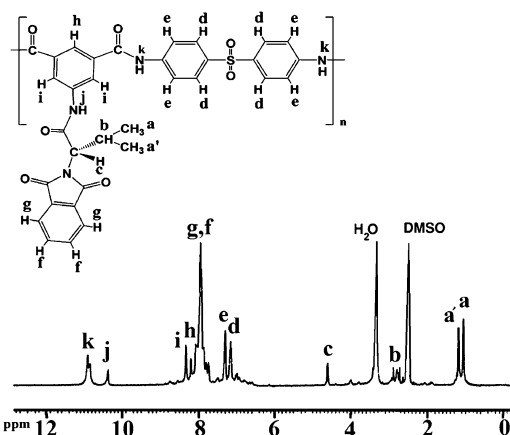

Figure 1. ^1H NMR (500 MHz) spectrum of **PA1** in DMSO-d_6 at rt.
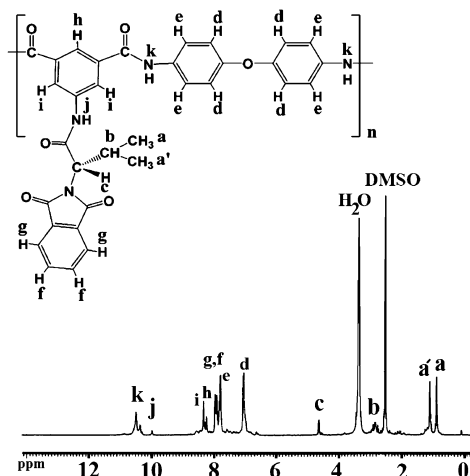

Figure 2. ^1H NMR (500 MHz) spectrum of **PA2** in DMSO-d_6 at rt.

^1H NMR Study. Figures 1 and 2 show the ^1H NMR (500 MHz) spectra of polymers **PA1**, **PA2**. In the ^1H NMR spectra of these two polymers, appearance of the two N-H protons of amide groups around 10.00–11.00 ppm indicate two different amide groups in the polymer's chain. The absorption of aromatic protons appeared at a range of 7.00–8.50 ppm. The proton of the chiral center appeared at 4.63 ppm. The peak of C-H isopropyl group of S-valine appeared at 2.80 ppm as a multiple peak. The absorption of the two diastrotopic CH_3 protons groups of S-valine appeared around 1.00 and 1.15 ppm.

Solubility of the PAs. One of the main objectives of this study was producing modified **PA**s with improved solubility. The incorporation of bulky side (pendent) groups into the monomer, reduces molecular packing, and restricts the formation of interchain hydrogen bonds, which are responsible of the **PA**s intractability. Because of flexible bulky groups in polymer's pendent, these polymers are expected to have higher solubility.

The solubility of **PA**s was tested at a concentration of 0.5 g/dL and at ambient temperature in various solvents. Almost all of the **PA**s are soluble in organic polar aprotic solvents such
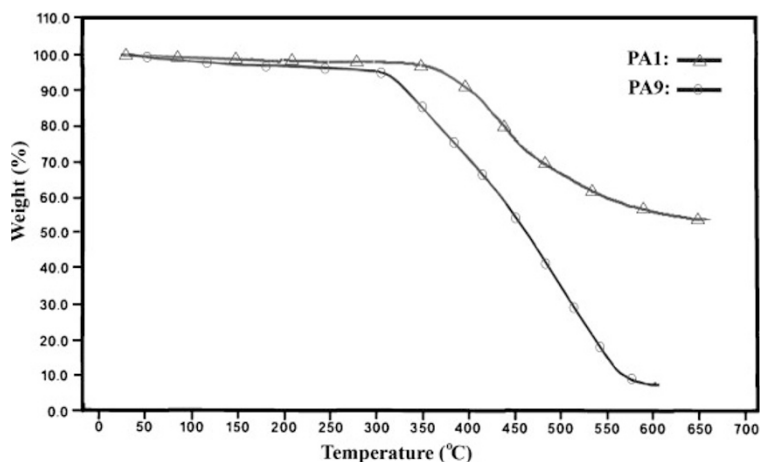
Figure 3. TGA thermograms of **PA1** and **PA9** under N$_2$ atmosphere and a heating rate of 10 °C/min.
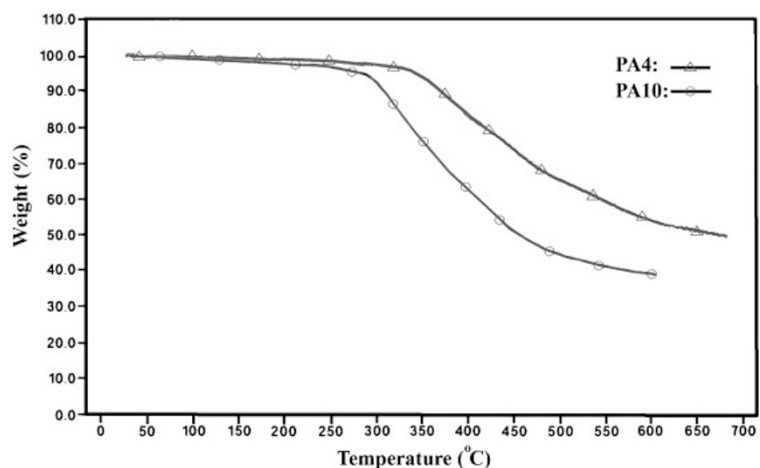

