

Ionic liquids as green reaction media for synthesis of poly(aryl ether ketone)s

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Poly(aryl ether ketone)s (PAEKs) were successfully synthesized via nucleophilic aromatic substitution (S_NAR) mechanism, using ionic liquids as green reaction media. The influence of various reaction parameters including monomer concentration, dehydration time, polymerization temperature and duration, IL's cations and anions nature, upon PAEKs molecular weight was investigated. In addition, the peculiarities of hydrogen-bonding ability of ILs were investigated. The interaction of 2,2-bis(4-hydroxyphenyl) propane (bisphenol A) with ILs has a strong influence on PAEKs synthesis. Various moderate molecular weight PAEKs have been obtained in high yields with molecular weights ranging from 10000 to 18000 g mol^{-1} .

high performance polymers, ionic liquids, poly(aryl ether ketone)s, polycondensation

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Poly (aryl ether ketone)s (PAEKs) belong to a category of materials known as special engineering thermoplastics, which exhibit many outstanding characteristics including excellent mechanical, thermo-oxidative and chemical resistance properties [1–3]. These polymers are expected to find use in engineering applications and membrane technology. One of the most recently developed of these materials is poly (ether ether ketone) (PEEK). Owing to the semi-crystalline structure, high melting point and poor solubility in classical organic solvents, the application of this high performance polymer has been limited. It is well known that the incorporation of aliphatic chain into the polymer backbone is a tool to improve polymer solubility. Therefore, attempts have been made to develop new varieties of this material such as bisphenol A type PAEKs to improve the processing characteristics [4,5]. Generally, PAEKs were synthesized by the reaction of bisphenoxides with bis (aryl halides) via nucleophilic aromatic substitution (S_NAR) mechanism [6]. The choices of solvents are usually *N,N*-

dimethylacetamide and *N*-methyl-2-pyrrolidone, which are volatile, flammable, toxic and harmful. Thus, removing organic solvents in polymer synthesis is a very important topic in the drive towards environmentally friendly technologies.

Recently, ionic liquids (ILs) attract more attention due to their low volatility, chemical stability, high thermal stability and ionic conductivity, etc [7–9]. Thus, ILs have become an alternative replacement for volatile organic compounds. In the last decades, high performance polymers such as polyimides and poly [naphthoylene bis-(benzimidazole)]s with high molecular weight were obtained in ILs as reaction medium [10]. A series of polyamides are generated in ILs coupling with microwave heating [11]. Moreover, aliphatic polyesters were successfully synthesized in sulfonic acid group-containing ILs [12]. Recently, our group developed a novel strategy to prepare high molecular weight polysulfone in imidazolium-based ionic liquids [13]. These forementioned studies demonstrate that the use of ILs has reactive effects on polymerization and make it possible to introduce ILs into polymer synthesis as green reaction media. However,

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the syntheses of high performance polymers especially PAEKs are still difficult. This is the first report of PAEKs synthesis in ionic liquids.

Herein, we present the development of new synthetic method for high performance PAEKs by using ILs as reaction media. Optimization of reaction conditions including the monomer concentration, dehydration time, polymerization temperature and duration was investigated. The interaction of ILs with bisphenol A was also studied. We intend to find an efficient way to gain high molecular weight of PAEKs. The structure of resulting polymers was confirmed by Elemental Analysis, FTIR and ^1H NMR spectroscopies.

1 Experimental

1.1 Materials and methods

N-methylimidazole was distilled under reduced pressure. All alkyl halides (aladdin, 99%), 1-butylimidazole (Aldrich, 98%), 4,4'-difluorobenzophenone (DFB) and 2,2-bis(4-hydroxyphenyl) propane (bisphenol A) (aladdin, 98%) were purified by recrystallizing from hot toluene. Ionic liquids and potassium carbonate were dried under vacuum before usage to eliminate the trace amount of water. Other solvents were utilized as received. ^1H NMR spectra were recorded on a Bruker Advance DRX-500 NMR spectrometer in DMSO- d_6 solutions. The molecular weight analysis was performed using a Polymer Laboratories gel permeation chromatograph (PL-GPC50) equipped with UV detector. The columns used are PL gel mixed-B by using chloroform as eluent with a flow rate of 1.0 mL min^{-1} . Polystyrene standards were used to calibrate the system.

1.2 Preparation of ionic liquids

All of the imidazolium based-ionic liquids used in this work were synthesized according to known procedures [14,15]. The structures of the ionic liquids were confirmed by ^1H NMR, FTIR and Elemental Analysis.

