

A QUICK AND GREEN IONIC LIQUID-MEDIATED APPROACH FOR THE SYNTHESIS OF HIGH-PERFORMANCE, ORGANOSOLUBLE AND THERMALLY STABLE POLYIMIDES

Mehdi Taghavi, Mousa Ghaemy*, Marjan Hassanzadeh and Seyed Mojtaba Amini Nasab

*Polymer Chemistry Research Laboratory, Department of Chemistry,
University of Mazandaran, Babolsar 47416-95447, Iran*

Abstract Three diamine monomers with different derivatives of imidazole heterocyclic ring and meta-linked aryl ethers were synthesized and used in polycondensation reaction with various commercial dianhydrides for preparation of a series of novel poly(ether-imide) (PEI)s. The polycondensation reactions were carried out by using conventional method and in a green medium of ionic liquid (IL) without using NMP-pyridine-acetic anhydride. The PEIs were obtained in good yields (80%–96%) with moderate viscosity (0.48–0.66 dL/g) in a shorter reaction time (10 h) in IL as compared with the conventional method (36 h). All of the polymers were amorphous in nature, showed excellent solubility in amide-type polar aprotic solvents with ability to form tough and flexible films, and excellent thermal stability with T_g s in the range of 212–340 °C and 10% weight loss temperature (T_{10}) up to 570 °C in N_2 and 528 °C in air.

Keywords: Ionic liquids; Poly(ether-imide); Polycondensation; Green media; Thermal properties.

INTRODUCTION

Aromatic polyimides, because of their many desirable physicochemical and mechanical characteristics such as high thermal stability, excellent mechanical properties, low dielectric constant, wear resistance, and surface inertness and dissipation factor, have been used extensively as dielectric and electrical insulation materials in microelectronic, aircraft and space applications as structural and sub-structural materials^[1–4]. For these applications it is desirable to use polyimides that are soluble in casting and spin coating processes. However, most of the wholly aromatic polyimides are difficult to process because they have high softening or melting temperatures and are insoluble in most organic solvents^[5–7]. Thus, many studies have focused on designing such chemical structures of the rigid aromatic backbone so as to obtain aromatic polymers that are processable by conventional techniques, while maintaining desirable properties^[8–11]. Most of the approaches for soluble polyimides are aimed at reduction of several types of chain-chain interaction, such as chain packing, charge transfer and electronic polarization interactions. As well known, introduction of geometrically or molecularly unsymmetrical diamine components into the polyimide main chain has led to new polyimides with improved solubility, melt processability and other desirable properties^[12–14].

Ionic liquids (IL)s are designer molecules which can efficiently replace the conventional organic solvents used in chemical processes and have attracted much attention from polymer chemists in various fields because of their unique physical and chemical properties, such as non-flammability, negligible volatility, high ionic conductivity and thermal stability^[15–19]. The ambient temperature ILs especially those based on 1,3-

* Corresponding author: Mousa Ghaemy, E-mail: ghaemy@umz.ac.ir

Received July 11, 2012; Revised August 27, 2012; Accepted August 28, 2012

doi: 10.1007/s10118-013-1258-z

dialkylimidazolium cations have gained considerable interest as promising alternative green solvents in polymer synthesis. The miscibility of ILs with other solvents can also be controlled through a careful choice of the ions, making them attractive as easily containable solvents. In such a system, the advantages of both homogeneous and heterogeneous catalysis, good catalyst efficiency under mild reaction conditions and facile catalyst recovery, respectively, can be combined^[20–23]. Analyzing the application of ILs in polymer synthesis proves their efficiency, so various polycondensation processes were successfully accomplished in ionic medium as well. There have been many reports that the reaction of different diamines with dicarboxylic acids in ILs resulted in the formation of high molecular weight polyamides^[24–26].

In this paper, we wish to report a convenient and environmentally benign green route for the synthesis of novel high-performance PEIs by using imidazolium-based ILs under classical heating conditions. Therefore, three kinds of aromatic unsymmetrical diamine monomers containing different imidazolium-based chemical functional groups and meta-linked aryl ether linkages in their structures were synthesized and used in polycondensation reaction with commercial dianhydrides to obtain optical poly(ether imide)s with good solubility and high thermal stability. These new polyimides were prepared in two different conditions and their properties were investigated.

EXPERIMENTAL

Materials and Measurements

All chemicals were purchased from Fluka and Merck Chemical Co. (Germany) through a local agency. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 0.4 nm molecular sieves. Dianhydrides such as 3,3',4,4'-benzophenone tetracarboxylic dianhydride, pyromellitic dianhydride, 4,4'-oxydiphthalic anhydride and bicyclo[2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic dianhydride were dried in a vacuum oven at 110 °C for 5 h.

