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ORIGINAL ARTICLE

Synthesis and characterization of novel, optically active polyamides derived from *S*-valine natural amino acid and bulky anthracenic side chain

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Abstract This is the first description of the application of molten tetrabutylammonium bromide (TBAB) in the presence of triphenyl phosphite (TPP) for the synthesis of novel polyamides (PAs). Monomer diacid, 5-[(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-methylbutanoylamino]isophthalic acid (**4**), having anthracenic and amino acid S-valine pendant group, was synthesized in four steps. Several novel, optically active PAs were prepared by the condensation of synthesized diacid monomer **4** with various aromatic diamines using two different techniques: a mixture of *N*-methyl-2-pyrrolidone (NMP)/TPP/pyridine/calcium chloride (method I) and combination of TPP with TBAB (method II). The main goal of the present paper was to prepare novel PAs in a green media by removal of toxic reagents. Therefore, TBAB/TPP was used as a novel, easy, safe and eco-friendly method for the preparation of aromatic PAs. This method is compared with the polymerization reaction under conventional solvent and in the case of TBAB as a new method, higher yields, inherent viscosities and thermally stable of PAs are gained. The resulting polymers showed good solubility in polar aprotic solvents such as dimethyl sulfoxide, NMP, *N,N*-dimethylacetamide and *N,N*-dimethylformamide. These polymers are characterized with respect to chemical structure and purity by means of specific rotation experiments, FT-IR, ^{1}H NMR spectroscopy techniques and elemental analysis. The obtained PAs exhibit good thermal stability up to 335°C for 10% weight loss in nitrogen atmosphere and glass transition temperatures fell in the rang of 177–185°C.

Keywords Green chemistry · Tetrabutylammonium bromide · Optically active polyamides · Phosphorylation polycondensation · *S*-Valine

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Introduction

Amino acids are extensively used for human and animal sustenance, as pharmaceuticals, cosmetics, agrochemicals and as other derivates for industrial applications. The α-amino acids are revealed to be a flexible building block for biodegradable and biocompatible materials. The amalgamation of α-amino acid into the backbone or side chain of different macromolecular structures results in multitalented polymers with attractive properties including optical activity, solubility in aqueous and highly polar solvents, electrical conductivity through ion movement and uses to templated polymers (Bourke and Kohn 2003; Bush and North 1998; Kovácsa et al. 2009). Recently, we have focused on amino acids as a key component of the optically active polymers, because it can lead to new biomaterials with a wide range of properties that can be easily modulated by varying the components in the building block of the polymer backbone during synthesis (Buruiana et al. 2007; Mallakpour and Taghavi 2009). Several optically active polymers have been used for enantiomeric high-performance liquid chromatography separation as the chiral stationary phase for resolution of racemic compounds (Kanazawa et al. 2006). A variety of optically active polymers have been prepared, which consist of asymmetric carbons, chiral hetero atoms

(Morisaki et al. 2007), chiral oxazoline substituent (Fu et al. 2007; Xi et al. 2009), one-handed helical structures (Kaneko et al. 2009) and amino acids (Mallakpour and Rafiee 2008, 2009; Mallakpour and Seyedjamali 2008; Mallakpour and Zadehnazari 2010).

One of the most promising areas of green technology is the abolition of solvents in chemical developments or the substitution of harmful solvents with environmentally friendly media. However, if a solvent is essential to a process, we should choose from alternative solvents that will have no or partial impact on healthiness and environment. The utilization of alternative solvents such as water, ionic liquids (ILs), supercritical media and their various mixtures is quickly increasing (Anastas 2007).

ILs are achieving universal academic and industrial attention as substitution for volatile organic solvents (VOS) in extraction, electrochemistry and chemical reactions (Fan et al. 2009). They are substances composed of cations and anions, which melt around 100°C or below as a random temperature limit (Hapiot and Lagrost 2008). The physicochemical properties of ILs can be proscribed by using dissimilar cations and anions (Singh et al. 2007). In addition to their potential for green chemistry, mostly owing to their low vapor pressure, reconsideration of organic synthesis in these new media lead to a shining series of credible examples of increases in chemical yields, chemo-, regio- and stereo-selectivity, as well as recycling of catalysts (Plaquevent et al. 2008; Yeom et al. 2007). Another aspect of ILs is their important role in controlling reactions as solvent or catalysts (Martins et al. 2008; Wasserscheid et al. 2001). Advantages of employing ILs as solvent are that they are nonvolatile and noncorrosive and have capability to dissolve a large variety of organic and inorganic substances including polymer materials in high concentrations (Ogoshi et al. 2008). These liquids have many of the properties of conventional organic solvents, such as outstanding solvation qualities and a broad liquid range. One factor that they do not share with classical organic solvents is their negligible vapor pressure and high thermal stability. Hence, room temperature ILs are regarded as novel, environmentally friendly solvents (Fan et al. 2009; Huddleston et al. 2001).

