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Ionic liquid catalyzed synthesis of organosoluble wholly aromatic optically active polyamides

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Abstract A series of optically active wholly aromatic polyamides (**PA**s) with amino acid moieties in the pendant groups have been synthesized through polycondensation of a chiral diacid and aromatic diamines in an ionic liquid (IL) as a green, safe and eco-friendly medium and also reactions catalysis agent (method I). Furthermore, the polymerization reactions were performed via conventional polycondensation (method II) and obtained results have been compared. Evaluation of data shows that IL is the better polyamidation medium and catalysis stand on the higher inherent viscosities and yields of the obtained **PA**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 ^{1}H-NMR and FT-IR spectroscopy, elemental analysis, thermogravimetric analysis and differential scanning calorimetric techniques.

Keywords Ionic liquids · Polyamides · Green chemistry · Amino acid · Optically active polymers

Introduction

Optically active polymers are one of the most important classes of high performance engineering materials which are suitable candidates for use as the chiral stationary phases in high performance liquid chromatography (HPLC) [1–5] as well as asymmetric catalysis applications [6–10].

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Unique properties of aromatic polyamides (**PA**s) such as superior resistance toward chemicals and high temperatures and elevated mechanical strength [11, 12], characteristics which exactly are match with those are essential for HPLC column packing materials, have made them one of the categories of macromolecules with critical significance and widespread applications. Unfortunately the exploit of **PA**s are associated with some processing difficulties because of either their weak solubility behavior in common organic solvents or high melting or softening temperatures [13]. Resolve the processing problems while maintaining wanted properties of **PA**s attracted a grate deal of researches. Insertion of flexible bulky groups along the polymer backbones or as pendant groups is the common strategy for subtracting these complexities [14–17].

On the other hand polycondensation reactions are traditionally performed in polar high-boiling-point organic solvents such as *N*-methyl-2-pyrrolidone (NMP) [16, 18], *N*,*N*-dimethyacetamide (DMAc) [19], *N*,*N*-dimethyformamide (DMF) [20], which are generally cause several ecological disadvantages further than the impose of the over cost on synthetic methods. In this regard, development of the effective techniques for replacing or removing hazardous materials is one of the recent environmental issues [21, 22]**.** 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. [23–27]. Nonvolatile nature and stability at high temperature make the ILs excellent candidates for the use as polycondensation reactions medium [20, 28–30]. 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 [17, 31, 32]. Herein, we presented the combinations of exclusive properties of polyamides with optical activity in such manner that improves the processability of PAs without the sacrifice of their thermal resistance via direct polycondensation of previously synthesized optically active diacid [33] and several aromatic diamines using either IL medium (method I) and traditional polycondensation agent (method II).

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.). 5-Aminoisophthalic acid was recrystallized from a mixture of DMF/water (v/v ratio 3:1). 4,4′-Diaminodiphenylmethane (**2g**) and 4,4′-diaminobiphenyl (**2h**) were purified by recrystallization from water. 2,5-Diaminotoluene (**2b**), 1,3-phenylenediamine (**2d**), 1,4-phenylenediamine (**2e**) and 4,4′-Diaminodiphenylether (**2f**) were purified by sublimation. Naphthalene-1,5-diamine (**2a**) and 4,4′-diaminodiphenylsulphone (**2c**) was used without purification. DMAc was purified by distillation under reduced pressure over barium oxide.

Equipments

Proton nuclear magnetic resonance ^{1}HNMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument (Bruker, Rheinstetten, Germany) using DMSO-d_6 as solvent. The FT-IR adsorption spectra were recorded on a JASCO 400_D IR spectrophotometer with KBr pellets. Vibration bands were reported as wavenumber (cm^{-1}). The band intensities were classified as weak (w), medium (m) and strong (s). 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). The specific rotations were measured by a Jasco polarimeter (Japan). Thermal Gravimetric Analysis (TGA) data for polymers were taken on a TGA-Perkin Elmer (Pyris 1) at a heating rate of 10 °C/min under N_2 atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). DSC data were recorded on a DSC-PL-1200 instrument under N_2 atmosphere by IPPI.

Synthesis of monomer (**1**)

5-(4-Methylthio-2-phthalimidybutanoylamino)isophthalic acid (**1**) as optically active diacid monomer has been synthesized according to our previous work [33].