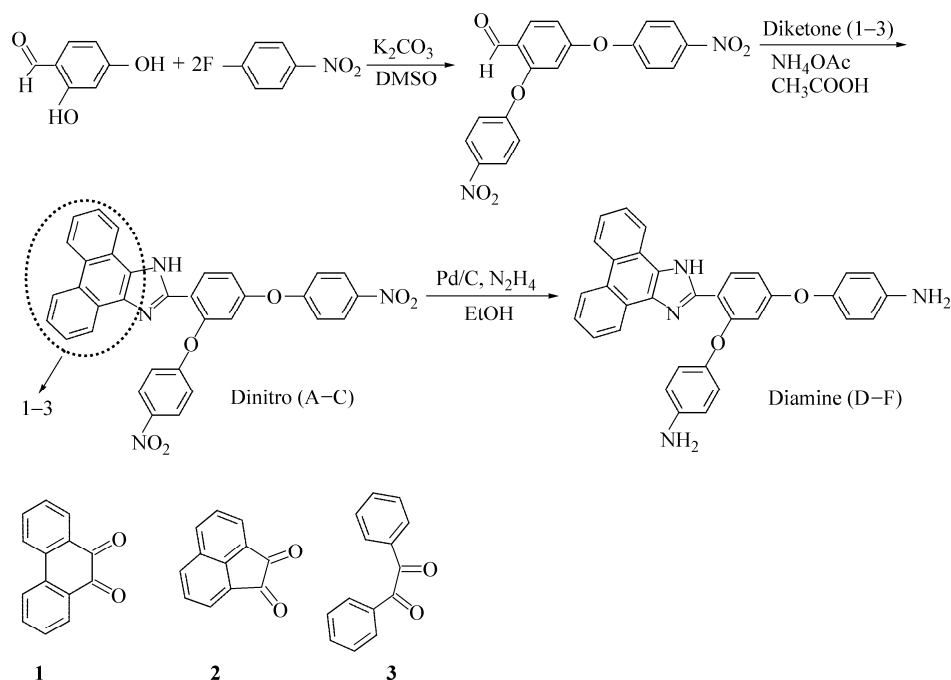
¹H-NMR spectra were recorded on a 400 MHz Bruker (Ettlingen, Germany) instrument using DMSO-*d*₆ as solvent and tetramethylsilane as an internal standard. Elemental analyses were performed by a CHN-600 Leco elemental analyzer. Melting point (uncorrected) was measured with a Barnstead Electrothermal engineering LTD 9200 apparatus. Inherent viscosities (at a concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 25 °C using NMP as solvent. Qualitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. Thermogravimetric analysis (TGA) was performed with the DuPont Instruments (TGA 951) analyzer well equipped with a PC at a heating rate of 10 K/min under nitrogen atmosphere. Differential scanning calorimeter (DSC) was recorded on a Perkin Elmer Pyris 6 DSC under nitrogen and air atmosphere (10 cm³/min) at a heating rate of 10 K/min. Glass-transition temperatures (*T*_g) values were read at the middle of the transition in heat capacity and were taken at a heating rate of 10 K/min in nitrogen atmosphere. Ultraviolet-visible and fluorescence emission spectra were recorded on Cecil 5503 (Cecil Instruments, Cambridge, UK) and Perkin-Elmer LS-3B spectrophotometers (Norwalk, CT, USA) (slit width = 2 nm), respectively, using a dilute polymer solution (0.10 g/dL) in NMP. X-ray powder diffraction patterns were recorded by an X-ray diffractometer (GBC MMA instrument) with Be-filtered CuK α radiation (0.15418 nm) operating at 35.4 kV and 28 mA. The 2θ scanning range was set between 4° and 50° at a scan rate of 0.05° per second.

Ionic Liquids Synthesis

All room temperature ILs were prepared by using procedures reported in the literatures^[20, 21]. The structure of the prepared ILs is given in Table 1, and they were all very viscose liquids at room temperature.

Monomer Synthesis

The synthetic pathway leading to the synthesis of target diamine D–F is outlined in Scheme 1. These diamines were synthesized previously and used in preparation of polyamides^[27].



Scheme 1 Synthesis of target diamines

Polymer Synthesis

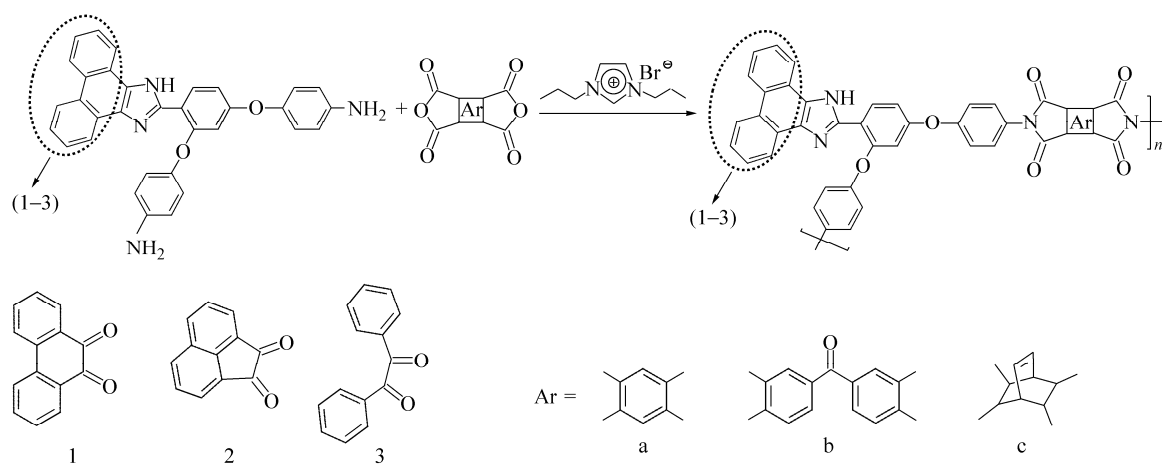
Method I: direct polycondensation using NMP/Py/ Ac_2O

The following general procedure was used for the preparation of PEIs from the diamines D–F and various aliphatic and aromatic dicarboxylic anhydrides. A 100 mL three-necked round-bottomed flask equipped with a condenser, a magnetic stirrer bar, a nitrogen gas inlet tube and a calcium chloride drying tube was charged with 1 mmol (0.51 g) diamine and 10 mL dry NMP, and the mixture was stirred at room temperature for 0.5 h. Thereafter, 1 mmol of a dried dianhydride was added and the mixture was stirred at room temperature for 24 h, forming a viscous solution of poly(amic acid) (PAA) in NMP. The chemical imidization of PAA was carried out by adding 3 mL of a mixture of acetic anhydride/pyridine (6/4, *V/V*) into the solution while stirring at room temperature for 1 h. The mixture was then stirred at 130 °C for 12 h to yield a homogeneous polymer solution, which was poured slowly into methanol to yield a precipitate that was collected by filtration, washed thoroughly with hot methanol and dried at 80 °C in a vacuum oven overnight. The yields were in the range of 72%–86%.

Method II: direct polycondensation using ILs

The following general procedure, as illustrated in Scheme 2, was used for the preparation of PEIs from the diamine and various aliphatic and aromatic dianhydrides.

