Amino Acids (2011) 40:533–542
DOI 10.1007/s00726-010-0667-3

ORIGINAL ARTICLE

Ionic liquid catalyzed synthesis and characterization of heterocyclic and optically active poly (amide-imide)s incorporating L-amino acids

Saeed Zahmatkesh

Received: 16 May 2010 / Accepted: 16 June 2010 / Published online: 7 July 2010

Abstract *N*,*N*′-Pyromelliticdiimido-di-L-alanine (**1**), *N*,*N*′-Pyromelliticdiimido-di-L-phenylalanine (**2**), and *N*,*N*′-Pyromelliticdiimido-di-L-leucine (**3**) were prepared from the reaction of Pyromellitic dianhydride with corresponding L-amino acids in a mixture of glacial acetic acid and pyridine solution (3/2 ratio) under refluxing conditions. A series of poly (amide-imide)s containing L-amino acids were prepared from the synthesized dicarboxylic acids with two synthetic aromatic diamines in an ionic liquid (**IL**) as a green, safe and eco-friendly medium and also reactions catalysis agent. Evaluation of data shows that **IL** is the better polyamidation medium than the reported method and the catalysis stand on the higher inherent viscosities of the obtained **PAI**s and the rate of polymerizations beyond the greener reaction conditions and deletion of some essential reagents in conventional manners. Characterization were performs by means of IR, MS and ^{1}H NMR spectroscopy, elemental analysis, specific rotation, thermogravimetric analysis and differential scanning calorimetric techniques. Molecular weights of the obtained polymers were evaluated viscometrically, and the measured inherent viscosities were in the range 0.43–0.85 dL/g. These polymers were readily soluble in many organic solvents. These polymers still kept good thermal stability with glass transition temperatures in the range of 94–154°C, and the decomposition temperature under the nitrogen atmosphere for 10% weight-loss temperatures in excess of 308°C.

Keywords Biodegradable · Amino acid · Green chemistry · Poly (amide-imide) · Ionic liquid

S. Zahmatkesh (✉)
Department of Science, Payame Noor University (PNU),
Tehran, Iran
e-mail: zahmatkesh1355@yahoo.com

Introduction

The synthesis and application of optically active polymers are the newly considerable topics, which have been paid more attention recently (Zahmatkesh and Hajipour 2009). Most of the natural polymers are optically active and have special chemical activities, such as catalytic properties that exist in genes, proteins, and enzymes. Some other applications are construction of chiral media for asymmetric synthesis, chiral stationary phases for resolution of enantiomers in chromatographic techniques (Akelah and Sherrington 1981), chiral liquid crystals in ferroelectrics and nonlinear optical devices (Wulff 1989). These synthetic polymers based on optically pure aminoacids can induce crystallinity with their ability to form higher ordered structures that exhibit enhanced solubility characteristics. These properties have caused them to be good candidate for drug delivery systems, biomimetic systems, biodegradable macromolecules, biomaterials, and also as chiral purification media (Mallakpour et al. 1998). So, more considerations to improve different synthetic procedures of optically active polymers exist. Recently, we have synthesized optically active polymers by different methods (Zahmatkesh and Hajipour 2010).

Polycondensation reactions to prepare polyamides are traditionally performed in aprotic polar high-boiling-point organic solvents such as *N*-methyl-2-pyrrolidone (NMP) (Caouthat et al. 2007), *N*,*N*-dimethyacetamide (DMAc) (Zulfiqar et al. 2008), *N*,*N*-dimethyformamide (DMF) (Mallakpour and Yousefian 2008), which are generally cause several ecological disadvantages and over cost on synthetic methods. In this regard, replacing or removing hazardous materials is one of the recent environmental issues (Talawar et al. 2009). Recently, ionic liquids (ILs) have been of interest in many fields of chemistry because of their exclusive properties such as solubility, nonvolatility, high reactivity, low flammability, and possibility of recycling, etc. (Shi et al. 2007). Nonvolatile nature and stability at high temperature make the ILs excellent candidates for the use as polycondensation reactions medium (Shaplov et al. 2008). Furthermore, it has been shown that ILs have catalytic effect on the polymerization progresses, resulting the removal of some of the additives which are essential in conventional polymerization methods (Mallakpour and Kowsari 2006).

In the present article, the synthesized dicarboxylic acids containing L-amino acids (Hajipour et al. 2007) were directly polycondensed with the two synthetic aromatic diamines (Hajipour et al. 2007) in an ionic liquid medium to produce a series of organosoluble poly (amide-imide)s. The properties of these polymers, such as specific rotation, viscosity, solubility, and thermal stability also discussed herein.

Materials and methods

Pyromellitic dianhydride (Merck) was recrystallised from acetic anhydride. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. The other chemicals (Merck) were used as received. ^{1}H NMR spectra were recorded on 300 MHz instrument, using DMSO-d_6 as solvent and tetramethylsilane as shift reference (tube diameter, 5 mm). IR spectra were recorded on a Shimadzu IR-435 instrument, using KBr pellets. Mass spectra were recorded on a Fisons (UK) mass spectrometer Model Trio 1000. Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermogravimetric analyses (TGA) were recorded on a Mettler TGA-50 with heating rate of 10°C min^{-1} under air atmosphere. Differential scanning calorimetry (DSC) analyses were recorded on a Mettler DSC-30 under nitrogen atmosphere. Inherent viscosities of polymer solution (0.5% w/v) in DMF were determined at 25°C by a standard procedure using a Cannon-Fenske Routine viscometer (Cannon, Mainz, Germany). Melting points were measured in open capillaries with a Qallenkamp instrument.

Monomer synthesis

Diacid synthesis (Hajipour et al. 2007)

The acidic compounds (1–4) were prepared by the reported procedure.

*N,N′-Pyromelliticdiimido-di-L-alanine (**1**)*

Yield (%) = 92; m.p. (°C) >250; $[\alpha]_D^{25} = +2.76$; IR (cm^{-1}): 3,400–2,700, 17,650–1,570, 1,455, 1,380, 1,365, 1,280, 1,250, 1,170, 1,060, 1,015, 930, 850, 730, 630; ^{1}H NMR δ (ppm): 1.60 (d, 6H), 4.98 (q, 2H), 8.45 (s, 2H), 13.7 (s, 2H); MS (*m/z*): 360, 345, 317, 316, 315 (100%), 288, 271, 244, 243, 199, 173, 172, 145, 135, 128, 75, 74, 45. Elemental analysis: calculated for $C_{16}H_{12}N_2O_8$: C (56.47%), H (3.55%), N (8.23%); found C (56.39%), H (3.60%), N (8.19%).

