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ORIGINAL ARTICLE

Synthesis of soluble poly(amide-ether-imide-urea)s bearing amino acid moieties in the main chain under green media (ionic liquid)

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Abstract In this study, an optically active diamine, *N,N′*-(pyromellitoyl)-*bis*{*N*-[4(4-aminophenoxy)phenyl]-2-(4-methyl)pentanamide} (**1**) containing amino acid L-leucine was prepared in three steps. The step-growth polymerization of this chiral diamine with several diisocyanates in room temperature ionic liquid (IL), 1,3-dipropylimidazolium bromide as an environmentally friendly solvent and in a volatile organic solvent, is investigated. The polymerization yields and inherent viscosities of the resulting poly(amide-ether-imide-urea)s are compared in both solvents. The results show that the IL to be the superior polymerization media. All of the obtained polymers exhibited good solubility in some polar aprotic organic solvents such as *N,N*-dimethyacetamide, *N,N*-dimethyformamide, dimethyl sulfoxide while thermal stability was not disturbed based on thermogravimetric analysis and differential scanning calorimetry experiments. X-ray diffraction analysis of polymers shows that they are amorphous. The observation of optical rotation confirms the optical activity of prepared polymers.

Keywords Chiral diamine · L-Leucine · Polyurea · Optically active polymers · Imidazolium ionic liquid · Green chemistry

Introduction

The synthesis of artificial chiral polymers and oligomers has recently been attracting considerable attention due to their various advanced functions. The application of optically active polymers in chiral recognition, liquid crystals, asymmetric catalysis, and linear optical devices has made them one of the most motivating material categories (Zhai et al. 2005; Zhong et al. 2005; Gasparrini et al. 2005; Lee et al. 2003; Lindholm and Forstedt 2005; Ikeuchi et al. 2009). Furthermore, the chemistry of polyureas (PU)s may potentially be in the interesting correlation with optical activity, since they are known as excellent candidates for the microencapsulation purposes (Ley et al. 2003) and their chiral structure may lead to the asymmetric recognition behavior.

PUs are commercialized since 1989 and may simply be prepared via the polymerization of diamines with diisocyanates (Li and Chen 2008; Jewrajka et al. 2009; Tamami et al. 2005). The adoptable mechanical properties of PUs caused by the tailoring of hard and/or soft moieties in the structures, in conjunction with excellent hydrolysis resistances, make them appropriate for plenty of various applications such as coating, roofs, bridges, etc. (Roland and Casalini 2007; Roland et al. 2007; Sarva et al. 2007; Ni et al. 2000; Du et al. 2001). In addition, the application of PUs as piezoelectric and ferroelectric polymers, second-order optical nonlinear polymers, biodegradable polymers, and polymer microcapsules has already been reported (Du et al. 2001; Sakai et al. 2008; Hong and Park 2000; Tao et al. 1995). On the other hand, chiral PUs an advanced category of macromolecules are useful precursors for preparation of polymeric chiral stationary phases in HPLC techniques (Huang et al. 2007).

However, the use of PUs is associated with some serious drawbacks as a consequence of their limited solubility and

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high glass transition or softening temperatures which have been attributed to the high polarity of urea functions and the construction of strong interchain hydrogen bond lattice (Sarva et al. 2007; Huang et al. 2007; Kurita et al. 1994; Sendijarevic et al. 2004; Yang et al. 1998). Generally, it has been accepted that the utilization of aromatic low molecular weight diamines make the resulting PUs highly stiff and poorly soluble in organic solvents, while the existence of further fractions with superior flexibilities, such as ether functionalities and aliphatic moieties cause major improvements in both rigidity and solubility behaviors (Sakai et al. 2008; Yang et al. 1998; Luo et al. 1996). Although the aforementioned soft functional groups may diminish the thermal resistance of PUs, it can be restored by the incorporation of further intrinsic thermo-resistance functions, such as amide or imide groups in the polymer backbone.

Many chemical processes involve volatile organic solvents (VOS)s that evaporate into the atmosphere with detrimental effects on human health and the environment. Obviously, considerable efforts have focused on the reduction and often elimination of VOSs as major environmental pollutants (Long and Hunt 1998). Ionic liquids (IL)s exhibit great promise as solvents for polymerization of a wide range of monomers. Their low volatility, high thermal and chemical stability, and potential to be recycled make ILs attractive as an environmentally friendly alternative to organic solvents (e.g., *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, toluene, xylene, dichloromethane) utilized in many industrial polymerization processes (Johnston-Hall et al. 2009; Andrzejewska et al. 2009; Kubisa 2009; Mallakpour and Kolahdoozan 2008).