Regarding accessibility and low cost, tetraalkylammonium salts are the most beneficial ILs. Among these, tetrabutylammonium bromide (TBAB) is an inexpensive, readily accessible IL with intrinsic properties such as environmental viability, operational simplicity, greater selectivity, non-corrosive nature, mildness, water tolerance and ease of reusability (Chary et al. 2008; Khurana and kumar 2009; Selvakumar et al. 2002). TBAB is also an exceptional hydrate promoter, which can form semiclathrate hydrates with water molecules and small gas molecules and moderate the hydrate formation condition drastically (Li et al. 2010). As a consequence of these superior advantages using TBAB, it is therefore of interest to scrutinize the behavior of TBAB as solvent and catalyst in polymerization reactions (Mallakpour and Sepehri 2008; Mallakpour and Yousefian 2008).

Aromatic polyamides (PAs) are widely used in technical applications as high-performance polymers because of their combination of distinctive properties such as excellent mechanical strength, high temperature stability, low flammability and good chemical resistance (Ferreiro et al. 2008; Maji and Banerjee 2008; Nechifor 2009; Zulfiqar et al. 2008). However, high melting or glass transition temperatures (T_gs), which are caused by the formation of strong intermolecular hydrogen bonding and regular and rigid polymer backbone, result in their poor processability and restricted solubility in most organic solvents. To conquer these shortcomings, a variety of approaches have been applied to obtain thermally stable, high molecular weight and organic-soluble aromatic PAs (Ghaemy and Barghamadi 2008; Liou and Fang 2007; Nechifor 2009).

Among many useful and dependable esterification, amidation and anhydridization methods available, condensation reaction is a well-organized and suitable one, in which a condensing reagent is employed to activate a carboxylic acid followed by the attack of an anion derived from an alcohol, amine or carboxylic acid. To date, a variety of condensing agents for this reaction have been developed in literature (Yoneyama et al. 1999; Mallakpour and Dinari 2009; Mallakpour and Kolahdoozan 2008; Mallakpour and Seyedjamali 2009). However, some of them are moisture sensitive and highly expensive, which limits their extensive application and gives rise to the search for new types of condensing agents. TBAB is air and moisture-tolerant and also commercially available and cost effective.

Aiming to provide good properties to polymers such as optical activity and high solubility with retention of excellent thermal stability, in the present work, the preparation of new PAs from chiral diacid containing anthracenic and natural amino acid, S-valine and appropriate commercial aromatic diamines are reported. Since the usage of several chemicals may increase the cost and pollution of polymerization reactions, this study also demonstrates the ILs-assisted synthesis of aromatic PAs by combination of TBAB and triphenyl phosphite (TPP) as a novel condensing agent for the first time. This procedure is compared with conventional heating solution polymerization in traditional organic solvents. This process is safe and green, since VOSs such as *N*-methyl-2-pyrrolidone (NMP) and pyridine are eliminated.

Experimental

Materials

Commercial products were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel–deHaen AG (Seelze, Germany) and Merck Chemical Co. *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP) and triethylamine (TEA) were dried over barium oxide and then distilled under reduced pressure. Maleic anhydride was purified by recrystallization from dichloromethane (CH_2Cl_2), 4,4′-diaminodiphenylmethane (**5a**) by recrystallization from water and benzidine (**5d**) by recrystallization from ethanol. 4,4′-Diaminodiphenylether (**5c**), 1,4-phenylenediamine (**5e**) and 2,4-diaminotoluene (**5f**) were purified by sublimation. TBAB (mp = 100–103°C) was purchased from Merck Co. (Darmstadt, Germany) and was used without further purification. The other materials were used as obtained without additional purification.