Figure 4. TGA thermograms of **PA4** and **PA10** under N$_2$ atmosphere and a heating rate of 10 °C/min.

as DMF, *N,N*-dimethylacetamide, dimethyl sulfoxide, NMP and polar protic solvent such as H$_2$SO$_4$ at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Thermal Properties. To get insight the thermal stability of this series of **PA**s, thermal properties of **PA1**, **PA4**, **PA9** and **PA10** were evaluated by means of TGA in a nitrogen atmosphere at a heating rate of 10 °C/min. The thermal stability of the polymers were assessed based on initial decomposition temperatures (T_i), temperature of 5% (T_5) and 10% (T_{10}) weight loss together with weight residue at 600 °C. Figure 3 shows the TGA thermograms of **PA1** and **PA9** and Figure 4 shows the TGA thermograms of **PA4** and **PA10** which indicate single step thermal degradation. The thermoanalysis data of these polymers are summarized in Table V. Comparison of thermograms of **PA1** with **PA9** and **PA4** with **PA10** demonstrate that the obtained polymers from **IL**s media method show higher T_i, T_5, T_{10} and char yields than **PA**s *via* phosphorylation reaction with the same diamines. So polymerizations in **IL**s, in addition of other advantages, give **PA**s with improved thermal stability.

Table V. Thermal properties of typical **PA**s

Polymer Code	T_i^a(°C)	T_5^b(°C)	T_{10}^c(°C)	Char Yield(%)^d
PA1	342	370	405	57
PA4	320	345	378	55
PA9	295	304	338	8
PA10	245	285	322	41

[a] Initial decomposition temperature. [b] Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 °C/min under N$_2$ atmosphere. [c] Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 °C/min under N$_2$ atmosphere. [d] Weight percent of the material left undecomposed after TGA at maximum temperature 600 °C in a N$_2$ atmosphere.

The TGA measurement of the polymers revealed that these polymers exhibited good thermal stability. **PA1** and **PA4** are stable up to 350 °C.

The introducing of heat resistant phthalimide groups as well as the presence of imide and amide group may counterbalance any loss of thermal stability that may cause by the existence of flexible aliphatic group.

CONCLUSIONS

In this work **IL**s in the presence of TPP were effectively used as a condensing agent for direct polyamidation reaction of chiral aromatic 5-(2-phthalimidyl-3-methylbutanoylamino)-isophthalic acid (**1**) with various diamines. Dicarboxylic acid **1** has a rigid phthalimide and flexible S-valine groups. In this method **IL**s act both as a media as well as catalyst for these polyamidation reactions. The main advantage of this method of polycondensation reaction is that, in this procedure there is no need of using volatile and toxic solvents and extra materials, consequently, would have less waste treatment after work-up. In addition, this method is one-pot reaction and It is not required to prepare diacid chloride and therefore, saves time and energy. Two typical **PA**s were also prepared *via* method **II**, using NMP/TPP/Py as a condensing agent. The results herein, show that **IL**s as a condensing media gave polymers with higher yields and inherent viscosity than phosphorylation reaction method. In addition, thermogravimetric analyses demonstrate that these **PA**s from **IL**s method have higher thermal stability in compare with **PA**s prepared by method **II**. The resulting **PA**s have S-valine in polymer chain and are optically active. The introduction of pendent bulky groups along the polymer backbone results in a less ordered polymer matrix hence disturbed the strong interchain and intrachain hydrogen bonding and inherent macromolecular rigidity, consequently increasing the solubility characteristics without affecting thermal properties to any great extent. These **PA**s could be considered as new processable high-performance polymeric materials. In addition because of the existence of amino acid in the polymer pendent group these polymers are expected to be biodegradable and therefore are classified under environmentally friendly polymers. Since the resulting polymers are optically active and have good thermal stability they have potential to be used as a chiral stationary phase in chromatography technique for the separation of chiral mixtures.

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