*N,N′-Pyromelliticdiimido-di-L-phenylalanine (**2**)*

Cream; Yield (%) = 98; m.p. (°C) >250; $[\alpha]_D^{25} = -4.08$; IR (cm^{-1}): 3,400–2,280, 1,775, 1,750–1,680, 1,495, 1,450, 1,380, 1,365, 1,275, 1,095, 940, 920, 870, 825, 730, 695; ^{1}H NMR δ (ppm): 3.30 (dd, 2H), 3.50 (dd, 2H), 5.20 (dd, 2H), 7.15 (s, 10H), 8.25 (s, 2H), 13.60 (s, 2H); MS (*m/z*): 364, 343, 318, 315, 149, 148 (100%), 103, 91, 77, 65, 51, 44. Elemental analysis: calculated for $C_{28}H_{20}N_2O_8$: C (65.62%), H (3.93%), N (5.47%); found C (65.55%), H (4.02%), N (5.38%).

*N,N′-Pyromelliticdiimido-di-L-leucine (**3**)*

White; Yield (%) = 98; m.p. (°C) = 235–237(d); $[\alpha]_D^{25} = +6.08$; IR (cm^{-1}): 3,200, 2,920, 1,765, 1,700, 1,555, 1,480, 1,385, 1,235, 1,180, 1,145, 1,080, 925, 855, 810, 725, 620; ^{1}H NMR δ (ppm): 1.00 (d, 12H), 1.50 (m, 2H), 1.90 (ddd, 2H), 2.20 (ddd, 2H), 4.88 (dd, 2H), 8.50 (s, 2H), 13.20 (s, 2H); MS (*m/z*): 447, 444, 402, 401, 399, 383, 371, 370, 257, 344, 343, 331, 315, 313, 287, 269, 255, 243, 229, 225, 199, 128, 114, 99, 75, 69, 53, 44, 43 (100%). Elemental analysis: calculated for $C_{22}H_{24}N_2O_8$: C (59.45%), H (5.44%), N (6.30%); found C (59.33%), H (5.52%), N (6.21%).

*N-Phthalicimido-L-phenylalanine (**4**)*

White; Yield (%) = 98; m.p. (°C) = 232; $[\alpha]_D^{25} = +0.5$; IR (cm^{-1}): 3,450–2,600, 1,765–1,705, 1,505, 1,425, 1,380, 1,275, 1,102, 945, 865, 725; ^{1}H NMR δ (ppm): 3.40 (dd, 1H), 3.50 (dd, 1H), 5.15 (dd, 1H), 7.20 (s, 5H), 7.85 (s, 4H), 13.40 (s, 1H); MS (*m/z*): 295 (M·+), 251, 249, 232, 149, 148 (100%), 147, 131, 130, 117, 105, 104, 92, 91, 89, 77, 76, 65, 51.

Diamine synthesis (Hajipour et al. 2007)

Compounds (5, 6) were prepared by the reported procedure.

4-Phenyl-2,6-bis(4-nitrophenyl) pyridine

Yield (%) = 60; m.p. (°C) >250; IR (cm^{-1}): 1,585, 1,543, 1,510, 1,375, 1,345, 1,090, 845, 815, 750, 740; ^{1}H NMR δ

(ppm): 7.56–7.62 (m, 8H), 7.77–7.79 (s, 2H), 8.07 (dd, 2H), 8.37–8.44 (m, 3H); MS (*m/z*): 399, 398, 397(M·+, 100%), 351, 306, 305, 304, 302, 152, 151.

4-(p-Methylthiophenyl)-2,6-bis(4-nitrophenyl) pyridine

Yellow; Yield (%) = 55; m.p. (°C) >250; IR (cm^{-1}): 3,400, 1,590, 1,545, 1,510, 1,425, 1,375, 1,345, 1,095, 850, 805, 750, 725, 680; ^{1}H NMR δ (ppm): 2.61 (s, 3H), 7.47 (d, 2H), 8.05 (d, 2H), 8.20 (s, 2H), 8.45 (d, 4H), 8.65 (d, 4H); MS (*m/z*): 445, 444, 443 (M·+, 100%), 415, 413, 397, 383, 367, 353, 352, 351, 337, 336, 335, 303, 302, 291, 252, 227, 207, 176, 167, 151, 145, 133, 117, 97, 73, 69, 57, 55.

*4-Phenyl-2,6-bis(4-aminophenyl) pyridine (**5**)*

Yield (%) = 92; m.p. (°C) = 155; IR (cm^{-1}): 3,335, 3,200, 1,620, 1,580, 1,535, 1,505, 1,440, 1,385, 1,280, 1,235, 1,175, 825, 750, 680; ^{1}H NMR δ (ppm): 7.00–8.20 (m, 15H), 3.99 (NH2, s, 4H); MS (*m/z*): 340, 338, 337 (M·+, 100%), 336, 322, 245, 169.

*4-(p-Methylthiophenyl)-2,6-bis(4-aminophenyl) pyridine (**6**)*

Bright yellow; Yield (%) = 90; m.p. (°C) = 130–132; IR (cm^{-1}): 3,350, 3,280, 1,620, 1,580, 1,535, 1,510, 1,480, 1,430, 1,405, 1,375, 1,295, 1,235, 1,175, 1,090, 800; ^{1}H NMR δ (ppm): 2.50 (s, 3H), 5.41 (s, 4H), 6.65 (d, 4H), 7.4 (d, 2H), 7.75 (s, 2H), 7.90 (d, 2H), 8.00 (d, 4H); MS (*m/z*): 386, 385, 383 (M·+, 100%). 368, 366, 336, 192, 117.