Polymerization

Method I: synthesis of ***PA****s via IL catalysis polycondensation*

The **PA**s were prepared by the following general procedure: as an example for the preparation of **PA3aI**, 0.1000 g (0.226 mmol) of diacid **1** and 0.0357 g (0.226 mmol) of diamine **2a** were dissolved in 0.15 g of [1,3-$(pr)_2$im]Br, then 0.15 mL (0.565 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 polymerization reaction. The resulting product was dissolved in 1 mL of DMF and was poured in 30 mL of methanol, filtered, dried under vacuum to give 0.121 g (89%) of **PA3aI**.

Method II: synthesis of PAs via conventional polycondensation

The **PA**s were synthesized using direct polycondensation following general procedure: Taking polymer **PA3aII** as an example, into a 5 mL round-bottomed flask fitted with a water cooled condenser and a magnetic stirrer, was placed 0.100 g (0.226 mmol) of diacid **1**, 0.06 g of calcium chloride, 0.15 mL (0.565 mmol) of TPP, 0.15 mL of Py, 0.0357 g (0.226 mmol) of diamine **2a** and 0.5 mL of NMP. The stirrer was operated and the mixture was heated under nitrogen atmosphere in an oil bath at 110 °C for 5 h. The viscous reaction mixture was poured into 30 mL of methanol. The precipitated polymer was collected by filtration, and was dried at 80 °C for 10 h under vacuum to leave 0.123 g (91%) of white solid **(PA3aII)**; The other **PA3bII–PA3hII** were prepared in a procedure similar to that mentioned above.

PA3a White solid; FT-IR (KBr): 3318 (m), 2965 (w), 1714 (s), 1666 (s), 1600 (s), 1526 (s), 1384 (s), 720 (m) cm^{-1}**.** $(C_{31}H_{24}N_4O_5S)_n$ (654.12): Calc. C 65.95, N 9.92, H 4.28. Found C 65.26, N9.37, H 4.41.

PA3b: White solid; FT-IR (KBr): 3300 (m), 3069 (w), 1715 (s), 1671 (s), 1595 (s), 1526 (s), 1384 (s), 720 (m) cm^{-1}.

PA3c: White solid; FT-IR (KBr): 3340 (m), 3100 (m), 1716 (s), 1677 (s), 1590 (s), 1524 (s), 1399 (m), 719 (m) cm^{-1}. $C_{33}H_{26}N_4O_7S_2$ (654.12): Calc. C 60.54, N 8.56, H 4.00. Found C 30.13, N 8.37, H 4.26.

PA3d: White solid; FT-IR (KBr): 3318 (m), 2916 (w), 1715 (s), 1672 (s), 1604 (s), 1538 (s), 720 (m) cm^{-1}.

PA3e: White solid; FT-IR (KBr): 3329 (m), 2920 (w), 1715 (s), 1671 (s), 1596 (m), 1513 (s), 720 (m) cm^{-1}.

PA3f: White solid; FT-IR (KBr): 3394 (m), 2915 (w), 1716 (s), 1670 (m), 1594 (m), 1225 (m), 719 (w) cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): 2.05 (s, 3H), 2.38 and 2.55 (m, 2H, diastereotopics), 2.57–2.59 (m, 2H diastereotopics), 5.07–5.08 (m, 1H, chiral center) 7.03–7.05 (d, 4H, $J = 8.5$ Hz), 7.78–7.79 (d, 4H, $J = 8.7$ Hz), 7.90–7.94 (d, 4H, $J = 8.9$ Hz), 8.24 (s, 1H), 8.31 (s, 2H), 10.35 (s, 1H, amidic), 10.58 (s, 2H, amidic).

PA3g: White solid; FT-IR (KBr): 3351 (m), 2915 (w), 1715 (s), 1671 (m), 1593 (s), 1512 (s), 1383 (m), 719 (w) cm^{-1}.

PA3h: White solid; FT-IR (KBr): 3330 (m), 2921 (w), 1715 (s), 1672 (s), 1590 (m), 1514 (s), 719 (m) cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6): 2.05 (s, 3H), 2.40 and 2.54 (m, 2H, diastereotopics), 2.55–2.57 (m, 2H diastereotopics), 5.08–5.10 (m, 1H, chiral center), 7.66–7.71 (d, 4H, $J = 7.8$ Hz), 7.89–7.95 (m, 8H), 8.30 (s, 1H), 8.36 (s, 2H,, 10.38 (s, 1H, amidic), 10.57 (s, 2H, amidic).