In a 50 mL round-bottomed three-necked flask equipped with a dropping funnel, a reflux condenser and a magnetic stirrer bar, 1 mmol (0.51 g) diamine (D–F), 1 mmol tetracarboxylic dianhydride and 3 g of IL were stirred at room temperature for 10 min. The temperature was gradually elevated to 180 °C under an inert gas atmosphere and the reaction mixture was held at such temperature and stirring for 10 h. An additional 0.5 g IL was added to the mixture. As the reaction proceeded, the solution became viscous. The reaction mixture was then cooled to room temperature and the resulting polymers were precipitated in 100 mL methanol. The precipitate was filtered and washed with hot water, and then was further purified by washing with refluxing methanol for 24 h in a soxhlet apparatus to remove the low molecular weight oligomers. The inherent viscosity (η_{inh}) of the resulting PEIs was in the range of 0.48–0.66 dL g^{−1}, measured at a concentration of 0.5 g/dL in NMP at 25 °C. The above procedure was used for the preparation of all PEIs given below.



Scheme 2 Polycondensation reactions of the diamine with different dianhydrides

PEI1a

This PEI was prepared from the diamine (D) and pyromellitic dianhydride. Yield = 91% and η_{inh} (dL/g) = 0.62. FT-IR (KBr disk) at cm^{-1} : 3482 (N—H imidazole), 3046 (C—H aromatic), 1777 and 1728 (C=O imide), 1609 (C=N), 1504 (C=C), 1372 (C—N), 1264 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.45 (s, 1H), 6.49–8.33 (m, 21H). Elemental analysis calculated for $(C_{43}H_{22}N_4O_6)_n$: C, 74.78%; H, 3.19%; N, 8.12%. Found: C, 74.69%; H, 3.28%; N, 8.09%.

PEI1b

This PEI was prepared from the diamine (D) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride. Yield = 95% and η_{inh} (dL/g) = 0.64. FT-IR (KBr disk) at cm^{-1} : 3468 (N—H imidazole), 3051 (C—H aromatic), 1782 and 1725 (C=O imide), 1720 (C=O ketone), 1603 (C=N), 1522 (C=C), 1367 (C—N), 1258 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.58 (s, 1H), 6.62–8.41 (m, 25H). Elemental analysis calculated for $(C_{50}H_{26}N_4O_7)_n$: C, 75.57%; H, 3.27%; N, 7.05%. Found: C, 75.47%; H, 3.38%; N, 7.02%.

PEI1c

This PEI was prepared from the diamine (D) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. Yield = 86% and η_{inh} (dL/g) = 0.56. FT-IR (KBr disk) at cm^{-1} : 3462 (N—H imidazole), 3060 (C—H aromatic), 2911 (C—H aliphatic), 1782 and 1714 (C=O imide), 1607 (C=N), 1512 (C=C), 1380 (C—N), 1210 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.37 (s, 1H), 7.11–8.24 (m, 19H), 6.31 (m, 2H), 2.63 (m, 4H), 2.19 (m, 2H). Elemental analysis calculated for $(C_{45}H_{28}N_4O_6)_n$: C, 75.00%; H, 3.89%; N, 7.78%. Found: C, 74.96%; H, 4.00%; N, 7.78%.

PEI2a

This PEI was prepared from the diamine (E) and pyromellitic dianhydride. Yield = 88% and η_{inh} (dL/g) = 0.57. FT-IR (KBr disk) at cm^{-1} : 3482 (N—H imidazole), 3059 (C—H aromatic), 1780 and 1726 (C=O imide), 1606 (C=N), 1502 (C=C), 1375 (C—N), 1260 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.50 (s, 1H), 6.39–8.34 (m, 19H). Elemental analysis calculated for $(C_{41}H_{20}N_4O_6)_n$: C, 74.10%; H, 3.01%; N, 8.43%. Found: C, 74.01%; H, 3.15%; N, 8.45%.

PEI2b

This PEI was prepared from the diamine (E) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride. Yield = 90% and η_{inh} (dL/g) = 0.59. FT-IR (KBr disk) at cm^{-1} : 3466 (N—H imidazole), 3041 (C—H aromatic), 1776 and 1734 (C=O imide), 1728 (C=O ketone), 1605 (C=N), 1522 (C=C), 1369 (C—N), 1259 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.44 (s, 1H), 6.49–8.28 (m, 23H). Elemental analysis calculated for $(C_{48}H_{24}N_4O_7)_n$: C, 75.00%; H, 3.12%; N, 7.30%. Found: C, 74.88%; H, 3.19%; N, 7.30%.

PEI2c

This PEI was prepared from the diamine (E) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. Yield = 80% and η_{inh} (dL/g) = 0.48. FT-IR (KBr disk) at cm^{-1} : 3459 (N—H imidazole), 3053 (C—H aromatic), 2914 (C—H aliphatic), 1785 and 1711 (C=O imide), 1600 (C=N), 1503 (C=C), 1382 (C—N), 1219 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.47 (s, 1H), 7.23–8.38 (m, 17H), 6.36 (m, 2H), 2.69 (m, 4H), 2.27 (m, 2H). Elemental analysis calculated for $(C_{43}H_{26}N_4O_6)_n$: C, 74.35%; H, 3.75%; N, 8.07%. Found: C, 74.29%; H, 3.84%; N, 8.02%.

PEI3a

This PEI was prepared from the diamine (F) and pyromellitic dianhydride. Yield = 92% and η_{inh} (dL/g) = 0.64. FT-IR (KBr disk) at cm^{-1} : 3494 (N—H imidazole), 3059 (C—H aromatic), 1780 and 1729 (C=O imide), 1603 (C=N), 1507 (C=C), 1370 (C—N), 1264 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.42 (s, 1H), 6.30–8.21 (m, 23H). Elemental analysis calculated for $(C_{43}H_{24}N_4O_6)_n$: C, 74.57%; H, 3.47%; N, 8.09%. Found: C, 74.49%; H, 3.58%; N, 8.01%.