Preparation of model compound (7)

A mixture of *N*-phethalic imido-L-phenyl alanine (**4**) (0.295 g, 1.0 mmol) and 4-(*p*-methylthiophenyl)-2,6-bis(4-aminophenyl) pyridine (**6**) (1.914 g, 0.5 mmol) were dissolved in 0.33 g of [1-methyl-3-propyl imidzolium]Br, then 0.33 mL (1.25 mmol) of triphenyl phosphite (TPP) was added. The whole solution was heated at 110°C for 2.5 h. The solution becomes more viscous by progress of the reaction. The resulting product was dissolved in 3 mL of DMF and was poured into 30 mL of stirring methanol/H_2O, followed by filtration. It was washed several times with methanol and vacuum dried. Yellow; Yield (%) = 95; m.p. (°C) = 154; $[\alpha]_D^{25} = +5.65$; IR (cm^{-1}): 3,350, 1,735, 1,710, 1,600, 1,510, 1,485, 1,420, 1,375, 1,310, 1,240, 1,175, 1,080, 950, 815, 730; ^{1}H NMR δ (ppm): 2.55 (s, 3H), 3.40 (m, 2H), 3.65 (dd, 2H), 5.25 (dd, 2H), 7.20 (s, 10H), 7.4 (d, 2H), 7.75 (d, 4H), 7.82 (s, 8H), 8.00 (d, 2H), 8.13 (s, 2H), 8.30 (d, 4H), 10.2 (s, 2H). MS (*m/z*): 384, 383, 337, 234, 207, 149, 148, 126, 98, 94, 85, 69, 60, 57, 55 (100%).

Preparation of polymers

The polymers (**PAI$_{1-6}$**) were prepared by the modified procedure which is mentioned in the section of model compound preparation by using the mentioned starting materials.

PAI$_1$ *(using diacid **1** and diamine **5**)*

Light yellow; Yield (%) = 95; η'_{inh} (dL g^{-1}) = 0.56; $[\alpha]_D^{25} = +11.25$; IR (cm^{-1}): 3,390, 3,040, 2,900, 1,780, 1,715, 1,595, 1,520, 1,490, 1,450, 1,380, 1,360, 1,320, 1,245, 1,180, 1,125, 1,075, 1,015, 930, 830, 755, 725, 685; ^{1}H NMR δ (ppm): 1.70 (d, 6H), 5.05 (q, 2H), 7.30 (m, 1H), 7.50 (d, 2H), 7.70 (d, 4H), 8.00 (d, 2H), 8.10 (s, 2H), 8.25 (d, 4H), 8.35 (s, 2H), 10.3 (s, 2H); CHNS: Calculated for $(C_{39}H_{27}N_5O_6)_n$ (661.669) C (70.79%), H (4.11%), N (10.58%); found C (70.51%), H (4.25%), N (10.32%).

PAI$_2$ *(using diacid **2** and diamine **5**)*

Light yellow; Yield (%) = 95; η'_{inh} (dL g^{-1}) = 0.73; $[\alpha]_D^{25} = +12.35$; IR (cm^{-1}): 3,380, 3,050, 2,900, 1,770, 1,725, 1,590, 1,535, 1,490, 1,450, 1,385, 1,350, 1,315, 1,245, 1,180, 1,105, 945, 845, 760, 725, 695; ^{1}H NMR δ (ppm): 3.65 (dd, 4H), 5.30 (dd, 2H), 7.20 (s, 11H), 7.55 (d, 2H), 7.75 (d, 4H), 8.03 (d, 2H), 8.15 (s, 2H), 8.28 (s, 2H), 8.35 (d, 4H), 10.20 (s, 2H); CHNS: Calculated for $(C_{51}H_{35}N_5O_6)_n$ (813.865) C (75.26%), H (4.33%), N (8.60%); Found C (74.87%), H (4.40%), N (8.57%).

PAI$_3$ *(using diacid **3** and diamine **5**)*

Light yellow; Yield (%) = 95; η'_{inh} (dL g^{-1}) = 0.85; $[\alpha]_D^{25} = +15.80$; IR (cm^{-1}): 3,350, 3,005, 2,950, 1,765, 1,720, 1,590, 1,515, 1,490, 1,375, 1,350, 1,315, 1,245, 1,175, 1,075, 945, 840, 755, 715, 690; ^{1}H NMR δ (ppm): 0.92 (d, 12H), 1.52 (br, 2H), 2.05 (br, 2H), 2.30 (br, 2H), 5.20 (dd, 2H), 7.40 (m, 1H), 7.55 (d, 2H), 7.75 (d, 4H), 8.05 (d, 2H), 8.12 (s, 2H), 8.30 (d, 4H), 8.40 (s, 2H), 10.2 (s, 2H); CHNS: calculated for $(C_{45}H_{39}N_5O_6)_n$ (745.831) C (72.47%), H (5.27%), N (9.39%), S (8.20%); found C (72.26%), H (5.32%), N (9.31%).

PAI$_4$ *(using diacid **1** and diamine **6**)*

Bright yellow; Yield (%) = 95; η'_{inh} (dL g^{-1}) = 0.43; $[\alpha]_D^{25} = +19.56$; IR (cm^{-1}): 3,380, 2,900, 1,770, 1,720, 1,595, 1,510, 1,492, 1,425, 1,380, 1,375, 1,312, 1,240, 1,178, 1,080, 1,005, 940, 812, 755, 725, 690; ^{1}H NMR δ (ppm): 0.90 (d, 6H), 2.55 (s, 3H), 5.05 (m, 2H), 7.40 (d, 2H), 7.70 (d, 4H), 8.00 (d, 2H), 8.10 (s, 2H), 8.30 (d, 4H), 8.40 (s, 2H), 10.20 (s, 2H); CHNS: calculated for $(C_{40}H_{29}N_5O_6S)_n$ (707.762) C (67.88%), H (4.13%), N

Scheme 1 Preparation of diacids (**1**–**3**)