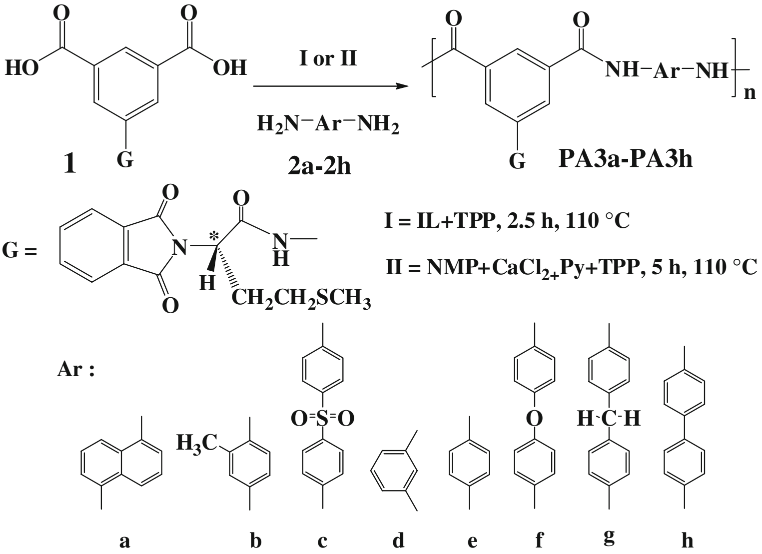
Results and discussion

Polymer synthesis

Wholly aromatic optically active **PA**s have been synthesized via direct polycondensation of diacid monomer **1** and several aromatic diamines using two different methods (Scheme 1). At first the benefits of **IL**/TPP as both polyamidation catalysis and reaction medium has been investigated. Figures 1 and 2 are consisting of FT-IR and ^{1}H-NMR spectra of representative **PA**s, respectively.

Some physical properties of **PA**s produced under this condition are collected in Table 1. In order to compare this contemporary method with a classical instance, the polycondensation reactions have been examined using NMP/TPP/$CaCl_2$/Py system as the conventional condensing agent too. Some physical data belong the polymers prepared under this conditions are collected in Table 2. The use of [1,3-$(pr)_2$im]Br as the best reaction medium and catalysis was based on our previous works [31, 32].

In addition to provide a safe and green reaction medium, **IL** has also catalytic effect on polymerization reaction because polyamidations did not progress in the



Scheme 1 Polycondensation reactions of optically active diacid **1** with diamines **2a–h**

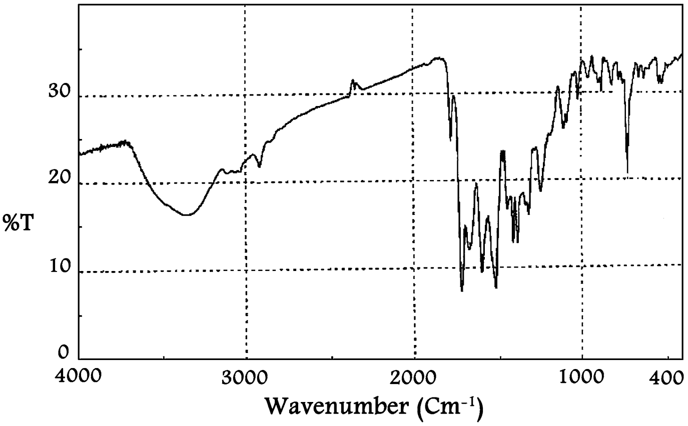


Fig. 1 FT-IR spectrum of **PA3h**

absence of either **IL** or TPP and the existence of both **IL** and TPP at the same time was essential for the polycondensation.

A comparison between presented data in Tables 1 and 2 proves that the **PA**s prepared via **IL** method encompass higher inherent viscosities and yields respect to whom that prepared under conventional method. Furthermore, the use of **IL** has led to reduce the overall cost of synthesis and cleaner reaction conditions by the removal of some chemicals which are indispensable in conventional methods.