Techniques

Proton nuclear magnetic resonance (^{1}H NMR, 500 MHz) spectra were recorded in dimethylsulfoxide (DMSO-d_6) solution using a Bruker (Germany) Avance 500 instrument, and also carbon nuclear magnetic resonance (^{13}C NMR, 125 MHz) spectrum was recorded on a Bruker (Germany) advance 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 potassium bromide (KBr) pellets. Vibration bands were reported as wave number (cm^{-1}). The band intensities were classified as weak (w), medium (m), strong (s) and broad (br). Inherent viscosities of polymer solution (0.5% w/v) in *N*,*N*-dimethylformamide (DMF) were determined at 25°C by a standard procedure using a Cannon–Fenske routine viscometer (Cannon, Mainz, Germany). The specific rotations were measured by a Jasco polarimeter (Japan). Thermogravimetric analysis (TGA) data for polymers were taken on V5.1A DuPont 2000 at a heating rate of 10°C/min under a N_2 atmosphere. Differential scanning calorimetric (DSC) data were recorded on a NETZSCH DSC 200 F3 instrument under a nitrogen atmosphere by the Research Institute of Polymer and Petrochemical of Iran. $\underline{T}_g$s were read at the middle of the transition in the heat capacity taken from the heating DSC traces. Elemental analyses were performed by Tarbit Moalem University, Tehran, Iran.

Monomer synthesis

Chiral dicarboxylic acid monomer, 5-[(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-methylbutanoylamino]-isophthalic acid (**4**) was prepared according to our previous work (Mallakpour and Mirkarimi 2010).

Polymer synthesis

Method I: conventional polycondensation using NMP/TPP/Py/$CaCl_2$ system

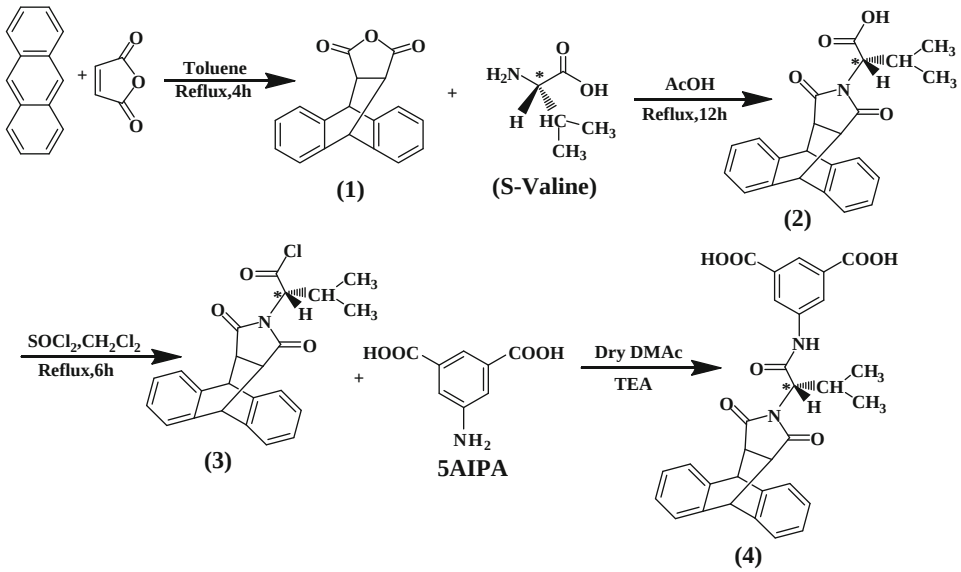
The polymers reported here were prepared by the phosphorylation polymerization method. An illustrative example is described in detail.