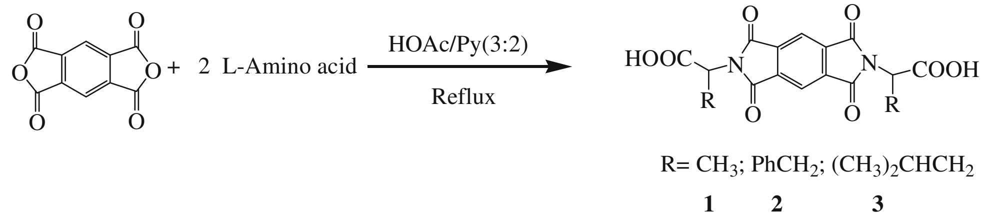
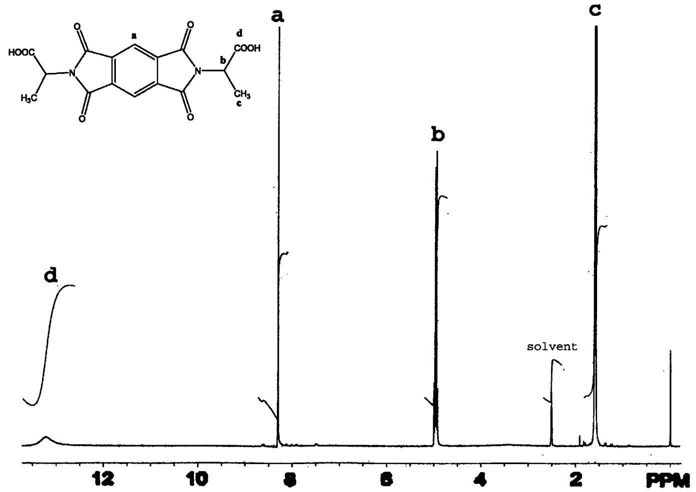
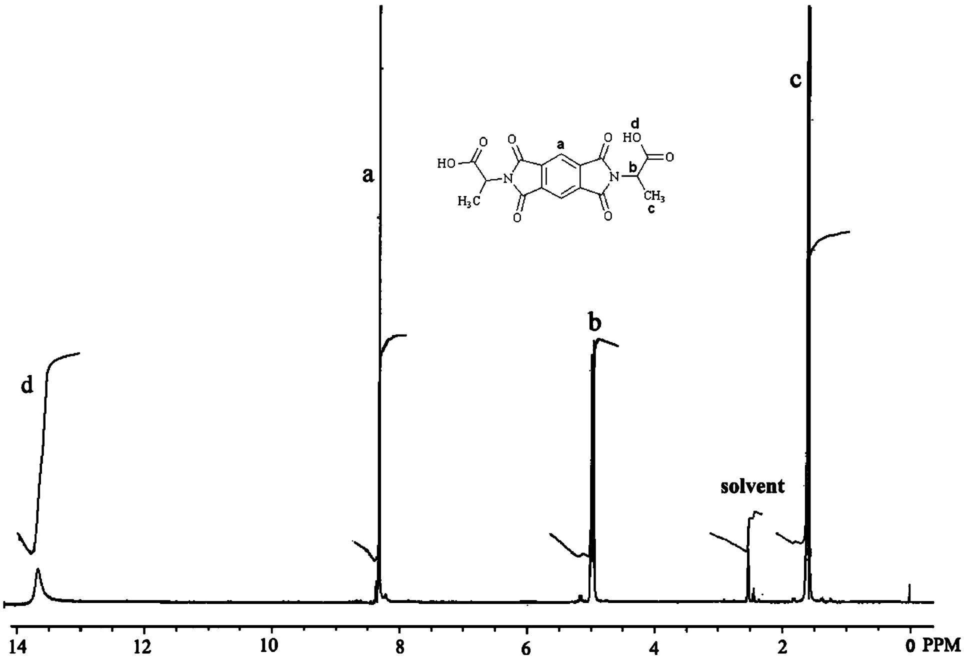


Fig. 1 ^{1}H NMR of diacid **1**





(9.89%), S (4.53%); found C (67.63%), H (4.21%), N (9.78%), S (4.36%).

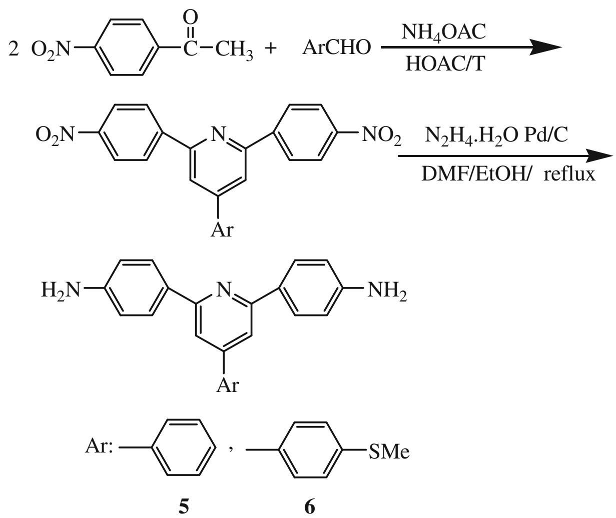
*PAI$_5$ (using diacid **2** and diamine **6**)*

Bright yellow; Yield (%) = 95; η'_{inh} (dL g^{-1}) = 0.48; $[\alpha]_D^{25}$ = +20.54; IR (cm^{-1}): 3,360, 3,005, 2,880, 1,766, 1,725, 1,655, 1,595, 1,510, 1,490, 1,450, 1,420, 1,380, 1,310, 1,235, 1,185, 1,095, 1,010, 940, 810, 745, 720, 685; ^{1}H NMR δ (ppm): 2.05 (s, 3H), 3.25–3.42 (m, 4H), 5.3 (dd, 2H), 7.10–7.60 (m, 10H), 7.85 (d, 2H), 8.05 (d, 4H), 8.17 (s, 2H), 8.30 (s, 2H), 8.40 (d, 4H), 8.55 (s, 2H), 10.60 (s, 2H); CHNS: calculated for $(C_{52}H_{37}N_5O_6S)_n$ (859.958) C (72.63%), H (4.34%), N

(8.14%), S (3.73%); found C (72.55%), H (4.46%), N (7.96%), S (3.68%).

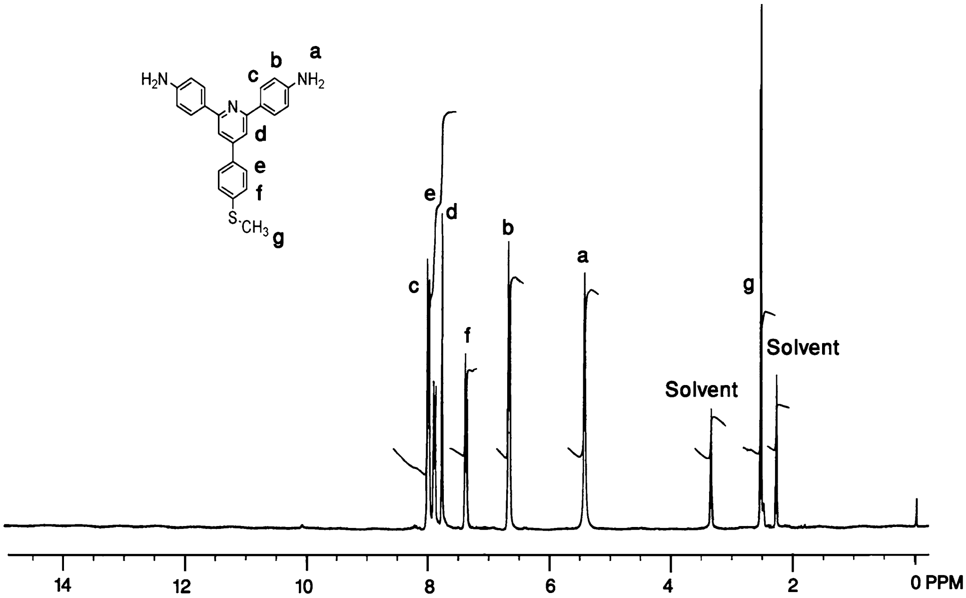
***PAI$_6$* (using diacid 3 and diamine 6)**