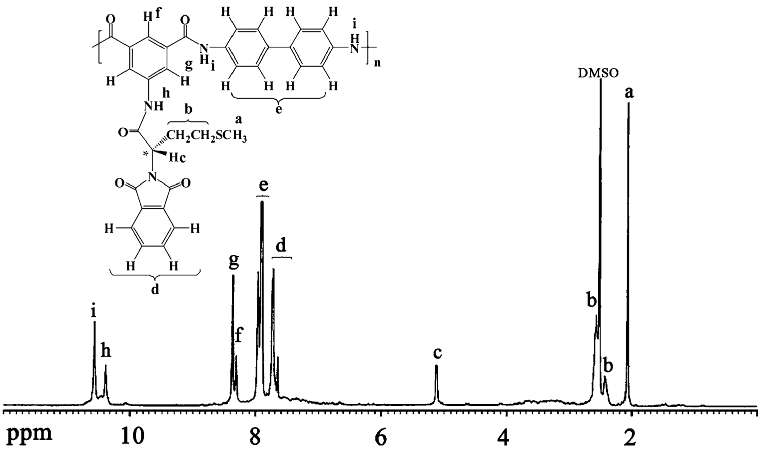


Fig. 2 ^{1}HNMR spectrum of **PA3h** in DMSO-d_6 at RT

Table 1 Synthesis and some physical properties of **PA**s prepared via method **I**

Diamine	Polymer	Yield[a] (%)	η_{inh} (dL/g)[b]	$[\alpha]_{Na,589}^{25,b}$
2a	**PA3aI**	93	0.53	−23.05
2b	**PA3bI**	93	0.57	−21.76
2c	**PA3cI**	95	0.65	−28.62
2d	**PA3dI**	95	0.52	−21.03
2e	**PA3eI**	94	0.50	−26.65
2f	**PA3fI**	93	0.47	−24.93
2g	**PA3gI**	91	0.55	−19.03
2h	**PA3hI**	95	0.52	−26.80

[a] Isolated yields

[b] Measured at a concentration of 0.5 g/dL in DMF at 25 °C

Table 2 Synthesis and some physical properties of **PA**s prepared via method **II**

Diamine	Polymer	Yield[a] (%)	η_{inh} (dL/g)[b]	$[\alpha]_{Na,589}^{25,b}$
2a	**PA3aII**	87	0.45	−20.15
2b	**PA3bII**	90	0.51	−18.65
2c	**PA3cII**	89	0.57	−26.08
2d	**PA3dII**	91	0.42	−20.11
2e	**PA3eII**	92	0.35	−23.68
2f	**PA3fII**	86	0.35	−24.79
2g	**PA3gII**	89	0.44	−17.56
2h	**PA3hII**	90	0.41	−23.65

[a] Isolated yields

[b] Measured at a concentration of 0.5 g/dL in DMF at 25 °C

Thermal properties

The aim of this work was based on the perfection of process abilities, namely increasing the organosolubility, of **PA**s while keeping up their thermal properties, thus we evaluated the thermal resistance of **PA**s based on TGA and DSC analysis.

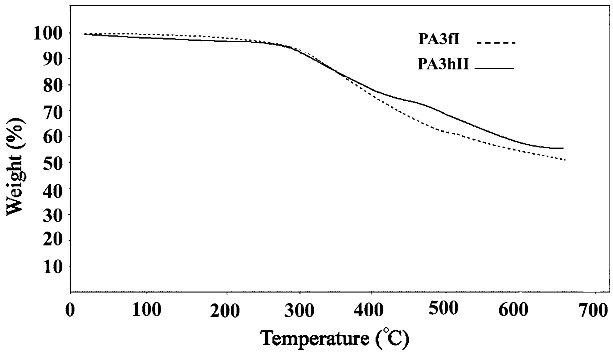


Fig. 3 TGA thermograms of **PA3fI** and **PA3hII**

Table 3 Thermal behavior of **PA**s

Polymer	Decomposition temperature (°C) T_5^a	Decomposition temperature (°C) T_{10}^b	Char yield (%)[c]
PA3fI	275	325	53
PA3hII	272	318	58

[a] Temperature at which 5% weight loss respectively was recorded by TGA at heating rate 10 °C/min in a nitrogen atmosphere

[b] Temperature at which 10% weight loss respectively was recorded by TGA at heating rate 10 °C/min in a nitrogen atmosphere

[c] Percentage weight of material left undecomposed after TGA analysis at maximum temperature 600 °C in a nitrogen atmosphere

The 5% weight loss temperatures for some typical **PA**s were measured by means of TGA analysis and find to be above 270 °C. In addition more than half of the polymers weight remained at 600 °C (char yields). Two exemplar TGA thermograms of **PA**s have been illustrated in Fig. 3. Glass transition temperatures (T_gs) of some **PA**s were considered based on DSC technique and the results show that the T_gs were in the range of 196–198 °C. Good thermal resistance of **PA**s can be attributed to the aromatic nature of polymer backbones. Table 3 contains thermal property details of some typical **PA**s.