1.3 Synthesis of PAEK in ionic liquid

For a typical preparation of PAEK in ionic liquid, PAEK was synthesized within a 100 mL three-necked round flask

equipped with a Dean-Stark trap, reflux-condenser, mechanical stirrer and nitrogen inlet. The flask was charged with 4,4'-difluorobenzophenone (0.646 g, 2.8 mmol) and bisphenol A (0.639 g, 2.8 mmol) in 1.25 g of IL. The mixture was stirred vigorously with a constant purge of nitrogen and heated. After the homogeneous solution was heated up to 140°C , anhydrous potassium carbonate (0.46 g, 3.2 mmol) was added followed by 3 mL of toluene. The reaction mixture was refluxed under a Dean-Stark system with toluene at 150°C for 0.5 h until the accumulation of water was no longer evident in the Dean-Stark trap. Then toluene was removed by nitrogen atmosphere. The reaction mixture acquired a white and turbid suspension at the initial stage of the reaction due to the formation of the phenoxide. The reaction mixture was gradually heated to 180°C for 1.5 h, and polymer was precipitated with the increase of viscosity of the polycondensation system. Then the reaction system was cooled down to room temperature. The product was obtained by simple filtration to separate the PAEKs and ILs. The resulting polymer was washed with methanol and hot water several times in order to remove inorganic salts and ILs, and then dried in vacuum at 60°C for 8–12 h. IR (KBr, cm^{-1}): 3200–3000 (Ar), 2963 ($-\text{CH}_3$ asym-), 2845 ($-\text{CH}_3$ sym-), 1591, 1497 (C=C), 1654 (C=O), 1240 (C–O–C), 1169 ($-\text{C}(\text{CH}_3)_2$), 837 (Ar–H). ^1H NMR (DMSO- d_6 , ppm): $\delta = 6.97\text{--}7.79$ (16H, Ar–H), 1.70 (6H, $\text{C}(\text{CH}_3)_2$).

2 Results and discussion

As we know, the synthesis of PAEKs needs high reaction temperature ($160\text{--}200^\circ\text{C}$) and polar solvents such as DMAc, NMP and DMSO [16]. Need for usage of high boiling solvents makes it a highly energy reaction. The unique feature of our approach is the synthesis of PAEKs in ILs as reaction media (Figure 1).

In this work, PAEKs were synthesized by the reaction of 4,4'-difluorobenzophenone (DFB) with bisphenol A via $\text{S}_{\text{N}}\text{AR}$ mechanism in the presence of anhydrous potassium carbonate, using ILs as reaction media. 1,3-dialkylimidazolium-based ILs, which have been the focus of polymer synthesis as environmentally benign solvents [17–19], were employed for synthesis of PAEKs. Toluene and anhydrous potassium carbonate were used as azeotropic solvent and

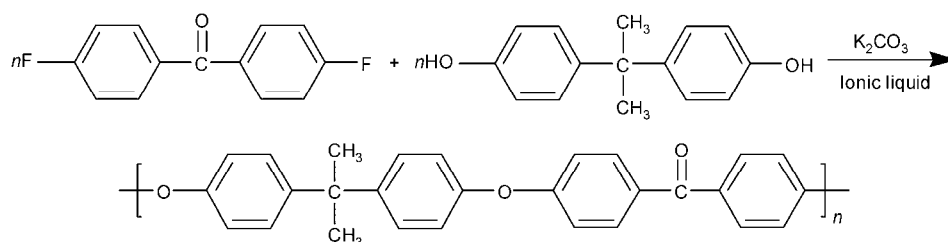


Figure 1 Synthesis of poly(aryl ether ketone)s in ionic liquids.

salt forming agent respectively.

2.1 Optimization of polycondensation conditions

As we know, monomer concentration plays an important role in polycondensation and high concentration is usually preferred. The influence of monomer concentration on properties of PAEKs was first examined by using *i*-pmim PF₆ as a model medium (Figure 2). The molecular weights of PAEKs gradually increased with increasing monomer concentration. The concentration dependence showed a maximum when the monomer concentration was 50% and high molecular weight PAEK ($M_n=16900 \text{ g mol}^{-1}$) was synthesized. When the monomer concentration was higher than 50%, the viscosity of reaction medium was very high leading to decreasing of the molecular weight of PAEKs.