Bright yellow; Yield (%) = 95; η_{inh} (dL g^{-1}) = 0.63; $[\alpha]_D^{25}$ = +21.43 IR (cm^{-1}): 3,390, 3,008, 2,995, 1,770, 1,720, 1,595, 1,512, 1,475, 1,420, 1,375, 1,350, 1,315, 1,245, 1,175, 1,170, 1,050, 945, 815, 750, 715, 685; ^{1}H NMR δ (ppm): 0.90–1.00 (d, 12H), 1.55 (br, 2H), 2.05 (br, 2H), 2.30 (br, 2H), 2.55 (s, 3H), 5.07 (br, 2H), 7.42 (d, 2H), 7.75 (d, 4H), 7.96 (s, 2H), 8.10 (d, 2H), 8.30 (d, 4H), 8.50 (s, 2H), 10.20 (s, 2H); CHNS: calculated for $(C_{46}H_{41}N_5O_6S)_n$ (791.924) C (69.77%), H (5.22%), N (8.84%), S (4.05%); found C (69.59%), H (5.34%), N (8.75%), S (3.93%).



Scheme 2 Preparation of diamines (**5**, **6**)

Fig. 2 ^{1}H NMR spectrum of diamine **6**



Scheme 3 Preparation of model compound **7**

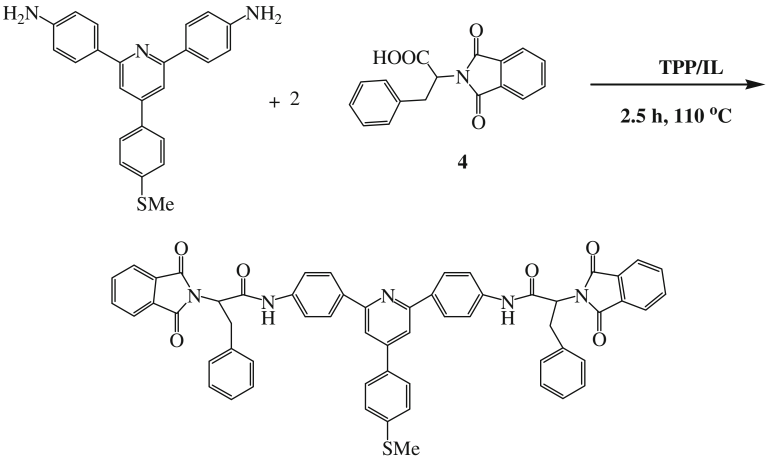
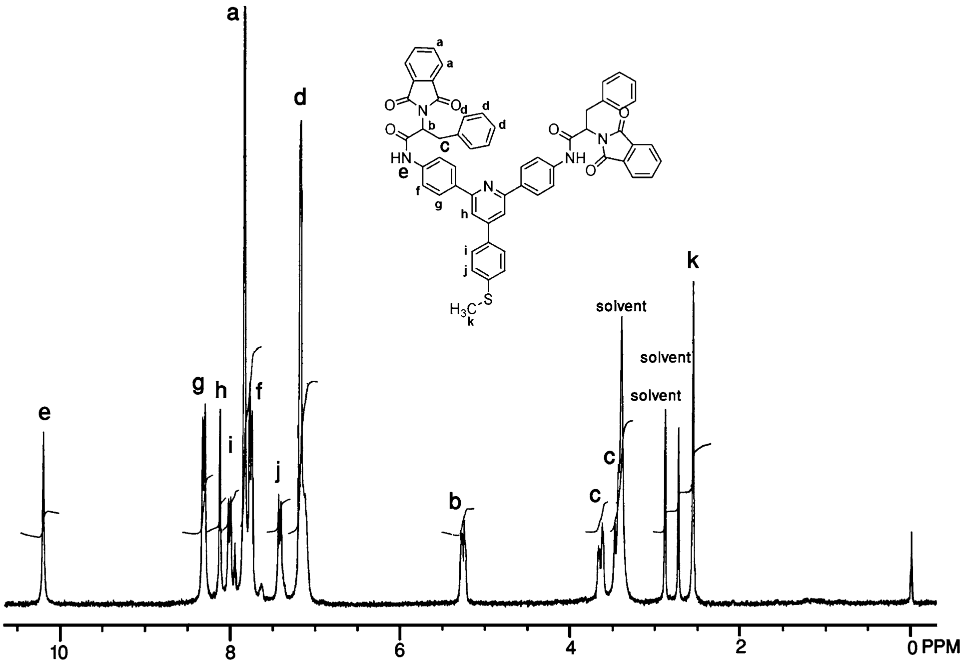
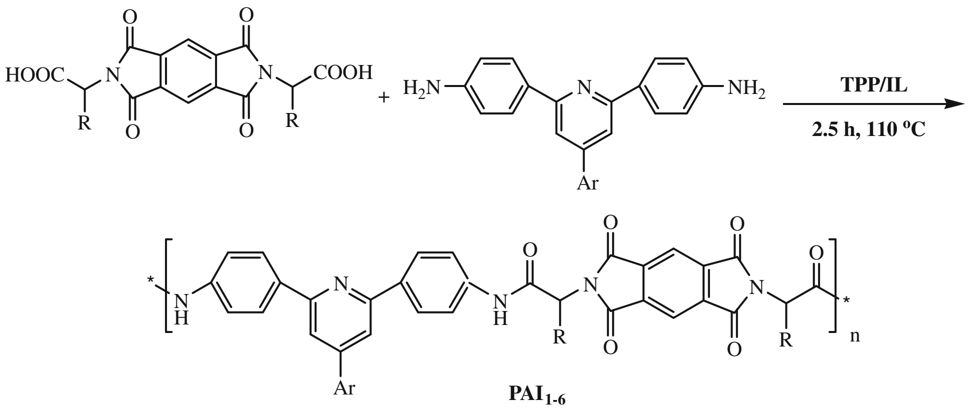