Organosolubility of **PA**s

The quantitative organosolubility of **PA**s have been examined in different organic solvents. All of the prepared **PA**s showed good solubility in common dipolar organic solvent such as DMF, DMAc, DMSO and NMP. Other organic solvents with lower polarity, such as acetone, cyclohexane, chloroform, methanol and water did not solve the **PA**s. High tendency to pack the polymer chains is the predominant origin of insolubility of common **PA**s because of ability to create high density of interchain H-bonds. In the case of our synthesized **PA**s, the solubility behavior could be explained by the existence of bulky pendant groups along the polymer chains which confuse the chains packing and thus increase the free volume and diffusion of the organic solvent between polymer chains

Conclusions

Synthesis of a series of **PA**s with superior features such as optical activity, thermal stability, wholly aromatic backbone and of course, organosolubility were the main questions of presented investigation. The combination of optical activity and thermal stability makes the **PA**s to be potentially useful HPLC column packing materials as chiral stationary phases for resolution of racemates. Wholly aromatic nature of polymer backbone cause some advanced characteristics such as high tolerance toward elevated temperatures and chemicals. Organosolubility takes **PA**s away from processing difficulties which are general drawback of common **PA**s. Replacement of the toxic volatile organic solvents with several ecological disadvantages by a green, safe and eco friendly reaction medium is the other aspect of this investigation. Attaining these wants, direct polycondensations of chiral diacid monomer containing L-methionine segment and several aromatic diamines have been investigated in both **IL** medium, which acts as a green solvent and a reaction catalyst, and classical organic solvent. Comparison of these two methods by means of the yields and inherent viscosities of resulting **PA**s 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 (e.g. NMP, $CaCl_2$ and Py), which are essential in conventional methodologies, decreases the cost of polymerization as well as the environmental pollutions, considerably. Moreover, polymerization reactions via method **I** have been completed in shorter period of time (2.5 vs. 5 h) and it can be a desired aspect from energy saving and commercial point of views specially in the industrial large scales polymerization.

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References

1. Nakano T (2001) Optically active synthetic polymers as chiral stationary phases in HPLC. J Chromatogr A 906:205–225
2. Cirilli R, Di Santo R, Artico M, Roux A, Gallinella B, Zanitti L, La Torre F (2003) Enantioselective liquid chromatography of C3-chiral 2, 3-dihydro-1, 2, 5-benzothiadiazepin-4(5H)-one and thione 1, 1-dioxides on polyacrylamide- and polysaccharide-based chiral stationary phases. J Chromatogr A 993:17–28
3. Coa J, Yang NF, Li JC, Yang LW (2007) Helical polymers from optically active epoxides with bulky pendants. Polym Bull 59:481–490
4. Mallakpour S, Kowsari E (2005) Synthesis of organosoluble and optically active poly(ester-imide)s by direct polycondensation with tosyl chloride in pyridine and dimethylformamide. Polym Bull 55:51–59

