

A Facile and Highly Efficient Protocol for Synthesis of Poly(ether sulfone)s in Ionic Liquid/Zwitterion^{*}

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Abstract A benign approach for efficient preparation of poly(ether sulfone) (PES) ($\eta_{\text{inh}} = 0.10\text{--}0.31 \text{ dL}\cdot\text{g}^{-1}$) has been presented by using ionic liquid (IL)/zwitterion (ZI) as reaction medium. It has been found that the interaction between 4,4'-dihydroxydiphenylsulfone (Bisphenol-S) and ZI at elevated temperatures results in efficient reduction of dehydration time, which is confirmed by TGA curves, melting point of the mixture and FTIR spectra. Furthermore, no agglomeration is observed at dehydration stage, which is attributed to the high solubility of Bisphenol-S dipotassium salt in IL/ZI. This also makes the polymerization temperature (150 °C) much lower than a conventional method (220–300 °C). In order to demonstrate the efficiency of IL/ZI as reaction medium, the polymerization was also performed in sulfolane under the same reaction condition as that in IL/ZI.

Keywords: Poly(ether sulfone); Benign synthesis; Ionic liquid; Zwitterion.

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INTRODUCTION

Aromatic poly(ether sulfone)s (PESs) with high thermal stability, excellent mechanical properties, high heat distortion temperature and easy processability belong to a class of special engineering plastics. In recent years, PESs have gained considerable attention for application in many fields, especially polymer electrolyte membrane fuel cells (PEMFCs)^[1–6]. In 1967, Johnson *et al.* described synthesis of poly(aryl ether sulfone) *via* nucleophilic aromatic substitution reaction ($\text{S}_{\text{N}}\text{AR}$)^[7] for the first time. Later, ICI Company of UK commercialized an aromatic poly(ether sulfone), which contributed to increasing scientific interest in this class of materials. From then on, the synthetic method has been developed rapidly, including dehydrochlorination method, smelting desalting method, monophenol desalting method, bisphenol desalting method in solution, and microwave assisted process^[8]. Reaction media was also investigated, and polar aprotic solvents, such as DMAc, DMSO and sulfolane were highly effective^[9]. Taking a wide view of the research on synthetic technology, there are a few studies addressing using green and eco-friendly reaction media for preparation of PES.

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PES is generally synthesized through the reaction between 4,4'-dichlorodiphenyl sulfone (DCDPS) or 4,4'-difluorodiphenyl sulfone (DFDPS) with 4,4'-dihydroxydiphenylsulfone (Bisphenol-S) *via* S_NAR in the presence of aqueous potassium carbonate^[10]. Three crucial issues need to be emphasized here. Firstly, sulfolane (TMS) is the reaction solvent as it can dissolve PES efficiently. Secondly, the reaction is usually conducted at temperatures exceeding 250 °C of 2–12 h for the preparation of PESs ($\eta_{inh} = 0.20\text{--}0.35\text{ dL}\cdot\text{g}^{-1}$)^[9]. Thirdly, water generated during phenoxide formation reaction should be rigorously excluded, which usually needs sufficient dehydration time of 2.5–8.5 h^[11]. Water removal and use of polar organic solvent with high boiling point makes the reaction consume a high energy and time. Therefore, development of novel reaction media which can solve these problems is of great importance for synthesis of PES.

Ionic liquids (ILs), bearing a series of cations and anions, are promising alternative to organic solvents due to their unique properties such as low volatility, chemical stability, high thermal stability, and so on^[12–14]. During the past decades, high performance polymers such as polyimides and polyamides were successfully prepared in 1,3-dialkylimidazolium based ionic liquids which were used as dual solvent and catalyst^[15, 16]. In particular, the molecular weight of polyimide can be improved by addition of zwitterionic type IL (ZI)^[17]. Synthesis of poly(1,3,4-oxadiazole)s, polyureas, poly(glycolic acid), phenol polymers and poly(methyl methacrylate) in ionic liquids were reported recently^[18–25]. These reports have demonstrated that ionic liquids have strong influence upon the reaction improvement and solubility of monomers. In our previous researches, aliphatic polyesters and aromatic poly(ethylene terephthalate)s have been obtained in ionic liquids, especially high molecular weight polysulfones were efficiently synthesized based on Bisphenol-A and DFDPS using ionic liquid/zwitterion (IL/ZI) as reaction medium^[26–31]. Considering the similar properties of Bisphenol-S and Bisphenol-A, the reaction between Bisphenol-S and DFDPS can take place in the same reaction medium. However, usage of ionic liquids generally exists problems for the synthesis of PES. Indeed, elimination of water and solubility of intermediate salt are two main and crucial prerequisites in this study.