Fig. 3 ^{1}H NMR of the model compound (**7**)



Scheme 4 Ionic liquid catalyzed synthesis of $\mathbf{PAI_{1–6}}$



R: CH_3; $PhCH_2$; $(CH_3)_2CHCH_2$, Correspondingly

Ar: Ph; CH_3SPh, Correspondingly

Table 1 Optimization of the direct polycondensation in **IL** on $\mathbf{PAI_1}$

Temperature	TPP/monomer	η_{inh} (dL g^{-1})	$[\alpha]_D^{25}$
100	2	0.31	+12.56
110	2	0.35	+12.11
120	2	0.35	+10.43
100	2.5	0.37	+12.43
110	2.5	0.56	+11.25
120	2.5	0.60	+6.53
100	3	0.34	+13.67
110	3	0.39	+11.02
120	3	0.39	+5.67

Results and discussion

We synthesized the optically active diimide-diacid monomers (**1–3**) from condensation of pyromellitic dianhydride with the corresponding L-amino acids (1:2) in a refluxing solution of acetic acid/pyridine (3:2) (Scheme 1). IR spectra of these compounds showed the characteristic absorptions at around 3,400–2,250 cm^{-1}, peculiar to carboxylic acid groups, and two peaks at around 1,770 and 1,700 cm^{-1}, peculiar to carbonyl stretching of imide and acid moieties. All of these compounds exhibited strong absorptions at 1,388 and 725 cm^{-1}, which indicates the presence of the cyclic imide group in these monomers. The corresponding peaks included acidic groups at around

Table 2 Comparison between IL catalyzed and the conventional reported (Hajipour et al. 2007) method

Polymer	IL catalyzed method				The conventional reported method			
	Viscosity	Specific rotation	Reaction time	Reaction temperature	Viscosity	Specific rotation	Reaction time	Reaction temperature
PAI_1	0.56	+11.25	2.5 h	110°C	0.49	+3.84	1 h then 3 h	25°C then 100°C
PAI_2	0.73	+12.35	2.5 h	110°C	0.40	+4.04	1 h then 3 h	25°C then 100°C
PAI_3	0.85	+15.80	2.5 h	110°C	0.97	+6.88	1 h then 3 h	25°C then 100°C
PAI_4	0.43	+19.56	2.5 h	110°C	0.36	+4.80	1 h then 3 h	25°C then 100°C
PAI_5	0.48	+20.54	2.5 h	110°C	0.45	+4.60	1 h then 3 h	25°C then 100°C
PAI_6	0.63	+21.43	2.5 h	110°C	0.38	+9.52	1 h then 3 h	25°C then 100°C

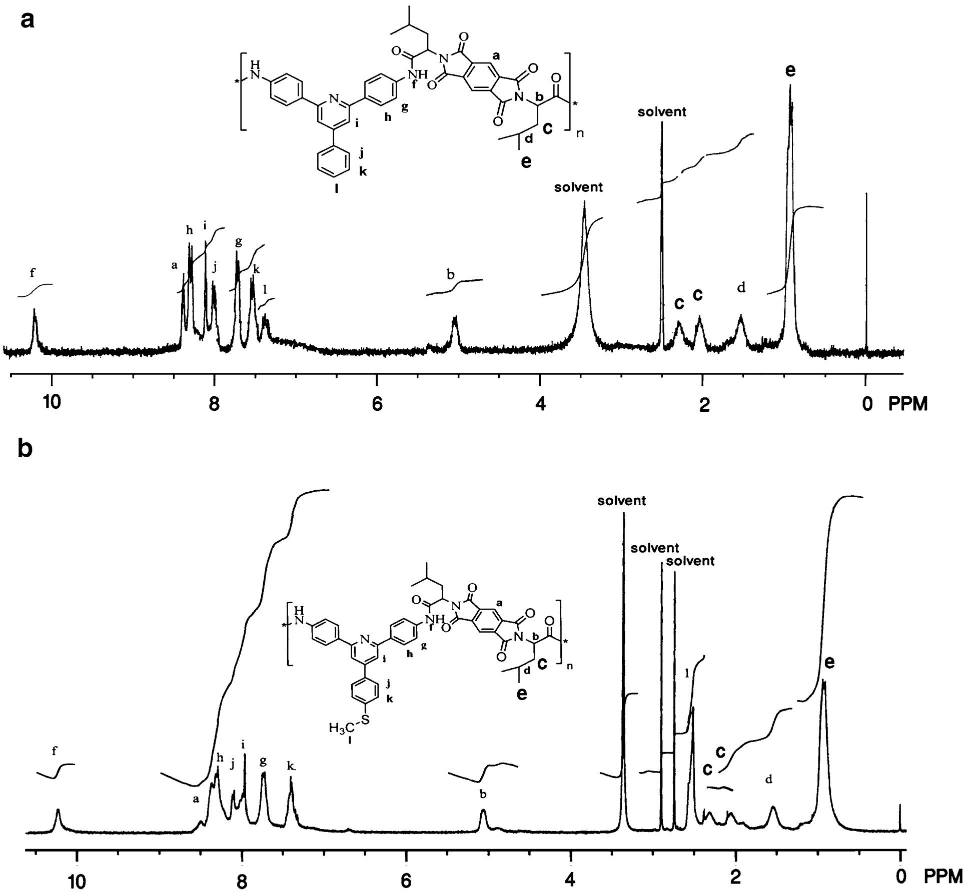


Fig. 4 **a** ^{1}H NMR spectrum of **PAI_3**. **b** ^{1}H NMR spectrum of **PAI_6**

Table 3 Solubility of **PAI_{1-6}**

Polymer	DMAc	DMF	NMP	DMSO	H_2SO_4
PAI_1	+	+	+	+	+
PAI_2	+	+	+	+	+
PAI_3	+	+	+	+	+
PAI_4	+	+	+	+	+
PAI_5	+	+	+	+	+
PAI_6	+	+	+	+	+

+ soluble at room temperature

13.4 ppm have been detected by ^{1}H NMR. ^{1}H NMR of diimide-diacid **1** is presented in Fig. 1. Mass spectra showed the appropriate molecular ion peaks and/or fragments.