Following the extensive investigation of the synthesis and characterization of the new optically active macromolecules (Mallakpour and Seyedjamali 2008; Mallakpour and Rafiee 2008, 2009; Mallakpour and Zadehnazari 2010; Mallakpour and Khani 2010; Mallakpour and Shamoahammadi 2004), in this article, we wish to report the synthesis and characterization of a series of optically active, poly(amide-ether-imide-urea)s, (**PAEIU**)s, with modified solubility and thermal properties via the **IL**-mediated polymerization of high molecular weight chiral diamine containing natural amino acid, L-leucine moieties in the polymer backbone with several diisocyanates.

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI, USA), Riedel–deHaen AG (Seelze, Germany) and Merck Chemical Co. Pyromellitic dianhydride (benzene-1,2,4,5-teracarboxilic dianhydride) was recrystallized from acetic anhydride and then dried in a vacuum oven at 125°C overnight. *N,N*-Dimethylacetamide (DMAc) was dried over barium oxide, followed by fractional distillation. 4,4′-Oxydianiline (ODA) was purified by sublimation and then dried in a vacuum oven at 125°C overnight. 2,4-Tolylene diisocyanate (TDI) (**a**) (Merck), hexamethylene diisocyanate (HDI) (**b**) (Merck), 4,4′-methylene-*bis*-(4-phenylisocyanate) (MDI) (Aldrich) (**c**) and isophorone diisocyanate (IPDI) (**d**) (Fluka) were employed as received. IL, 1,3-dipropylimidazolium bromide ($[1,3\text{-(pr)}_2\text{im}]\text{Br}$) was prepared according to the literature procedure (Lindholm and Forstedt 2005).

Instruments

Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz and ^{13}C-NMR, 125 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), and multiplet (m). FT-IR spectra were recorded on 400D IR spectrophotometer (Japan). 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 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). Quantitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. Thermogravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a heating rate of 20°C min^{-1} by the Iranian Polymer and Petrochemical Institute of Iran (IPPI). Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument at a heating rate of 20°C min^{-1} in nitrogen atmosphere by IPPI. Glass-transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. The X-ray diffraction (XRD) patterns were recorded by employing a Philips X'PERT MPD diffractometer (Cu Kα radiation: $\lambda = 0.154056$ nm at 40 kV and 30 mA) over the 2θ range of 20–80° at a scan rate of 0.05° min^{-1}.

Monomer synthesis

N,N′-(Pyromellitoyl)-*bis*{*N*-[4(4-aminophenoxy)phenyl]-2-(4-methyl)pentanamide} (**1**) was synthesized according to previous work (Mallakpour and Seyedjamali 2010).

Polymerization of diamine **1** with MDI in IL

A 25 mL three neck round bottomed flask was charged with 0.300 g (3.71 × 10^{-4} mol) of diamine **1** and 0.15 g of [1,3-(pr)$_2$im]Br, the nitrogen atmosphere was equipped, 0.093 g (3.71 × 10^{-4} mol) of MDI was added and the temperature was slowly raised up to 80°C. The mixture was stirred mechanically for 2 h. After that time, the viscose solution was poured into the 30 mL of methanol, polymer precipitated rapidly as a white solid, filtered-off to yield 0.373 g (95%) of **PAIEU3c**.