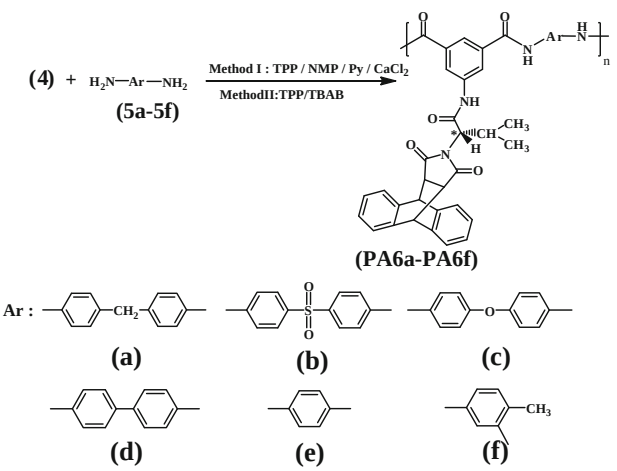
4,4′-Diaminodiphenylether (**5c**) (0.038 g, 1.90×10^{-4} mol) and diacid **4** (0.10 g, 1.90×10^{-4} mol) were dissolved in a mixture of NMP (0.30 mL, 3.12×10^{-3} mol), TPP (0.10 mL, 7.60×10^{-4} mol) and pyridine (Py) (0.10 mL, 1.24×10^{-3} mol) containing calcium chloride ($CaCl_2$) (0.05 g). The solution was heated with stirring at 130°C for a further 4 h under a gentle flow of nitrogen atmosphere to avoid humidity from air. In some cases, the solvent had to be added to dilute the solutions before precipitation because of their very high viscosity. After cooling, the obtained polymer solution was trickled into a large amount of methanol with stirring. The precipitated polymer was washed successively with methanol and hot water, collected by filtration and dried under vacuum at 100°C for 8 h. Yields over 85% were obtained in all cases. The following are representative examples: the elemental analyses calculated for **PA6a** $(C_{44}H_{36}N_4O_5)_n$ (700.78 g/mol): C 75.41%, H 5.18%, N 7.99%; found: C 72.72%, H 5.33%, N 8.03%. For **PA6b** $(C_{43}H_{34}N_4O_7S)_n$ (750.82 g/mol): C 68.79%, H 4.56%, N 7.46%; found: C 67.91%, H 4.45%, N 7.65%.

Method II: polyamidation using TPP/TBAB as a condensing agent

The **PA**s were prepared using TPP/TBAB as activator by the following general procedure. Into a 25-mL flask fitted with a mechanical stirrer, diacid **4** (0.10 g, 1.90×10^{-4} mol), diamine **5a** (0.038 g, 1.90×10^{-4} mol) and TBAB (1.40 g, 7.60×10^{-4} mol) were added. After the mixture was completely ground, TPP (0.10 mL, 7.60×10^{-4} mol) was added, and then the reaction temperature was raised to 120°C and held for 12 h. On cooling to room temperature, the viscous polymer solution was dropped into a large volume of methanol giving rise to 0.125 g (91%), a pearl-like polymer precipitate. The results clearly indicate that

Scheme 1 Synthesis of monomer **4**





Scheme 2 Polycondensation reactions of monomer **4** with different diamines

reactions can tolerate a wide range of differently substituted amines.

Results and discussion

Monomer synthesis

Scheme 1 outlines the synthetic route applied for the synthesis of the monomer **4**. Thus, *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride (**1**) was converted to imide acid (**2**) by reaction with S-valine. Compound **2** was converted to the acid chloride (**3**) by reaction with thionyl chloride and then treated with 5-aminoisophthalic acid (5AIPA) in dry *N,N*-dimethylacetamide to obtain 5-[(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido)-3-methylbutanoylamino]isophthalic acid (**4**). The resulting monomer was characterized with FT-IR, ^{1}H NMR and ^{13}C NMR techniques (Mallakpour and Mirkarimi 2010).

Polymer synthesis

Two different methods of polymerization were evaluated for the preparation of novel PAs, either in the presence of TPP/$CaCl_2$/Py/NMP or TBAB/TPP as condensing agents, by the reaction of new chiral diacid **4** and different aromatic diamines (Scheme 2).

Initially, in method I we used the direct polycondensation of aromatic diamines with corresponding dicarboxylic acid in the presence of TPP as a well-known convenient method to prepare aromatic PAs. Py is employed consistently to activate TPP through a complex formation (Aharoni et al. 1984; Yamazaki et al. 1975; Yang et al. 2000). Addition of $CaCl_2$ salt as a solubility enhancer increases both the solubility of the polymers in the reaction media and their viscosity by forming the complex $CaCl_2$.nPy too. The polycondensation reactions proceeded in homogeneous solutions and giving high yields. All the polymers precipitated in a tough form when the resulting polymer solutions were slowly poured with stirring into methanol. The resulting polymers showed white colors and exhibited inherent viscosities of 0.27–0.46 dL/g in DMF at 25°C (Table 1).