There are several methods for preparation of the pyridine ring, but the Chichibabin method is one of the best (Scheme 2). IR spectra of dinitro compounds showed characteristic bands of nitro groups at around 1,345 and 1,540 cm^{-1}. In addition C=C and C=N bands of phenyl and pyridine rings at 1,590 cm^{-1} were presented. ^{1}H NMR

Table 4 Thermal properties of **$PAI_{1–6}$**

Polymer	$T_{10\%}$ (°C)[a]	T_g[b]	Ch.Y[c]
PAI_1	350	125	5.9
PAI_2	345	154	0.0
PAI_3	340	98	19.0
PAI_4	320	94	4.7
PAI_5	340	128	14.8
PAI_6	308	112	6.0

[a] Temperature of 10% weight loss, obtained from TGA

[b] Glass transition temperature, obtained from DSC

[c] Char yield percentage at 600°C, obtained from TGA

spectra showed the corresponding peaks which confirmed the formation of pyridine rings. ^{1}H NMR spectrum of diamine **6** is shown in Fig. 2. Mass spectra showed the appropriate molecular ion peaks and fragments. Hydrazine monohydrate with the catalytic amount of palladium on charcoal (10%) was used for reduction. IR spectra of diamines (**5**, **6**) showed characteristic bands of amino group at ca. 3,350–3,200 cm^{-1} (N–H stretching) and 1,620 cm^{-1} (N–H out-of-plane bending). ^{1}H NMR spectra of diamines (**5**, **6**) showed NH_2 protons at ca. (4.0 and 5.4 ppm). Molecular ion peaks and fragment peaks were shown by MS.

Model compound (**7**) was prepared via direct polycondensation in [1-methyl-3-propyl imidzolium]Br both as solvent and catalyst outlined in Scheme 3. In addition to provide a safe and green reaction medium, **IL** has also catalytic effect on polymerization reaction because the amidation did not progress in the absence of either **IL** or TPP and the existence of both **IL** and TPP at the same time was essential for the condensation. The IR spectrum of the model compound (**7**) showed amide bands at 3,350 cm^{-1} (N–H stretching), 1,710 cm^{-1} (C=O stretching) and 1,600 cm^{-1} (combined N–H bending and C–N stretching). In its ^{1}H NMR spectrum an amidic proton was observed at ca. 10.3 ppm (Fig. 3) and its elemental analysis data $(C_{58}H_{43}N_5O_6S)_{938.072}$ are given below:

Calculated C 74.26%, H 4.62%, N 7.4%, S 3.42%; Found C 74.17%, H 4.72%, N 7.31%, S 3.31%.

Polymerization of diacids (**1–3**) with stoichiometric amount of different aromatic diamines (**5**, **6**) was carried out in [1-methyl-3-propyl imidzolium]Br both as solvent and catalyst outlined in Scheme 4. In addition to provide a safe and green reaction medium, **IL** has also catalytic effect on polymerization reaction because polyamidation did not progress in the absence of either **IL** or TPP and the existence of both **IL** and TPP at the same time was essential for the polycondensation. In optimizing the