PAIEU3c: Off-white solid; FT-IR (KBr): 3,477 (m), 3,374 (s), 2,967 (m), 2,933 (m), 2,875 (w), 1,774 (m), 1,723 (s), 1,626 (m), 1,593 (s), 1,525 (m), 1,503 (m), 1,383 (m), 1,349 (m), 1,312 (m), 1,148 (s), 1,105 (s), 1,075 (m) 553 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.87–0.88 (d, 3H, CH$_3$, $J = 6.7$ Hz), 0.89–0.90 (d, 3H, CH$_3$, $J = 6.7$ Hz), 1.52 (m, 1H, CH), 1.87–1.92 (m, 1H, CH$_2$), 2.16–2.21 (m, 1H, CH$_2$), 3.81 (s, 1H, CH$_2$), 4.85–4.88 (dd, 1H, CH chiral, $J_1 = 11.1$, $J_2 = 3.91$), 6.72 (d, 1H, Ar–H, $J = 4.8$), 6.84 (d, 1H, Ar–H, $J = 4.6$), 6.91–6.93 (d, 2H, Ar–H, $J = 8.3$), 7.10–7.12 (d, 2H, Ar–H, $J = 7.7$), 7.35–7.36 (d, 2H, Ar–H, $J = 7.67$), 7.42–7.43 (d, 2H, Ar–H, $J = 8.52$), 8.33 (s, 1H, Ar–H), 8.50–8.54 (d, 1H, Ar–H, $J = 4.6$) 8.50–8.53 (s, broad, 2H, NH), 8.78–8.83 (s, broad, 2H, NH), 8.90 (s, 2H, NH) ppm. Elemental analysis calculated for $C_{61}H_{54}N_8O_{10}$ (1,059.13 g mol^{-1}): C, 69.18%; H, 5.14%; N, 10.58%. Found: C, 68.61%; H, 5.92%; N, 10.74%.

The other PAEIUs derived from different diisocyanates such as TDI, HDI and IPDI were prepared in this **IL** according to the procedure described above.

PAEIU3a: off-white solid; FT-IR (KBr): 3,275 (br), 2,800–3,000 (br), 1,773 (w), 1,695 (m), 1,600 (m), 1,537 (s), 1,448 (m), 1,223 (m) cm^{-1}.

PAEIU3b: off-white solid; FT-IR (KBr): 3,353 (br), 2,932 (m), 2,856 (m), 1,791 (m), 1,745 (s), 1,613 (m), 1,524 (s), 1,421 (m), 1,357 (m), 1,253 (m), 1,187 (m) cm^{-1}.

PAEIU3d: off-white solid; FT-IR (KBr): 3,364 (br), 2,954 (s), 2,925 (s), 2,900 (m), 1,775 (m), 1,736 (m), 1,639 (s), 1,558 (s), 1,462 (m), 1,239 (m), 747 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.86–0.93 (m, 18H, CH$_3$), 1.05 (s, 3H, CH$_3$), 1.49–1.52 (m, 2H, CH), 1.87–1.94 (m, 4H, CH$_2$), 2.15–2.21 (m, 4H, CH$_2$), 2.70 (s, 2H, CH$_2$), 3.29–3.32 (t, 2H, CH$_2$, $J = 7.08$), 3.78–3.81 (m, 1H, CH) 4.85–4.88 (dd, 2H, CH chiral, $J_1 = 11.30$, $J_2 = 4.41$), 6.56–6.58 (d, 2H, Ar–H, $J = 7.668$), 6.70–6.72 (d, 4H, Ar–H, $J = 6.77$), 6.75–6.78 (d, 4H, Ar–H, $J = 6.80$), 7.27–7.31 (d, 4H, Ar–H, $J = 6.77$) 7.33–7.36 (d, 4H, Ar–H, $J = 6.97$), 8.32 (s, 2H, NH), 8.43 (s, 2H, NH), 8.54 (s, 2H, NH) ppm. Elemental analysis calculated for $C_{58}H_{62}N_8O_{10}$ (1,031.16 g mol^{-1}): C, 67.56%; H, 6.06%; N, 10.87%. Found: C, 66.80%; H, 5.25%; N, 10.67%.

Polymerization of diamine **1** with MDI in organic solvent media

PAIEU3a–PAIEU3c were synthesized according to previous work (Mallakpour and Seyedjamali 2010).

Results and discussion

Monomer synthesis

Optically active diamine **1** was prepared according to the synthesis sequence illustrated in Scheme 1. Dehydration of pyromellitic dianhydride and excess L-leucine in acetic acid reflux led to the preparation of corresponding imide acid. In continuation, imide acid was converted to its acid chloride derivative using thionyl chloride and then was dissolved in dry THF and added very slowly to the slightly excess amount of ODA to avoid polymerization as an unwanted side reaction. Resulting chiral diamine was characterized by means of FT-IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis techniques.