Because of the rapid emergence of ILs as green solvents and replacement of a volatile and toxic organic solvent in the polymerization with a nonvolatile solvent, we decided to synthesize PAs in IL media (Method II) and the results were then compared with a similar preparation using an organic solvent (Method I). The use of TBAB/TPP is a new

Table 1 Synthesis and some physical properties of **PA6aI–PA6fI** prepared using NMP/TPP/Py/$CaCl_2$ (method I)

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh} (dL g^{-1})[a]	$[\alpha]^{25,a}_{Na,589}$	$[\alpha]^{25,a}_{Hg}$	Color
5a	**PA6aI**	93	0.35	−31.36	−63.06	W
5b	**PA6bI**	96	0.32	−33.14	−78.18	W
5c	**PA6cI**	94	0.46	−34.62	−73.52	W
5d	**PA6dI**	97	0.42	−44.90	−80.68	LY
5e	**PA6eI**	85	0.31	−37.44	−83.04	W
5f	**PA6fI**	86	0.27	−36.74	−67.10	W

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

W white, *LY* light yellow

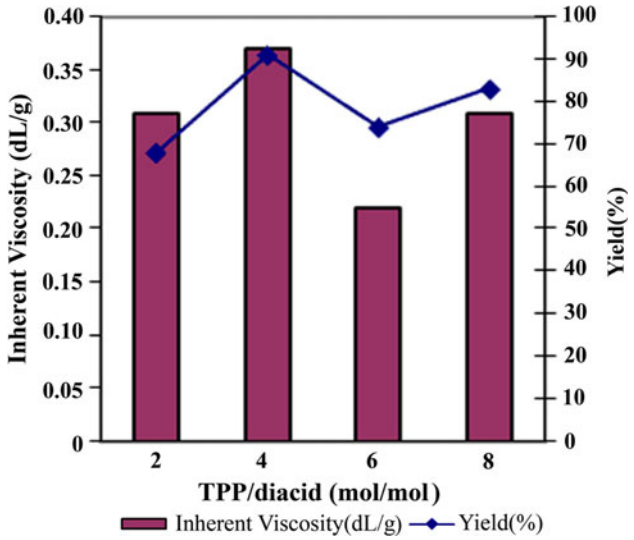


Fig. 1 Effect of ratio of TPP/diacid on the inherent viscosity and yield of PA6aII at 120°C for 12 h

method for the preparation of PAs. In this procedure, the TPP/TBAB system was used in place of the NMP, TPP, $CaCl_2$ and Py systems. At first, for understanding the role of TBAB and TPP in polymerization, two reactions were carried out in the presence of all materials except TBAB and in another trial reaction in the absence of TPP. No precipitations in methanol were obtained at the end of the reactions, revealing that both their presence is necessary in polycondensation reaction. The following explain these findings: TPP is necessary, since it can activate dicarboxylic acid via formation of a complex with it (Aharoni et al. 1984) and TBAB can make proper orientation for all the starting materials by electrostatic attraction as well as homogenizing the reaction mixture. The ratio between TPP and monomer was also optimized (Fig. 1). As can be seen in Fig. 1, a molar ratio of diacid over TPP equal to 1:4 is required to produce a polymer with high inherent viscosity

Table 2 Optimum condition for polyamidation using TPP/TBAB

TBAB/diacid (mol/mol)	TPP/diacid (mol/mol)	Reaction temperature (°C)	Reaction time (h)
4	4	120	12

Table 3 Synthesis and some physical properties of **PA6aII–PA6fII** prepared using TPP/TBAB (method II)

Diamine	Polymer					
	Polymer	Yield (%)	η_{inh} (dL g^{-1})[a]	$[\alpha]^{25,a}_{Na,589}$	$[\alpha]^{25,a}_{Hg}$	Color
5a	**PA6aII**	84	0.35	−32.83	−76.22	W
5b	**PA6bII**	89	0.30	−51.14	−119.36	W
5c	**PA6cII**	91	0.37	−12.82	−55.70	W
5d	**PA6dII**	87	0.38	−42.20	−52.56	Y
5e	**PA6eII**	72	0.56	−42.40	−53.22	W
5f	**PA6fII**	72	0.23	−20.11	−41.12	W

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

W white, *Y* yellow

and good yield. The optimum conditions for the preparation of PAs are listed in Table 2 and these conditions have been applied for the preparation of other PAs. The PAs were obtained in almost high yields and moderate inherent viscosities (Table 3). The use of TBAB as reaction media for this polymerization helps to avoid the necessity of high temperature and toxic solvents. It is worth mentioning that the reaction mixture was homogenous in molten TBAB as homogenizer throughout the polyamidation; while in method I, NMP was used as a solvent that was volatile and caused a change in the concentration of the reaction mixture during the polymerization process.