PEI3b

This PEI was prepared from the diamine (F) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride. Yield = 96% and η_{inh} (dL/g) = 0.66. FT-IR (KBr disk) at cm^{-1} : 3494 (N—H imidazole), 3059 (C—H aromatic), 1780 and 1734 (C=O imide), 1724 (C=O ketone), 1608 (C=N), 1521 (C=C), 1370 (C—N), 1259 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.46 (s, 1H), 6.32–8.33 (m, 27H). Elemental analysis calculated for $(C_{50}H_{28}N_4O_7)_n$: C, 75.38%; H, 3.52%; N, 7.03%. Found: C, 75.39%; H, 3.65%; N, 7.02%.

PEI3c

This PEI was prepared from the diamine (F) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride. Yield = 90% and η_{inh} (dL/g) = 0.57. FT-IR (KBr disk) at cm^{-1} : 3453 (N—H imidazole), 3064 (C—H aromatic), 2928 (C—H aliphatic), 1780 and 1714 (C=O imide), 1603 (C=N), 1507 (C=C), 1380 (C—N), 1219 (C—O). ^1H -NMR (400 MHz, DMSO- d_6 , δ): 12.35 (s, 1H), 7.16–8.33 (m, 21H), 6.29 (m, 2H), 2.67 (m, 4H), 2.20 (m, 2H). Elemental analysis calculated for $(C_{45}H_{30}N_4O_6)_n$: C, 74.79%; H, 4.15%; N, 7.76%. Found: C, 74.67%; H, 4.30%; N, 7.73%.

RESULTS AND DISCUSSION

Synthesis and Characterization of Diamines and PEIs

The aim of this study was the preparation of new thermally stable and organosoluble PEIs containing different substituted bulky pendants and unsymmetrically meta-arylether linkage in the backbone of polymer. First, compound 1 was successfully synthesized from 1-fluoro-4-nitrobenzene and 2,4-dihydroxy benzaldehyde as starting materials by the nucleophilic fluorodisplacement reaction according to the synthetic route shown in Scheme 1. The structure of this compound was identified by elemental analysis, FT-IR and ^1H -NMR spectroscopy^[27].

Polycondensation in NMP/Py/ Ac_2O , is one of the effective methods for the synthesis of aromatic PIs. However, the usage of such aggressive solvents and partial hydrolysis of the formed polymers during their isolation and purification complicate this process. For the advancement of ecological safety and improvement of technological ability of this process, IL solvents based on the imidazolium cations were used as a reaction medium. The reaction proceeded efficiently in ILs allowing PEIs synthesis by direct polycondensation of dianhydride and diamines without using NMP, Ac_2O and pyridine (Py). Room temperature ILs, predominantly those based on the substituted imidazolium cations which can be prepared simply from the commercially available starting materials, *N*-trimethylsilylimidazole and alkyl halides, were used in this investigation^[20, 21]. Thus, different symmetrical 1,3-dialkylimidazolium ILs bearing Br^- , PF_4^- and BF_4^- anions, shown in Table 1, were prepared and used as polycondensation media. These ILs are soluble in the polar solvents such as water and methanol, which allowed the complete isolation of obtained polymers. In order to find out the effect of ILs nature on the yield and viscosity of the polymer, the synthesis of PEI1 was carried out in different imidazolium

type ILs at a selected reaction temperature. IL needs to be liquid and thermally stable near the reaction temperature and a good solvent for initial monomers and the resulting polymers. These ILs were all very viscose liquids at room temperature. Therefore, the choice of polycondensation temperature (130 °C) was being determined by the viscosity of the ILs and solubility of the diamine and the corresponding polymers. Although PEI1 was soluble in all used ILs, but as alkyl chain in IL increased the yield and viscosity of the polymer decreased. This may be due to the decrease of polarity of IL as a result of increase in the alkyl chain which explains the lower mobility of polymer chains in ILs of longer alkyl chain. The polymer PEI3b with the highest yield and viscosity was obtained when [1,3-(Pr)₂im]Br was used as the reaction media, as shown in Table 1, and this IL was also selected for the synthesis of other PEIs. As far as anions were concerned, the best results were achieved in ILs with Br⁻. The optimum time of polycondensation was determined by measuring the yield and viscosity of PEI3b in the selected IL and temperature, the results are shown in Fig. 1. Therefore, all of the PEIs (1a–3c), as designated in Scheme 2, were prepared in two different reaction conditions; in direct polycondensation reactions by using NMP/Py/Ac₂O and by using only IL of [1,3-(Pr)₂im]Br.

Table 1. The influence of IL cation and anion upon yield and viscosity (η_{inh}) of PEI3b

Polymer	IL	Yield (%)	η_{inh}^a (dL/g)
PEI3b	1,3-Dipropyl imidazolium bromide	96	0.66
PEI3b	1,3-Diisopropyl imidazolium bromide	90	0.64
PEI3b	1,3-Dibutyl imidazolium bromide	88	0.59
PEI3b	1,3-Dipentyl imidazolium bromide	83	0.58
PEI3b	1,3-Dihexyl imidazolium bromide	72	0.55
PEI3b	1,3-Diheptyl imidazolium bromide	72	0.53
PEI3b	1,3-Dibutyl imidazolium tetrafluoroborate	70	0.54
PEI3b	1,3-Dibutyl imidazolium hexafluorophosphate	64	0.41