Polymer synthesis in IL media

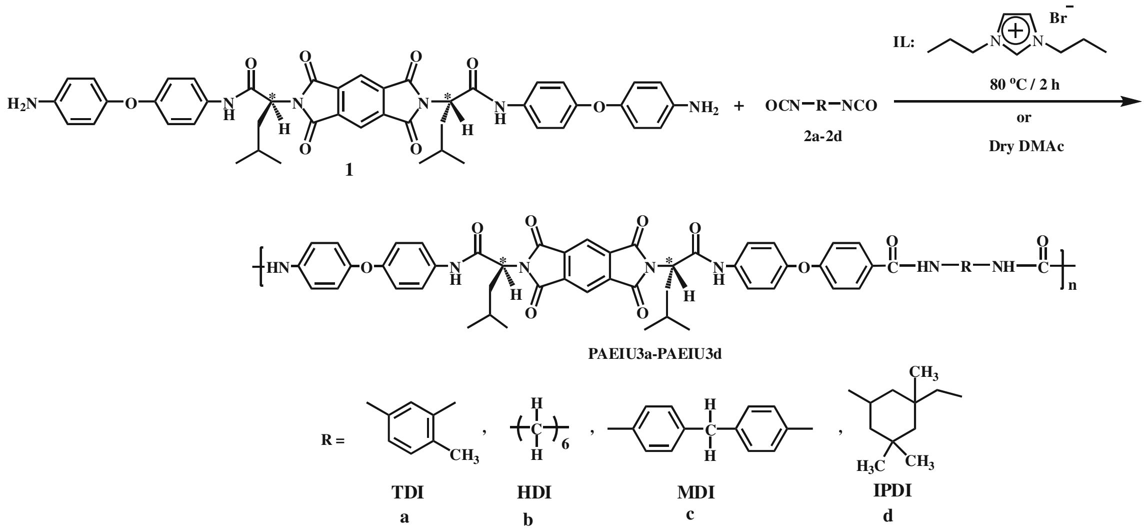
Equal molar ratios of diamine **1** and different diisocyanates (**2a–2d**) were polymerized in **IL** medium as an advanced alternate for VOS (Scheme 1). The reaction time and temperature were optimized separately and the optimum conditions were preferred by means of the superior reaction yields and the viscosity of resulted macromolecules.

The use of [1,3-(pr)$_2$im]Br as the best **IL** was base on the optimization data in our previous work (Mallakpour and Kolahdoozan 2008). Synthesis and some physical properties of obtained polymers are collected in Table 1. FT-IR spectrum of **PAEIU3c** and ^{1}H-NMR spectrum of **PAEIU3d** as typical examples are illustrated in Figs. 1 and 2.

According to the optical activity of synthesized **PAEIUs**, they may be potentially suitable materials for column packing in HPLC techniques as chiral stationary phases. The magnitude and the sign of specific rotation of **PAEIUs** were not predictable since optical rotation is extremely reliant on the chemical structure and a tiny variance in the configuration as well as molecular weight of polymers has significant random consequence on the optical rotation.

Polymer synthesis in organic solvent media

In order to make a reasonable comparison, the polycondensation reactions were compared with those progressed in organic solvent which have been reported recently (Mallakpour and Seyedjamali 2010). According to the



Scheme 1 Polymerization reactions of monomer **1** with several aromatic and aliphatic diisocyanates in **IL** or organic solvent

Table 1 Synthesis and some physical properties of polymers prepared in IL

Entry	Polymer	Diisocyanate	Yield (%)	η_{inh} (dL g^{-1})^{a}	$[\alpha]_{Na,589}^{25,a}$
1	**PAEIU3a**	TDI	94	0.53	−28.4
2	**PAEIU3b**	HDI	92	0.49	−23.2
3	**PAEIU3c**	MDI	95	0.55	−39.5
4	**PAEIU3d**	IPDI	91	0.44	−29.1

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

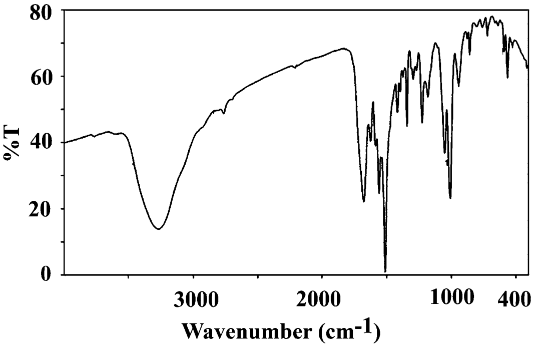


Fig. 1 FT-IR spectrum of **PAEIU3c** as a typical example

referenced publication, the yields and inherent viscosities of resulting macromolecules ranged between 85–91% and 0.37–0.46 dL g^{-1}, respectively.