Elemental analysis was carried out on the two representative polymers and was found to be in good agreement with the expected values.

Polymer characterization

Key structural features of PAs were demonstrated by FT-IR based on their characteristic absorption bands. These PAs contained amidic groups, and so the amide I band consisting of the amidic C=O stretching and the amide II band consisting of the N–H bending appeared at 1,670 and 1,590 cm^{-1}, respectively, and the absorption band at 3,350 cm^{-1} corresponded to the stretching vibration of amidic N–H. The presence of bands at 1,775 (asymmetry C=O) and 1,705 cm^{-1} (symmetry C=O) in the FT-IR spectra confirmed the presence of the imide heterocyclic ring.

To get more structural information, ^{1}H NMR spectra of the polymers have been measured. The **PA6a** presented

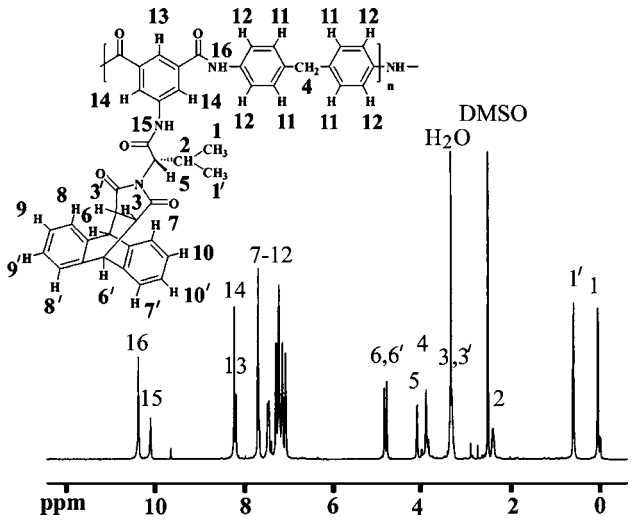


Fig. 2 ^{1}H NMR (500 MHz) spectrum of **PA6a** in DMSO-d_6 at RT

signals due to aromatic groups at 7.13–8.21 ppm and those due to N–H protons of amide group at 10.09 and 10.37 ppm. The multi-peak of methyne proton of *S*-valine residue appeared around 2.37–2.41 ppm (Fig. 2). Also, the resonances of diastereotopic methyl groups were observed at 0.04 and 0.59 ppm. The resonance peak as doublet at 4.10 ppm is assigned to the chiral center of the polymer. Resonance singlet peak that appeared at 3.90 ppm corresponded to the methylene group of diamine. The FT-IR and ^{1}H NMR data are shown in Table 4.

Solubility of PAs

The solubility characteristics of PAs were tested qualitatively (5 mg of polymer in 1 mL of solvent) using various solvents including DMF, DMSO, CH_2Cl_2, tetrahydrofuran, chloroform, acetone, methanol, ethanol and concentrated H_2SO_4. All of the PAs had good solubility in polar aprotic solvents, such as DMSO, DMF and NMP, and protic solvents, such as concentrated H_2SO_4, but they were not soluble in solvents such as CH_2Cl_2, tetrahydrofuran, chloroform, acetone, methanol and ethanol. The presence of bulky pendant moiety as well as amide and imide groups in the polymers side chain increased the solubility of the resulting polymers due to the lower rigidity.

Thermal properties

The thermal behavior data of the **PA6cI**, **PA6dI**, **PA6cII** and **PA6dII** were determined by DSC and TGA. TGA thermograms of **PA6dI** and **PA6dII** under N_2 atmosphere and a heating rate of 10°C/min are shown in Fig. 3. Table 5 shows the data for the thermal degradation of these PAs, including the temperature at which 5% (T_5 wt%) and 10% degradation occurs (T_{10} wt%), and the char yield at 800°C.