^a Measured at a concentration of 0.5 g/dL in NMP at 25 °C

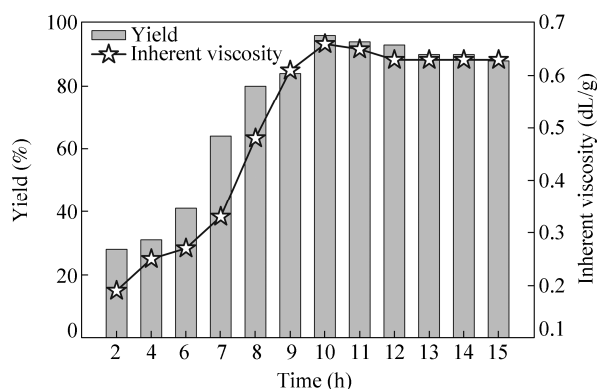


Fig. 1 Optimum conditions for the synthesis of PEI3b in IL

The results in Table 1 demonstrated the beneficial effect of using IL in the synthesis of PEIs in addition to other useful properties such as non-volatility and reusability of ILs. Furthermore, removal of some chemicals (e.g. NMP, Py and Ac₂O) which are essential in conventional direct polycondensation and also longer period of time (36 h versus 10 h) increase the cost of polymerization as well as the environmental pollution which all together are the desired aspects for energy saving. The PEIs were obtained as light brown powders with good yields, 80%–96%, after extraction with refluxing methanol for 24 h to remove low fraction oligomers, and their inherent viscosities were in the range of 0.48–0.66 dL/g indicating medium molecular weights. The aforementioned results can serve as evidence that ILs are the effective alternative to the previously used aggressive and toxic media. Because of their nature the ILs have very low vapor pressure and are characterized by the absence of strong acid or alkaline properties; therefore, the risk of polymer's hydrolysis at the isolation

along with the necessity of its thorough purification are no longer relevant. The polymer structures were confirmed by elemental analysis, FT-IR and $^1\text{H-NMR}$ spectroscopic techniques. The characteristic absorption bands of the five-membered imide ring appeared at 1785 and 1723 cm^{-1} , corresponding to asymmetric and symmetric $\text{C}=\text{O}$ stretching, at 1375 cm^{-1} related to $\text{C}-\text{N}$ stretching, and at 1094 and 763 cm^{-1} because of imide ring deformation. The $^1\text{H-NMR}$ spectrum of PEI1 in DMSO-d_6 , Fig. 2, showed peaks of aromatic protons at $\delta = 7.06\text{--}8.85$ and N-H of imidazole ring at $\delta = 12.61$, all of which were well assigned to the supposed chemical structure and no peaks attributable to amic acids were detected. The integration ratio of these peaks also agreed with the structure. The elemental analysis values generally agreed with the calculated values for the proposed structures of polymers.

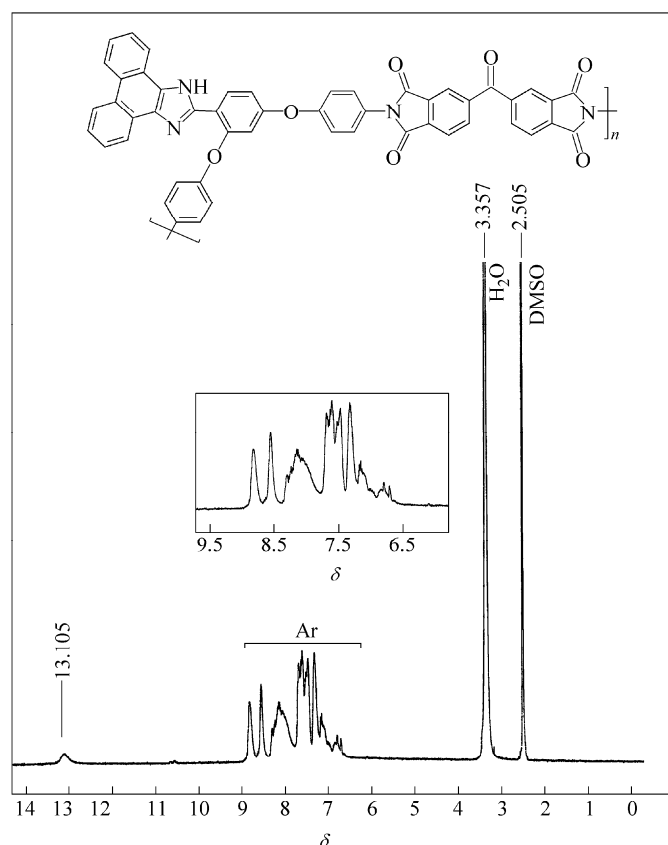


Fig. 2 $^1\text{H-NMR}$ spectrum of PEI2b in DMSO-d_6

Polymer Properties

X-ray diffraction and solubility of the PEIs

The prepared PEIs powder samples were examined for crystallinity by using X-RD analysis with graphite-monochromatized $\text{CuK}\alpha$ radiation and with 2θ ranging from 0° to 50° . The representative X-ray diffractograms in Fig. 3 indicate that all the PEIs are amorphous in nature and this can be mainly explained by the unsymmetrical macromolecular chain and presence of bulky diarylimidazole pendant. The amorphous nature of the PEIs was also reflecting their good solubility in polar organic solvents. The solubility behavior of the PEIs was tested qualitatively in several organic solvents at 50 g/L, and the results are summarized in Table 2. In general, these polymers exhibited good solubility in a variety of aprotic polar solvents such as NMP, DMAc, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine and *m*-cresol at room temperature or upon heating at 60°C . This can be due to the unsymmetrical meta-ether linkages in the polymer backbone and also bulky pendant which prevent macromolecular chains to pack closely. The presence of distance between the

polymer chains leads to penetration of solvent polar molecules into the chains and interaction with the polar linkages in the polymer backbone. Therefore, we believe that the presence of imidazole and ether groups in the pendant and in the main chain, respectively, can contribute effectively in the solubility of these polymers by interacting with the polar molecules of solvents. In addition, the PEIs synthesized from aliphatic dianhydride and benzyl such as PEI3c showed better solubility in less polar solvents such as pyridine, THF and *m*-cresol which can be due to presence of less bulky pendant and particularly due to methylene units in the main chain. However, the average molecular weights of these PEIs were not detectable by GPC because of they did not have good solubility in THF eluent at room temperature.