Induction of chirality into the polymer backbone was proved by the specific rotation measurement. A comparison between the data presented in Table 1 and previously reported data, confirms that polycondensation of chiral diamine **1** with various diisocyanates proceeds more effectively in **IL** media, because of not only the higher reaction yields and the viscosity of resulted polymers but also due to the cleaner reaction conditions and concurrent green chemistry issues. Morphology of the resulting macromolecules via both methods has been evaluated by means of XRD technique and confirmed to have amorphous structures.

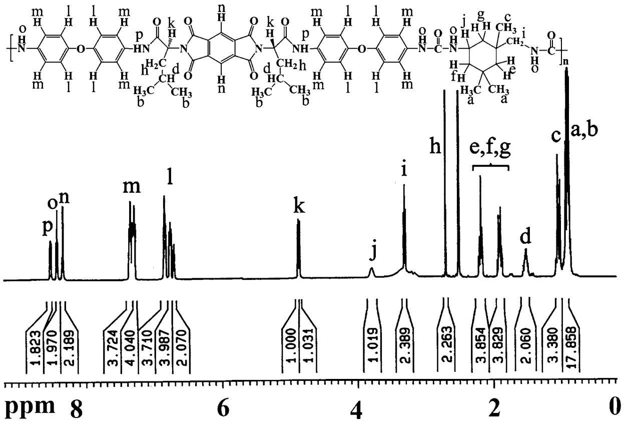


Fig. 2 ^{1}H-NMR spectrum of **PAEIU3d**

Solubility behaviors

Solubility of **PAEIU3**s was examined in common organic solvents quantitatively and it was confirmed that all of them are soluble in solvents such as DMF, NMP, DMAc, or dimethyl sulfoxide at room temperature, and found insoluble in acetone, cyclohexane, chloroform, and methanol. The isobutyl side group in the structure of monomer may be the cause of observed good solubility as they can depress the strong H-bond interaction, which is the common origin of limited PUs solubility. On the other hand, the incorporation of ether moieties along the polymer chains increases the flexibility of polymer backbone and facilitates their solubility as well as processability.

Thermal properties

Generally, the solubility enhancement agents are associated with reduction of the thermal stability of final products as an unwanted side effect. In the present study, this problem has been removed due to the existence of additional imide and amide functional groups which are known by their hardness and tolerance toward thermal shocks. It may be concluded that elastic soft divisions have regulated the rigidity of each amide, imide and urea functional groups, thus improving the solubility behaviors, and conversely such hard groups have improved the thermal stability of polymers.

The TGA and DSC thermograms of **PAEIU3c** and **PAEIU3d** as two examples of aromatic and aliphatic enriched polymers were examined at a heating rate of 20°C min^{-1} under a nitrogen atmosphere. For **PAEIU3c**, the 10% weight loss temperature was 325°C and about 37% of weight remained at 600°C (Char Yield). These quantities for **PAEIU3d**, were 175°C and 5%, respectively, which shows considerable differences in thermal behaviors between polymers based on aromatic and aliphatic diisocyanate. Examined polymers showed glass transition temperatures (T_g)s to be about 183°C for **PAEIU3**c and about 154°C for **PAEIU3**d based on DSC thermograms.

Conclusions

The synthesis and characterization of a chiral diamine containing naturally occurring amino acid (L-leucine) has been reported. The polymerization of this chiral diamine with several aromatic and aliphatic diisocyanates was performed via an **IL**-mediated polycondensation as a green process and the results have been compared with organic solvent analogous. Accordingly, the **IL** showed to be a superior polymerization media with higher reaction yields, elevated inherent viscosity of obtained polymer and the adjustment with environmental and biological concerns. The obtained **PAEIU**s have shown interesting characteristics such as optical activity, organosolubility and thermal stability, especially in the case of aromatic issues.

The existence of both soft and hard fractions together, increased the flexibility of polymer chain enough to be soluble in polar organic solvents while thermal resistance was not disturbed. Alternatively, the isobutyl side groups (in the structure of L-leucine) increased the free inter-chain volumes and the diffusion of solvent between the polymer chains as well as induction of asymmetric nature. The high molecular weight of prepared diamine monomer is contrasted to the fact that: *low molecular weight aromatic diamine monomers provide rigid PUs* (Long and Hunt 1998). The application of synthesized polymers of microencapsulation purposes may be the subject of further investigations.

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