Table 4 ^{1}H NMR and FT-IR characterization of **PA6a–PA6f**

Polymer	Spectral data	
PA6a	FT-IR Peaks (cm^{-1}): 3,317 (w, br), 3,111 (w), 3,040 (w), 2,962 (w), 2,931 (w), 1,775 (w), 1,704 (s), 1,671 (m), 1,595 (m), 1,512 (s), 1,408 (m), 1,383 (m), 1,316 (w), 1,246 (w), 1,192 (w), 1,132 (w), 1,020 (w), 911 (w), 842 (w), 813 (w), 759 (w), 724 (w), 634 (w), 614 (w), 551 (w), 507 (w), 446 (w)	^{1}H NMR Peaks (ppm): δ = 0.04 (d, 3H, CH_3, J = 6.35 Hz), 0.59 (d, 3H CH_3, J = 6.30 Hz), 2.37–2.41 (m, 1H, CH), 3.29–3.37 (m, 2H, 2CH), 3.90 (s, 2H, CH_2), 4.10 (d, 1H, J = 7.69 Hz CH, chiral center), 4.78 (s, 1H, CH), 4.83 (s, 1H, CH), 7.06 (s, 2H, Ar–H), 7.13 (s, 2H, Ar–H), 7.22 (d, 4H, Ar–H, J = 8.15 Hz), 7.27 (s, 2H, Ar–H), 7.47 (d, 2H, Ar–H, J = 13.46 Hz), 7.68 (d, 4H, Ar–H, J = 8.13 Hz), 8.17 (s, 1H, Ar–H), 8.21 (s, 2H, Ar–H), 10.09 (s, NH amidic), 10.37 (s, NH amidic)
PA6b	FT-IR Peaks (cm^{-1}): 3,458 (m), 3,252 (m, br), 3,099 (m), 2,961 (m), 2,930 (m), 2,873 (w), 1,775 (w), 1,710 (s), 1,663 (s), 1,590 (s), 1,527 (s), 1,443 (s), 1,386 (s), 1,316 (s), 1,251 (s), 1,182 (s), 1,151 (s), 1,104 (s), 1,024 (w), 970(w), 839 (m), 759 (m), 689 (s), 554 (m)	^{1}H NMR Peaks (ppm): δ = 0.04 (d, 3H, CH_3, J = 6.61 Hz), 0.59 (d, 3H CH_3, J = 6.50 Hz), 2.35–2.41 (m, 1H, CH), 3.29–3.33 (m, 1H, CH), 3.34–3.36 (m, 1H, CH), 4.10 (d, 1H, J = 7.84 Hz, CH, chiral center), 4.78 (s, 1H, CH), 4.83 (s, 1H, CH), 7.04 (s, 2H, Ar–H), 7.16 (s, 2H, Ar–H), 7.29 (s, 2H, Ar–H), 7.45 (s, 2H, J = 14.73 Hz Ar–H), 7.96 (d, 4H, J = 8.48 Hz, Ar–H), 8.01 (d, 4H, J = 8.66 Hz, Ar–H), 8.21 (s, 1H, Ar–H), 8.26 (s, 2H, Ar–H), 10.14 (s, NH amidic), 10.83 (s, NH amidic) ppm
PA6c	FT-IR Peaks (cm^{-1}): 3,318 (w, br), 3,068 (w), 2,962 (w), 2,932 (w), 1,775 (w), 1,705 (s), 1,598 (s), 1,497 (s), 1,382 (m), 1,343 (m), 1,225 (s), 1,132 (w), 1,037 (w), 1,012 (w), 970 (w), 832 (w), 759 (w), 614 (w), 550 (w), 430 (w)	
PA6d	FT-IR Peaks (cm^{-1}): 3,325 (w, br), 2,961 (w), 1,775 (w), 1,704 (s), 1,593 (s), 1,500 (s), 1,465 (m),1,383 (m), 1,318 (m), 1,240 (m), 1,192 (m), 1,164 (w), 1,132 (w), 1,003 (w), 896 (w), 819 (w), 759 (w), 614 (w), 559 (w)	
PA6e	FT-IR Peaks (cm^{-1}): 3,402 (m, br), 2,962 (m), 1,775 (w), 1,705 (s), 1,600 (m), 1,513 (s), 1,457 (m), 1,383 (s), 1,192 (s), 1,132 (w), 953 (w), 838 (w), 759 (w), 615 (w), 551 (w)	
PA6f	FT-IR Peaks (cm^{-1}): 3,328 (w, br), 2,962 (w), 1,775 (w), 1,705 (s), 1,597 (m), 1,526 (s), 1,457 (m), 1,383 (m), 1,245 (w), 1,193 (w), 1,164 (w), 1,133 (w), 891 (w), 759 (w), 614 (w), 551 (w)	