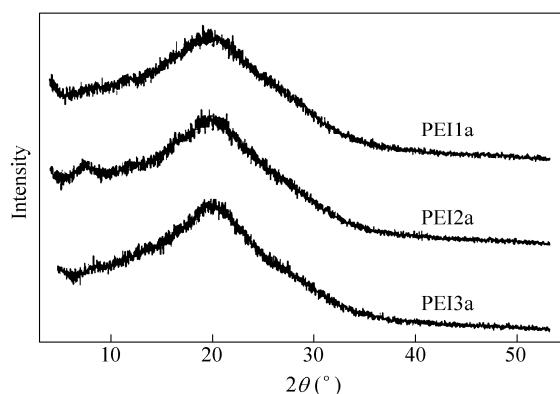


Fig. 3 X-ray diffraction patterns of PEI1a, PEI2a and PEI3a

Table 2. Solubility of synthesized PEI1a–PEI3c

Code	Solvent										
	Yield (%)	η_{inh} (dL/g) ^a	DMAc	DMF	NMP	DMSO	Py	THF	CHCl ₃	CH ₃ CN	<i>m</i> -Cresol
PEI1a	91	0.62	++	++	++	++	±	–	–	–	±
PEI1b	95	0.64	++	++	++	++	+	±	–	–	±
PEI1c	86	0.56	++	++	++	++	+	±	–	–	+
PEI2a	88	0.57	++	++	++	++	–	–	–	–	–
PEI2b	90	0.59	++	++	++	++	±	–	–	–	–
PEI2c	80	0.48	++	++	++	++	+	–	–	–	±
PEI3a	92	0.64	++	++	++	++	+	–	–	–	±
PEI3b	96	0.66	++	++	++	++	++	±	–	–	+
PEI3c	90	0.57	++	++	++	++	++	+	–	–	++
PEI3a'	86	0.54	++	++	++	++	+	–	–	–	±
PEI2b'	72	0.42	++	++	++	++	–	–	–	–	–
PEI1c'	81	0.56	++	++	++	++	±	–	–	–	±

++, soluble at room temperature; +, soluble on heating at 60 °C; ±, partially soluble on heating at 60 °C; –, insoluble on heating at 60 °C;

^a Measured at a polymer concentration of 0.5 g/dL in NMP at 25 °C;

PEI1a–PEI3c and PEI3a'–PEI1c' were synthesized in IL/TPP and NMP/TPP/Py/LiCl media, respectively.

Photophysical properties of PEIs

The photophysical properties of the PEIs were investigated by UV-visible and fluorescence spectroscopy in NMP solutions. The absorption and fluorescence spectra of PEIs films are shown in Figs. 4(a) and 4(b), respectively, and the data are listed in Table 3. These PEIs showed strong UV absorption in the range of $\lambda_{max} = 306–319$ nm in dilute (0.2 g/dL) NMP solutions and in the films. This absorption can be assigned mainly to $\pi-\pi^*$ and to some extent to $n-\pi^*$ transitions resulting from the conjugation between the aromatic rings and nitrogen

atom in the pendent group. The similarity of the absorption spectra of the polymers in the series of PEI1, PEI2 and PEI3 demonstrates the identical absorbing chromophore of the conjugated core of the pendent group in all of these polymers. The absorption spectra of the series of PEI2 are red-shifted between 2 nm to 5 nm in comparison with spectra of the series of PEI1 and PEI3 which can be due to the extension of conjugation of the backbone of these polymers.

Figure 4(b) shows the emission spectra of the polymers films, and the data extracted from the spectra of polymers in solutions and in films are in the range of 431–466 nm as listed in Table 3. The excitation wavelength was 310 nm in all cases. To measure the photoluminescence (PL) quantum yields (Φ_f), dilute polymer solutions (0.2 g/dL) in NMP were prepared. A 0.1 mol/L solution of quinine in H_2SO_4 ($\Phi_f = 0.53$) was used as a reference^[28]. Polymers of the PEI1 showed higher intensity in peak maximum and also higher values of quantum yields, in Table 3, in comparison with the polymers in the series of PEI2 and PEI3. Polymer PEI1 has fused phenyl rings in the pendent unit and is restricted in free rotation, thus a minimum amount of energy can be lost as heat and most of the received energy emits as light. Polymer PEI2 has low fluorescence intensity due to presence of naphthalene pendant which hinders extension of conjugation with the imidazole chromophore. Moreover, the emission intensity of aliphatic and aromatic PEIs was not exactly the same, which confirms that the fluorescence intensity is affected by incorporation of alkyl and phenyl groups into the polymer main chain. The aliphatic polymers (PEI1c, PEI2c, and PEI3c) exhibited blue shift with higher quantum yield. The higher quantum yield of these polymers can be attributed to the effectively reduced conjugation and capability of charge-transfer complex formation by aliphatic diacids with the electron-donating diamine moiety in comparison with that of the stronger electron-accepting aromatic diacids^[29].

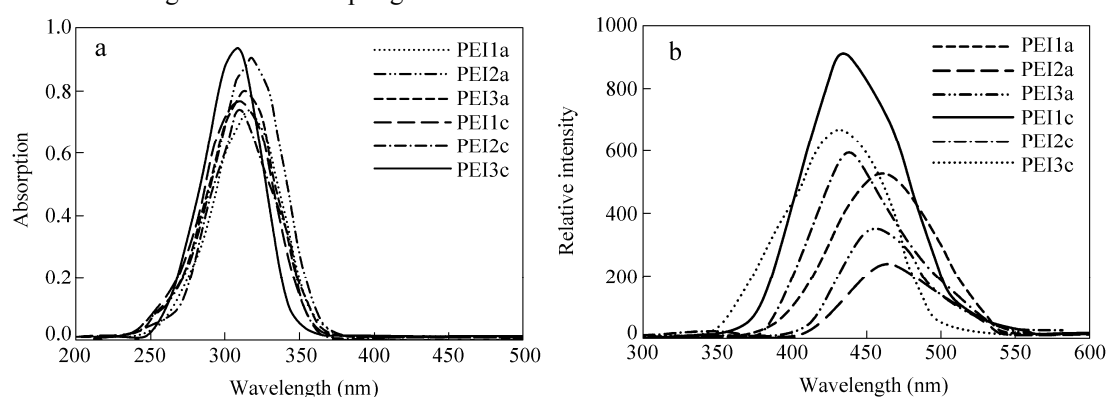


Fig. 4 UV-Vis (a) and fluorescence (b) spectra of PEI1a, PEI2a, PEI3a, PEI1c, PEI2c and PEI3c films