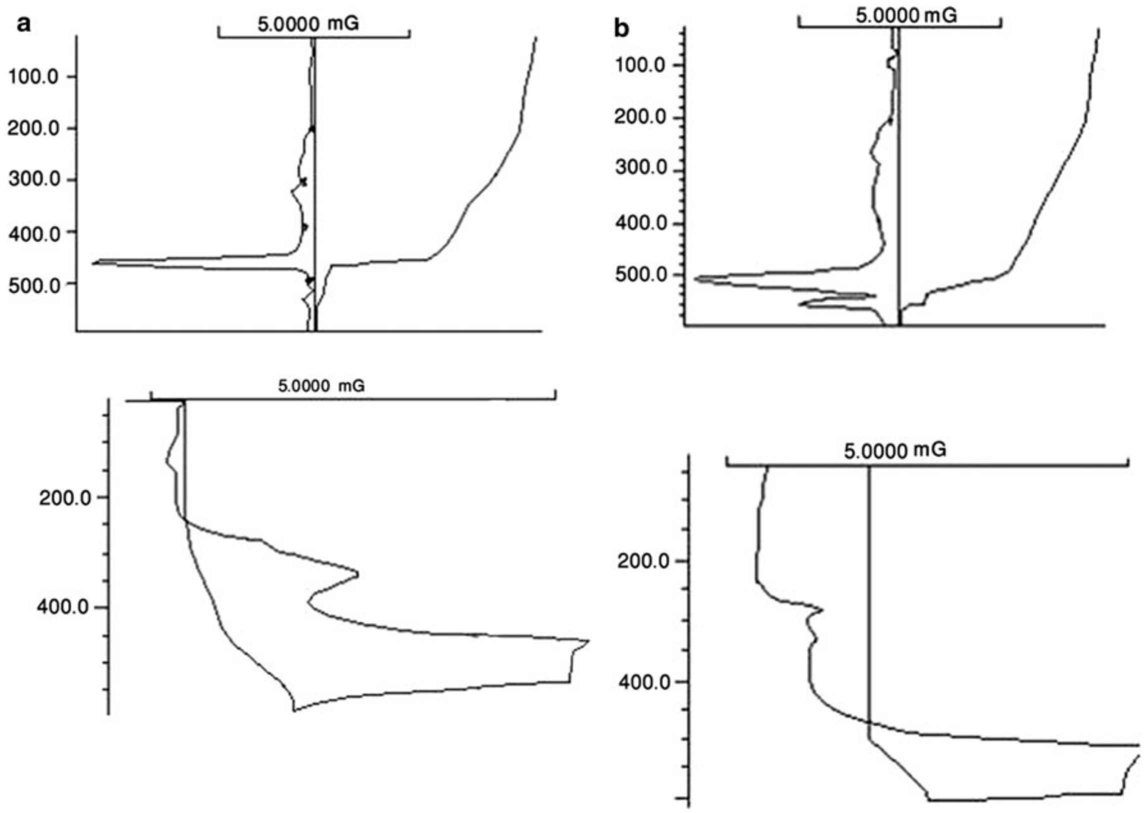


Fig. 5 **a** TGA/DSC diagrams of **PAI_3**. **b** TGA/DSC diagrams of **PAI_6**

polycondensation it is found that higher reaction temperature cause higher viscosity and lower specific rotation and more TPP/monomer ratio cause lower viscosity; the results are shown in Table 1. A comparison between this method and the conventional method (Hajipour et al. 2007) proves that the **PA**s prepared via direct polycondensation in **IL** encompass higher inherent viscosities and specific rotations (Table 2). Furthermore, the use of **IL** causes reduced overall cost of synthesis and cleaner reaction. All polyamidations proceeded in a homogeneous system throughout the reaction, and the polyamides were isolated in quantitative yields. Inherent viscosities of the polymers ranged from 0.43 to 0.85 dL/g, indicative of the formation of high molecular weights. The structures of these polyamides were confirmed by IR spectroscopy. The polymers ($\mathbf{PAI_{1\text{–}6}}$) were characterized by IR, ^{1}H NMR, and CHNS analyses. The presence of amidic bands at ca. 3,350 $\mathrm{cm^{-1}}$ (N–H stretching), 1,720 $\mathrm{cm^{-1}}$ (C=O stretching) and ca. 1,595 $\mathrm{cm^{-1}}$ (combined N–H bending and C–N stretching) in the IR spectra and the amidic proton at ca. 10.25 ppm in the ^{1}H NMR spectra confirm the amidic structure. ^{1}H NMR spectra of $\mathbf{PAI_3}$ and $\mathbf{PAI_6}$ are shown in Fig. 4.

The color of **PAI**s ranges from bright yellow to yellow. The inherent viscosities of the polymers are in the range of 0.43–0.85 dL/g, indicating moderate to high molecular weight. Transparent, flexile and tough films could be obtained from these polymers by casting from solution of polymers in DMF solvent, which shows good mechanical strength of the films and consequently high molecular weight. One of the major objectives of this work is to improve the solubility. The solubility behavior of the new aromatic polyamides was determined at concentration of 5% (W/V) in a number of solvents. Table 3 shows that these polymers are readily soluble in common polar aprotic solvents. The other objective was to study the optical activity of polymers from three different L-amino acids, which showed that L-leucine is one of the best and cause maximum rotation of the polarized light.

The thermal properties of $\mathbf{PAI_{1\text{–}6}}$ were evaluated by means of TGA/DTG under air atmosphere and DSC under nitrogen atmosphere at a heating rate of 10°C $\mathrm{min^{-1}}$ (Table 4). These polymers show similar decomposition behavior. The temperature of 10% weight loss for the polymers ($\mathbf{PAI_{1\text{–}6}}$) range from 308 to 350°C and the residual weight for these polymers at 600°C range from 0.0 to 19.0% under air atmosphere. The T_gs for these polymers ($\mathbf{PAI_{1\text{–}6}}$) range from 94 to 154°C. It seems that *p*-SMe substituent in diamine **6** causes the corresponding polymers to show improvement in solubility and somewhat sharper and lower T_gs. However, a slight decrease in thermal stability can also be seen with this modification. TGA/DSC diagrams of $\mathbf{PAI_3}$ and $\mathbf{PAI_6}$ are shown in Fig. 5.

Conclusions

Replacement of the toxic volatile organic solvents with several ecological disadvantages by a green, safe and eco-friendly reaction medium is the main aspect of this investigation. Therefore, direct polycondensations of diacids (**1–3**) and two aromatic diamines (**5**, **6**) have been investigated in **IL** medium, which acts as a green solvent and a reaction catalyst. Comparison with the reported direct method (Hajipour et al. 2007) indicates that **IL** in combination with **TPP** is the superior polyamidation agent. On the other hand, in the case of **IL** catalyzed polyamidation, removal of some chemicals such as NMP, $\mathrm{CaCl_2}$ and Py, which are essential in conventional methodologies, decreases the cost of polymerization as well as the environmental pollutions, considerably. Here six heterocyclic thermally stable and optically active **PAI**s with admirable inherent viscosities (0.43–0.85) and optical activity (+11.25–+21.43) were synthesized by phosphorylation polycondensation in an **IL** media. The properties of these polymers make them attractive for practical applications such as processable optically active polymeric materials.

Acknowledgments We gratefully acknowledge the funding support received for this project from Payame Noor University.

References

Akelah A, Sherrington DC (1981) Application of functionalized polymers in organic synthesis. Chem Rev 81:557–587

Caouthat A, Roger P, Tessier M, Chatti S, Blais JC, Bortolussi M (2007) Synthesis and characterization of new polyamides derived from di(4-cyanophenyl)isosorbide. Eur Polym J 43:220–230

Hajipour AR, Zahmatkesh S, Ruoho AE (2007) Synthesis and characterization of heterocyclic, and optically active poly (amide-imide)s by phosphorylation polycondensation. Polym Bull 59:145–159

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 derived from *N*,*N*′-(4,4′-hexafluoroisopropylidenediphthaloyl)-bis-lmethionineand various aromatic diamines. Iran Polym J 15:239–247

Mallakpour S, Yousefian H (2008) Direct polyamidation in molten tetrabutylammonium bromide: novel and efficient green media. Polym Bull 60:191–198

Mallakpour SE, Hajipour AR, Khoee S, Sheikholeslami B (1998) A new method for producing optically active polybutadiene. Polym Int 47:193–197

Shaplov AS, Lozinskaya EI, Odinets IL, Lyssenko KA, Kurtova SA, Timofeeva GI, Iojoiu C, Sanchez JY, Abadie MJM, Voytekunas VY, Vygodskii YS (2008) Novel phosphonated poly(1, 3, 4-oxadiazole)s: synthesis in ionic liquid and characterization. React Funct Polym 68:208–224

Shi Q, Zhang Y, Jing G, Kan J (2007) Properties of polyaniline synthesized in ionic liquid (1-ethyl-3-methylimidazoliumethyl sulphate). Iran Polym J 16:337–344

Talawar MB, Sivabalan R, Mukundan T, Gandhe BR, Subhananda Rao A (2009) Environmentally compatible next generation green energetic materials (GEMs). J Hazard Mater 161:589–607

Wulff G (1989) Main-chain chirality and optical activity in polymers consisting of CC chains. Angew Chem Int Engl Ed 28:21–37

Zahmatkesh S, Hajipour AR (2009) Microwave-assisted synthesis and characterization of some optically active poly (ester-imide) thermoplastic elastomers. e-polymers 068

Zahmatkesh S, Hajipour AR (2010) Microwave-assisted synthesis and characterization of optically active poly (ester-imide)s incorporating L-alanine. Amino acids 38:1253–1260

Zulfiqar S, Lieberwirth I, Sarwar MI (2008) Soluble aramid containing ether linkages: synthesis, static and dynamic light scattering studies. Chem Phys 344:202–208