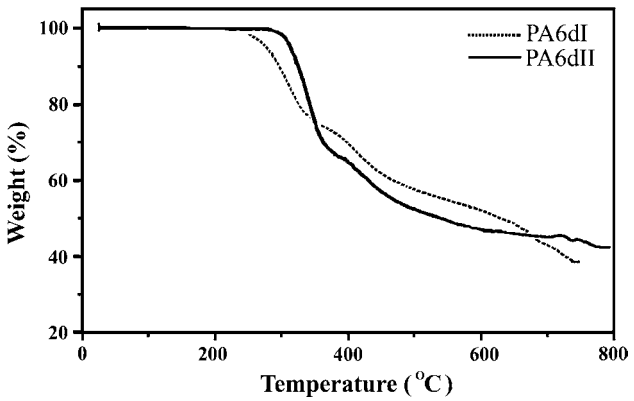


Fig. 3 TGA thermograms of (*dashed line*) **PA6dI** and (*solid line*) **PA6dII** under N_2 atmosphere and a heating rate of 10°C/min

Table 5 Thermal properties of **PA6cI, PA6dI, PA6cII** and **PA6dII**

Polymer	Decomposition temperature (°C)		Char yield (%)[c]	T_g^d (°C)	LOI[e]
	T_5^a	T_{10}^b			
PA6cI	210	230	25	177	28
PA6dI	265	290	38	185	33
PA6cII	315	335	38	–	33
PA6dII	310	320	43	–	35

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

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

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

[d] Glass transition temperature was recorded at a heating rate of 20°C/min in a nitrogen atmosphere

[e] Limiting oxygen index (LOI) evaluating char yield at 800°C

TGA curves of these PAs exhibited good thermal stability with significant weight loss up to 335°C in a nitrogen atmosphere. For the two fully aromatic **PA6cI** and **PA6dI**, the char yields are 25 and 38% at 800°C that are slightly lower than **PA6cII** and **PA6dII**. T_g varies widely with the structures, molecular weights and other thermodynamic parameters of the polymers, such as intermolecular force and chain flexibility. The T_g values of the **PA6cI** and **PA6dI** were observed in the range of 177–185°C by DSC and generally increased with decreasing conformational flexibility of the diamine used, because the flexible –O– groups in the backbone of the polymers decrease the rotational barrier than those with aromatic rings. Consequently, the motions in the main chain were easier when the temperature was increased (Wang and Shi 2006). In Table 5, T_5, T_{10}, char yield and limiting oxygen index (LOI) (Van Krevelen and Hoftyzer 1976) of these PAs prepared by both methods are compared.

$$\mathrm{LOI} = 17.5 + 0.4\,\mathrm{CR}$$

where CR = char yield.

PAs synthesized in TBAB media are more thermally stable than those prepared in the conventional solvent, which may be explained by the lower temperature of the polymerization reaction in TBAB. As a result, polymer chains with lower decomposition under mild IL conditions are formed, which may provide polymer chains with uniform structures.

Conclusions

Polymerization of novel, optically active diacid monomer bearing a voluminous anthracenic and S-valine-based optically active pendant group with aromatic diamines by two different methods yielded the corresponding PAs. In this study, for the first time, we studied the use of TBAB as an IL to remove harmful materials from the reaction. The present methodology offers several advantages such as safe, green, nature friendly, cost effective and one-pot protocol for the synthesis of organosoluble PAs. The reported procedure for the polycondensation of diacid monomer **4** with various diamines under green conditions demonstrated the potential of molten TBAB, a readily available IL, for further applications. Such new kind of media alternative to the traditionally used organic solvents will doubtlessly continue, gradually be adopted by the chemical industry and contribute to the efficiency of the latter. The combination of optically active amino acid, imide heterocycle and bulky anthracenic groups along the polymer side chains endow the current polymers with some special characteristics, such as optical activity, good solubility in organic aprotic solvents and good thermal resistance. Since these optically active polymers have amino acid in their polymer architecture, they are expected to be biodegradable and therefore classified as environmentally friendly. Also, they have the potential to be used as optically active packing materials in column chromatography for the resolution of racemic mixtures. Moreover, the solubility of these classes of PAs is better than those of PAs obtained from our previously reported works (Mallakpour and Kolahdoozan 2008; Mallakpour and Rafiee 2008). Incorporation of the bulky anthracenic group into the side chain caused difficulty in unlocking the polymer chains from each other and solvent molecules could penetrate to solubilize the polymer chain. Therefore, solubility of PAs increased. TGA analyses have shown that the polymers

prepared with IL have better thermal stability compared to those prepared with conventional solvents.

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