Since the existence of water may induce the hydrolysis of bisphenol A potassium salt disturbing the stoichiometry of monomers, removal of water generated during phenoxide formation is an important influencing factor. Hence, sufficient dehydration time (2.5–8.5 h) is usually required to remove the generated water completely. The influence of dehydration time on the molecular weight of PAEKs was studied (Table 1, runs 1–4). With 0.5 h of dehydration time, M_n of PAEKs was up to 16900 g mol^{-1} . The molecular weights of PAEKs were not improved by extending dehydration time. The dehydration property of the reaction process was monitored by visual inspection. A large amount of water was collected in Dean-Stark trap after 0.5 h of dehydration. Until 2.5 h, the accumulation of water was no longer evident. Thus phenoxide forming reaction was assumed to be complete after dehydration for 0.5 h, resulting in the highest molecular weight of PAEKs (Table 1, run 1). Then, experiments were carried out by optimization temperature. As the reaction temperature increased, molecular weights of PAEKs gradually increased. However, in the case of the reaction temperature at 190–200°C (Table 1, runs 6 and 7),

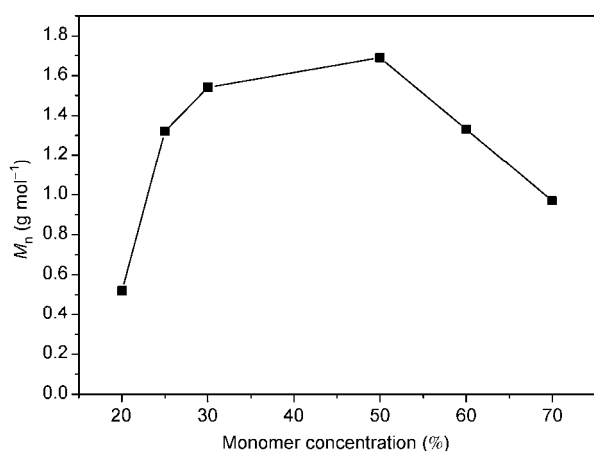


Figure 2 Influence of initial monomer concentration on molecular weight of PAEKs in *i*-pmim PF₆ at 180°C for 1.5 h.

Table 1 Effect of dehydration time, temperature and duration of polymerization on the synthesis of PAEKs^{a)}

Run	Dehydration time (h)	Temp. (°C) ^{b)}	Time (h) ^{b)}	M_n ^{c)}	PDI ^{c)}	Yield (%)
1	0.5	180	1.5	16900	2.09	>99
2	1.5	180	1.5	17000	2.70	>99
3	2.5	180	1.5	18100	2.26	>99
4	3.5	180	1.5	18000	2.17	>99
5	1.5	170	1.5	7900	2.08	93.5
6	1.5	190	1.5	15200	2.13	98.8
7	1.5	200	1.5	12300	2.30	96.4
8	1.5	180	0.5	6700	2.00	92.2
9	1.5	180	2.5	16500	2.23	>99
10	1.5	180	3.5	15700	2.31	>99

a) General polymerization conditions: equimolar of bisphenol A and DFB, a little excess of K₂CO₃, 50 wt% monomer concentration, dehydrate at 150°C. Polymers were washed by hot water without further purification. b) Temperature and duration of polymerization. c) Number-average molecular weight (M_n) and polydispersity index (PDI) were measured by GPC calibrated with polystyrene standards.

molecular weight of PAEKs significantly decreased and the color of polymers became dark. This was probably caused by decomposition of PAEKs and ILs at high salt concentration or side effects such as cyclization at elevated temperatures. Therefore, we monitored the polymerization at 180°C with different reaction time. After only 0.5 h reaction, PAEK of $M_n=6700 \text{ g mol}^{-1}$ was obtained. After 1.5 h, the molecular weight almost doubled. As the reaction reached equilibrium, the viscosity of reaction medium was very high hindering the movement of active functional group of oligomers, and the content of inorganic products increased, the molecular weight reached a plateau level after 2.5 and 3.5 h. It is noteworthy that the resulting polymers are precipitated from solution at initial stage of the polycondensation. So the molecular weight of PAEKs was no longer increased with increasing polycondensation time. The following reaction parameters providing the polymer with highest molecular weight were seemed to be optimal: 50wt% monomer concentration, dehydrate at 150°C for 0.5 h, and then polymerize at 180°C for further 1.5 h.