Table 3. Optical properties data of PEI1a–PEI3c

Polymer	λ_{abs} (nm) ^a	λ_{em} (nm) ^a	λ_{abs} (nm) ^b	λ_{em} (nm) ^b	Φ_f (%) ^c
PEI1a	315	457	316	462	15
PEI1b	315	452	317	454	11
PEI1c	306	433	309	435	26
PEI2a	316	462	318	466	7
PEI2b	317	453	319	456	5
PEI2c	308	436	310	437	17
PEI3a	311	450	314	454	10
PEI3b	312	446	316	451	7
PEI3c	306	430	308	431	19

Polymer concentration of 0.20 g/dL in NMP;

^{a, b} UV-Visible absorption and fluorescence emission spectra of the PEIs in solution (a) and in films (b), respectively;

^c Fluorescence quantum yield relative to 10^{-5} mol/L quinine sulfate in 0.5 mol/L H_2SO_4 (aq) ($\Phi_f = 0.55$) as a standard

Thermal properties

DSC and TGA methods were applied to evaluate thermal properties of the polymers. The DSC curves of the PEIs are shown in Fig. 5, and the thermal analysis data extracted from the original curves are summarized in Table 4. The measurements were performed at a heating rate of 10 K/min under nitrogen atmosphere. None of these polymers showed clear melting endotherms in the DSC thermograms, suggesting the amorphous nature of these polymers. The T_g values of these PEIs were measured by DSC (T_g was taken as the midpoint of the change in slope of the baseline), and ranged from 212 °C to 340 °C depending upon the stiffness of the main chain and thus the used dianhydride. Therefore, among the prepared polymers the series of PEIa based on pyromellitic dianhydride showed the highest T_g value and the series of PEIc based on alicyclic dianhydride showed the lowest T_g values. In general, the T_g values of these polymers are influenced and balanced by the net effect of two key factors: (1) The incorporation of bulky substituted imidazole side groups along the backbone restricts the free rotation of the macromolecular chains and leads to the enhancement of T_g values, and (2) the presence of flexible bonds such as ether linkage in the main chain of a polymer lowers the rigidity of its backbone and reduces the T_g values.

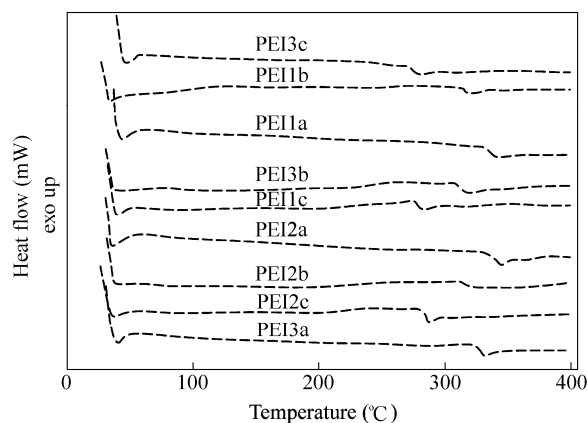


Fig. 5 DSC curves of PEI1a–PEI3c under N₂ at a heating rate of 10 K/min

Table 4. Thermal properties of new synthesized PEIs

Code	T_g (°C) ^a	T_{10} (°C) ^b	T_{10} (°C) ^c	Char yield ^d	LOI (%) ^e
PEI1a	336	552	521	65	44
PEI1b	315	538	469	64	43
PEI1c	279	454	429	45	36
PEI2a	340	570	528	69	45
PEI2b	317	544	471	65	44
PEI2c	285	461	451	49	37
PEI3a	330	540	512	64	43
PEI3b	322	530	463	62	42
PEI3c	212	450	420	42	34
PEI3a'	330	540	510	62	42
PEI2b'	310	535	458	61	42
PEI1c'	268	446	418	40	34

^a Glass transition temperature was recorded at a heating rate of 10 K/min in N₂;

^b Temperature at which 10% weight loss was recorded by TGA in N₂;

^c Temperature at which 10% weight loss was recorded by TGA in air;

^d Percentage weight of material left undecomposed after TGA analysis at a temperature of 800 °C in N₂;

^e Limiting oxygen index percent evaluating at char yield 800 °C;

PEI1a–PEI3c and PEI3a'–PEI1c' were synthesized in IL/TPP and NMP/TPP/Py/LiCl media, respectively.

Thermal stability of these polymers was evaluated by TGA in N₂ and air atmosphere, and the curves are shown in Figs. 6(a) and 6(b), respectively. TGA data presented in Table 4 show that the temperature of 10% weight loss ($T_{10\%}$) was in the range of 450–570 °C and 420–528 °C in N₂ and air atmosphere, respectively. All of these polymers exhibited good thermal stability with insignificant weight loss up to 420 °C in air. The residual weight retentions at 800 °C for the resulting PEIs were in the range of 42%–69% in N₂. Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation^[30]. $LOI = 17.5 + 0.4CR$ where CR = char yield. For all the polymers LOI values were calculated based on their char yield at 800 °C. According to Table 4, it is clear that aromatic PEIs have better thermal stability and higher LOI as compared to the aliphatic PEIs. This can be pertained to the rigid structure of aromatic diacids compared to the flexible structure of aliphatic diacids. Therefore, the PEI1 and PEI3 have the highest and the lowest thermal stability, respectively, which is due to the presence of rigid phenyl and flexible aliphatic units in their backbones.