5. Yuan LM, Xu ZG, Ai P, Chang YX, Fakhrul Azam AKM (2005) Effect of chiral additive on formation of cellulose triacetate chiral stationary phase in HPLC. Anal Chim Acta 554:152–155
6. Itsuno S (2005) Chiral polymer synthesis by means of repeated asymmetric reaction. Prog Polym Sci 30:540–558
7. Hu OS, Sun C, Monaghan CE (2001) Synthesis of optically active polymers with chiral units attached to rigid backbones and their application for asymmetric catalysis. Tetrahedron Lett 42:7725–7728
8. Hu OS, Sun C, Monaghan CE (2002) Optically active dendronized polymers as a new type of macromolecular chiral catalysts for asymmetric catalysis. Tetrahedron Lett 43:927–930
9. HB Y, Hu QS, Pu L (2000) Synthesis of a rigid and optically active poly(BINAP) and its application in asymmetric catalysis. Tetrahedron Lett 41:1681–1685
10. Canali L, Sherrington DC, Deleuze H (1999) Synthesis of resins with pendently-bound chiral manganese-salen complexes and use as heterogeneous asymmetric alkene epoxidation catalysts. React Funct Polym 40:155–168
11. Lopez-Nava R, Vazquez-Moreno FS, Pali-Casanova R, Aguilar-Vega M (2002) Gas permeability coefficients of isomeric aromatic polyamides obtained from 4, 4’-(9-fluorenylidene) diamine and aromatic diacid chlorides. Polym Bull 49:165–172
12. Bruma M, Schulz B, Kopnick T, Stiller B, Belomoina N, Mercer F (1999) Synthesis and study of aromatic polyamides containing silicon and phenylquinoxaline rings in the main chain. Eur Polym J 35:1253–1260
13. Oncio M (2007) Synthesis and properties of new polyamides based on a hydroxyethyl cinnamide extended from 3, 5-diaminobenzoic acid. J Appl Polym Sci 103:2013–2020
14. Kim YJ, Chung IS, In I, Kim SY (2005) Soluble rigid rod-like polyamides and polyamides containing curable pendent groups. Polymer 46:3992–4004
15. Spiliopoulos KI, Mikroyannidis JA (1998) Synthesis of soluble, blue-light-emitting rigid-rod polyamides and polyimides prepared from 2’, 6’, 3’’’, 5’’’-tetraphenyl- or tetra(4-biphenylyl)–4, 4’’’’-diamino-p-quinquephenyl. Macromolecules 31:515–521
16. Mallakpour S, Kolahdoozan M (2008) Synthesis and properties of novel soluble aromatic polyamides derived from 5-(2-phthalimidyl–3-methyl butanoylamino)isophthalic acid and aromatic diamines. React Funct Polym 68:91–96
17. Mallakpour S, Rafiee Z (2008) Use of ionic liquid and microwave irradiation as a convenient, rapid and eco-friendly method for synthesis of novel optically active and thermally stable aromatic polyamides containing N-phthaloyl-L-alanine pendent group. Polym Degrad Stab 93:753–759
18. 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
19. Zulfiqar S, Lieberwirth I, Sarwar MI (2008) Soluble aramid containing ether linkages: synthesis, static and dynamic light scattering studies. Chem Phys 344:202–208
20. Mallakpour S, Yousefian H (2008) Direct polyamidation in molten tetrabutylammonium bromide: novel and efficient green media. Polym Bull 60:191–198
21. 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
22. Paria S (2008) Surfactant-enhanced remediation of organic contaminated soil and water. Adv Colloid Interface Sci 138:24–58
23. Keskin S, Kayrak-Talay D, Akman U, Hortacsu O (2007) A review of ionic liquids towards supercritical fluid applications. J Supercrit Fluids 43:150–180
24. Nakagawa H, Fujino Y, Kozono S, Katayama Y, Nukuda T, Sakaebe H, Matsumoto H, Tatsumi K (2007) Application of nonflammable electrolyte with room temperature ionic liquids (RTILs) for lithium-ion cells. J Power Sources 174:1021–1026
25. Mallakpour S, Kolahdoozan M (2008) Microwave-accelerated preparation of aromatic polyamides containing phthalimide and *S*-valine pendant groups in ionic liquids. Iran Polym J 17:531–539
26. Abdolmaleki A (2007) Synthesis and characterization of some new polyhydrazides by direct polycondensationin ionic liquid. Iran Polym J 16:741–751
27. 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
28. Arbizzani C, Soavi F, Mastragostino M (2006) A novel galvanostatic polymerization for high specific capacitance poly(3-methylthiophene) in ionic liquid. J Power Sources 162:735–737
29. 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

30. Gorke JT, Okrasa K, Louwagie A, Kanzlauskas RJ, Srienc F (2007) Enzymatic synthesis of poly(hydroxyalkanoates) in ionic liquids. J Biotechnol 132:306–313
31. Mallakpour S, Kowsari E (2005) Ionic liquids as novel solvents and catalysts for the direct polycondensation of N, N'-(4, 4'-oxydiphthaloyl)-bis-L-phenylalanine diacid with various aromatic diamines. J Polym Sci Part A Polym Chem 43:6545–6553
32. 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
33. Mallakpour S, Seyedjamali H (2008) Synthesis and characterization of novel organosoluble and optically active aromatic polyesters containing L-methionine and phthalimide pendent groups. Amino Acid 34:531–538