2.2 IL's cations and anions nature

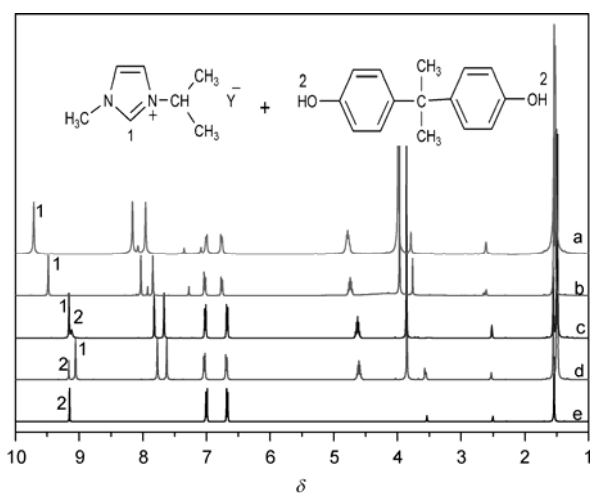
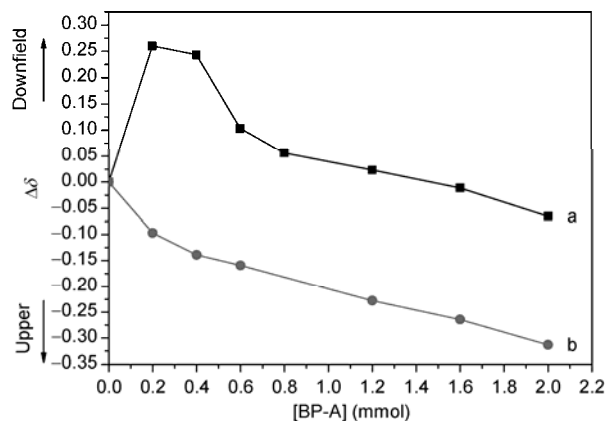
The influence of ILs structure on the synthesis of PAEKs was investigated under the optimal reaction conditions. It can be observed that the best result was obtained in ILs with *iso*-propyl or *iso*-butyl alkyl chain due to their steric hindrance (Table 2, runs 2 and 6). With the increase of aryl substitution length, the molecular weights of resulting polymers were decreased. This may be explained by the decrease of polarity and poor solubility of ILs with longer alkyl chain.

As far as anions were concerned, the best results were

Table 2 Effect of ILs nature on synthesis of PAEKs

Run	ILs			M_n	PDI	Yield (%)
	R ₁	R ₂	Y ⁻			
1	CH ₃	i-C ₃ H ₇	Br	7800	2.22	91.1
2	CH ₃	i-C ₃ H ₇	PF ₆	16900	2.09	>99
3	CH ₃	i-C ₃ H ₇	BF ₄	8600	1.91	89.7
4	CH ₃	i-C ₃ H ₇	Tf ₂ N	12900	1.78	93.5
5	CH ₃	C ₄ H ₉	PF ₆	13600	1.73	95.6
6	CH ₃	i-C ₄ H ₉	PF ₆	17700	2.00	91.6
7	C ₄ H ₉	C ₄ H ₉	PF ₆	10700	1.77	76.3
8	CH ₃	C ₆ H ₁₃	PF ₆	11200	2.00	97.3
9	CH ₃	C ₈ H ₁₇	PF ₆	9600	1.98	98.2

achieved in ILs with hexafluorophosphate counterion (Table 2, runs 1–4). It has been reported that C-2 proton activity of imidazole, which can react with KOH or phenol, has strong influence on polymer synthesis [20,21]. Therefore, we examined the ¹H chemical shifts of bisphenol A in a series of ILs with different anions (Figure 3). ¹H NMR was performed in nonpolar and aprotic solvent of DMSO-*d*₆. It was seen that the chemical shifts of protons in benzene ring and methyl slightly changed, while the chemical shifts of C-2 proton increased with increasing anion basicity and hydrogen bonding ability (PF₆⁻<Tf₂N<BF₄⁻<Br⁻) [22]. In addition, we found that no hydroxyl protons appeared in hydrophilic ILs such as i-pmim BF₄ and i-pmim Br. So we further examined the peak shifts of C-2 proton in the mixture of different amount of bisphenol A and ILs (i-pmim Br and i-pmim PF₆). As Figure 4 illustrated, when i-pmim Br was used, even with a small amount of bisphenol A, C2-position of imidazolium moiety significantly shifted to downfield, indicating strong interaction from electron-rich bisphenol A to electron-poor imidazolium cation. While the peak shifts were quickly decreased with the increase of the amount of bisphenol A. On the contrary, in the mixture of bisphenol A