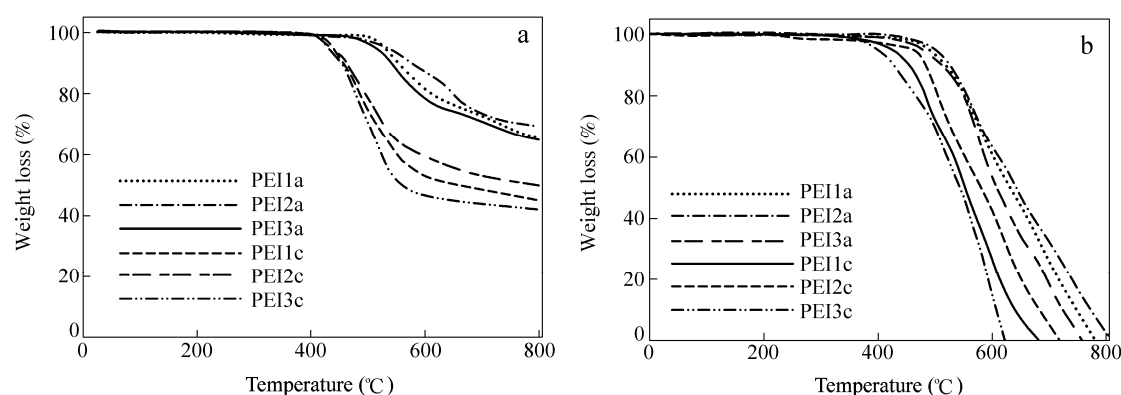


Fig. 6 TGA curves of PEI1a, PEI2a, PEI3a, PEI1c, PEI2c and PEI3c under N₂ (a) and air (b) at a heating rate of 10 K/min

CONCLUSIONS

Three diamine monomers bearing collective functional groups of flexible ether linkages and bulky derivatives of imidazole heterocyclic ring with an asymmetric molecular structure were synthesized and polymerized with commercially available aromatic and alicyclic dianhydrides *via* a conventional two-stage method using chemical imidization agents and a single-stage method in ionic liquid. In general, the results demonstrated the beneficial effects of using IL media, such as good yields and moderate viscosity, shorter period of reaction time, not being needed to remove some chemicals (*e.g.* NMP, Py and Ac₂O), and non-volatility. These amorphous polymers exhibited good solubility in common polar aprotic organic solvents and could be solution cast into transparent tough films. They also showed high thermal stability and light emitting properties because of the presence of aryl derivatives of imidazole ring. Therefore, these PEIs may be considered as promising processable high temperature materials for applications in microelectronic and optical devices.

REFERENCES

- 1 Wilson, D., Stenzenberger, H.D. and Hergenrother, P.M., "Polyimides", Chapman and Hall, New York, 1990
- 2 Ghosh, M.K. and Mittal, K.L., "Polyimides fundamentals and applications", Marcel Dekker, New York, 1996
- 3 Maier, G., Prog. Polym. Sci., 2001, 26: 3
- 4 Shao, Y., Li, Y., Zhao, X., Ma, T., Gong, C. and Yang, F., Eur. Polym. J., 2007, 43: 4389
- 5 Liu, J.G., He, M.H., Qian, Z.G. and Yang, S.Y., J. Polym. Sci. Part A: Polym. Chem., 2002, 40: 1572

- 6 Amini Nasab, S.M. and Ghaemy, M., *J. Polym. Res.*, 2011, 18:1575
- 7 Ghaemy, M. and Barghamadi, M., *J. Appl. Polym. Sci.*, 2009, 112: 815
- 8 Ghaemy, M. and Khajeh, S., *Chinese J. Polym. Sci.*, 2011, 29(4): 465
- 9 Faghihi, K. and Hajibeygi, M., *Chinese J. Polym. Sci.*, 2010, 28(4): 517
- 10 Ghaemy, M. and Bazzar, M., *J. Appl. Polym. Sci.*, 2011, 119: 983
- 11 Huang, X.H., Huang, W., Zhou, Y.F. and Yan, D.Y., *Chinese J. Polym. Sci.*, 2011, 29(4): 506
- 12 Liou, G.S., Hsiao, S.H., Huang, N.K. and Yang, Y.L., *Macromolecules*, 2006, 39: 5337
- 13 Ghaemy, M. and Amini Nasab, S.M., *Polym. J.*, 2010, 42: 648
- 14 Ghaemy, M. and Alizadeh, R., *Eur. Polym. J.*, 2009, 45:1681
- 15 Mohammad, A. and Inamuddin, A., "Green solvents I, properties and applications in chemistry", Springer, London, 2012
- 16 Wasserscheid, P. and Welton, T., "Ionic liquids in synthesis", Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2002
- 17 Przemyslaw, K., *Prog. Polym. Sci.*, 2004, 29: 3
- 18 Lu, J., Yan, F. and Texter, J., *Prog. Polym. Sci.*, 2009, 34: 431
- 19 Welton, T., *Chem. Rev.*, 1999, 99: 2071
- 20 Mallakpour, S. and Taghavi, M., *Polymer*, 2008, 49: 3239
- 21 Vygodskii, Y.S., Lozinskaya, E.I. and Shaplov, A.S., *Macromol. Rapid Commun.*, 2002, 23: 676
- 22 Lozinskaya, E.I., Shaplov, A.S., Kotseruba, M.V., Komarova, L.I., Lyssenko, K.A. and Antipin, M.Y., *J. Polym. Sci. Part A: Polym. Chem.*, 2006, 44: 380
- 23 Lozinskaya, E.I., Shaplov, A.S. and Vygodskii, Y.S., *Eur. Polym. J.*, 2004, 40: 2065
- 24 Kubisa, P., *J. Polym. Sci. Part A: Polym. Chem.*, 2005, 43: 4675
- 25 Yoneyama, M., *High. Perform. Polym.*, 2006, 18: 817
- 26 Vygodskii, Y.S., Ozinskaya, L.E.I., Shaplov, A.S., Lyssenko, K.A., Antipin, M.Y. and Urman, Y.G., *Polymer*, 2004, 45: 5031
- 27 Ghaemy, M., Amini Nasab, S.M., Taghavi, M. and Hassanzadeh, M., *J. Polym. Res.*, 2012, 19: 9905
- 28 Feng, K., Hsu, F.L., van DerVeer, D., Bota, K. and Bu., X.R., *J. Photochem. Photobiol. A: Chem.*, 2004, 165: 223
- 29 Liou, G.S. and Chang, C.W., *Macromolecules*, 2008, 41: 1667
- 30 van Krevelen, D.W. and Nijenhuis, K.T., "Properties of polymers", 4th Ed., Elsevier Scientific Publishing, Amsterdam, 2008