**Figure 3** ¹H NMR spectra of bisphenol A in different solvents. a, i-pmim Br/DMSO; b, i-pmim BF₄/DMSO; c, i-pmim Tf₂N/DMSO; d, i-pmim PF₆/DMSO; e, DMSO.**Figure 4** Values of peak shift of C2-position of imidazolium proton of i-pmim Br (a) and i-pmim PF₆ (b) with varying concentration of phenol; ionic liquids=0.25 g, [bisphenol A]=0–2 mmol L⁻¹.

and i-pmim PF₆, hydroxyl proton and C2-position of imidazolium moiety slightly shifted to downfield and upper, respectively. The values of the peak shift were gradually increased with increasing amount of bisphenol A. We can conclude that the interaction of bisphenol A with ILs plays an important role in PAEKs synthesis. In hydrophilic ILs, the strong interaction of bisphenol A with imidazolium cation should reduce electron density of phenoxide. Thus, nucleophilic reactivity of bisphenol A decreased and steric hindrance of phenoxide increased, resulting in lower molecular weight PAEKs. In contrast with i-pmim PF₆, the inter-action was too weak to inhibit the polymerization process, so high molecular weight PAEKs were prepared in ionic liquids with hexafluorophosphate counterion.

2.3 Recovery and reuse of ionic liquids

As an alternative to conventional organic solvents, recovery and reuse of ILs are absolutely important and necessary after polymerization. ILs in our study were separated with resulting polymers by soxhlet extraction. After that, the residual ILs in the filtrate were easily recovered by vacuum evaporation. The recycled i-pmim PF₆ after one reaction cycle was analyzed by FTIR (Figure 5). It can be seen that there was no obvious change of the absorption bands of i-pmim PF₆. Furthermore, the absorption peak at 838 cm⁻¹ was appeared, which was assigned to the P–F bond of PF₆⁻. The results showed that the ionic liquids underwent virtually no decomposition throughout the reaction. So the recycled ILs were used for a new polycondensation, and PAEK of slightly low molecular weight ($M_n=13100$ g mol⁻¹) was obtained. Therefore, the ILs recovered are able to be reused in new polymerization cycle.

3 Conclusions

In the present work, we describe a novel synthetic method

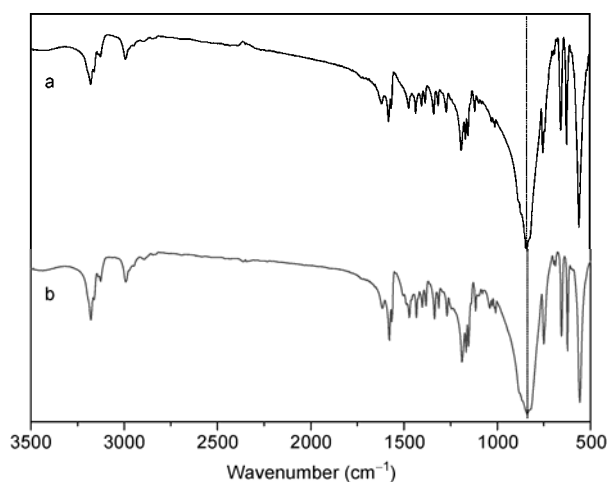


Figure 5 FTIR spectra of i-pmim PF₆ as prepared (a), recycled (b).

for high performance PAEKs by using ionic liquids as reaction media. This is an outstanding application of ILs in polymer synthesis.

The study of optimization of polycondensation conditions has showed that PAEKs can be successfully synthesized in ionic liquids (50 wt% monomer concentration, dehydrate at 150°C for 0.5 h, polymerize at 180°C for further 1.5 h). The number-average molecular weights of PAEKs are ranging from 10000 to 18000 g mol⁻¹ with high yields. The influence of ILs nature upon polymer molecular weight has been studied as well. The molecular weights of PAEKs decreased with the increase of aryl substitution length. The interaction of bisphenol A with ILs strongly influences the polymerization process. i-pmim PF₆ was utilized as the best choice of solvents. The ionic liquids used in this work can be recycled and reused for the new polymerization cycle.

Ionic liquids have not only the alternative to organic solvents but also potential to increase chemical reactivity leading to more efficient processes. The syntheses of the most wide possible range of new materials in ionic liquids are in progress.

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