Herein, we present a benign and efficient route toward high molecular weight PES using ionic liquids/Zwitterion as reaction medium. A series of polycondensation between Bisphenol-S and DFDPS were carried out in imidazolium-based ionic liquid/1-methylimidazolium-3-butylsulfonate zwitterion (MImBS). Toluene and anhydrous K₂CO₃ were employed as azeotroping solvent and salt forming agent, respectively. The optimal reaction conditions were obtained by varying the mass ratios of IL to ZI, amount of IL/ZI, amount of K₂CO₃, polymerization time and categories of ILs and got PES with high yield and molecular weight. The interaction between Bisphenol-S and MImBS was discussed by means of TGA, melting point of their mixtures and FTIR. We also compared the polymerization process in IL/ZI with that in sulfolane under the same reaction condition. Synthesis of PES in IL/ZI is not well-known, the polymerization condition is very mild, and this polymerization process will be industrially applicable.

EXPERIMENTAL

Materials

N-methylimidazole was distilled under reduced pressure. All alkylhalides (aladdin, 99%), 1-butylimidazole (Aldrich, 98%), 1,4-butylsulfone (99%) and 4,4'-difluorodiphenylsulfone (DFDPS) (Alfa Aesar, > 98%) were used without further purification. 4,4'-Dihydroxydiphenylsulfone (Bisphenol-S) (aladdin, 98%) was purified by recrystallizing from toluene. Ionic liquids and potassium carbonate were dried under vacuum before use. Other solvents were dried over 3 Å molecular sieves prior to use.

Characterization

¹H-NMR spectra were recorded on a Bruker Advance spectrometer (400 MHz) using CF₃COOD as the solvent. The FTIR spectra were obtained on an Omnic AVATAR 360 (Nicolet, USA) spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a METTLER STRAE SW 9.30 thermogravimetric analyzer at heating rate of 10 K/min in flowing nitrogen. Inherent viscosities were determined using an Ubbelohde viscometer (0.1 g polymer in 10.0 mL DMF at 25 °C).

Preparation of Ionic Liquid and Zwitterion

All of the imidazolium based-ionic liquids and Zwitterionic type IL (ZI) used in this work were synthesized according to known procedures^[32–35]. The structures of the ionic liquids were confirmed by ¹H-NMR, FTIR and elemental analysis.

Solubility of Bisphenol-S in IL or IL/ZI

Bisphenol-S (10 mg) was added to 0.6 g of IL or IL/ZI with different mass ratios, and stirred for 0.5–1 h. After that, solubility of the mixed solution was monitored by visual inspection. Later, Bisphenol-S was added to the mixtures again and repeated this process until the solution turned turbid. The suspensions, which contained insoluble fraction, were heated subsequently. The solubility was measured as the mentioned above at different temperatures. The solubility of Bisphenol-S was defined as the highest concentration observed at every temperature.

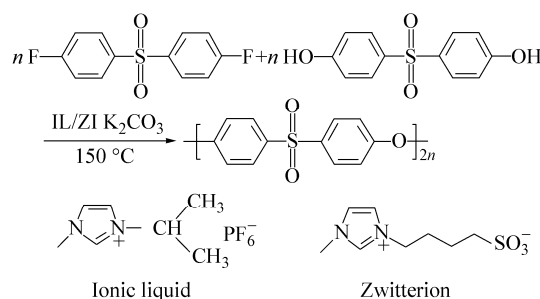
Synthesis of Poly(ether sulfone) in IL/ZI

PES 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 Bisphenol-S (0.350 g, 1.4 mmol), DFDPS (0.356 g, 1.4 mmol) and 1.06 g of IL/ZI. The mixture was stirred vigorously and heated up. After the homogeneous solution was heated up to 140 °C, anhydrous potassium carbonate (0.25 g, 1.8 mmol) was added followed by 3 mL toluene. The reaction mixture was refluxed 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. A transparent solution was obtained, and the reaction was continued at 150 °C for another 2 h. Polymer was gradually precipitated at the initial stage of the polymerization. Then the reaction system was cooled down to room temperature. The product was obtained by simple filtration to separate the PES from ILs. The crude product was washed with hot water several times to remove inorganic salts and other residual reactants, and then subjected to soxhlet extraction with ethanol. After that, they were filtered, and dried under vacuum at 60 °C for 12 h. The structure of PES was confirmed by FTIR and ¹H-NMR.

IR (KBr, cm⁻¹): 1575 and 1484 (s; ν (C=C)), 1325 and 1296 (m; ν_{as} (O=S=O)), 1236 (s; ν_{as} (C—O—C)), 1175 and 1146 (m; ν_s (O=S=O)), 873 and 852 (s; δ (C—H)); ¹H-NMR (400 MHz, CF₃COOD, δ): 8.04 (d, 4H, Ar—H), 7.23 (d, 4H, Ar—H).

RESULTS AND DISCUSSION

In general, synthesis of poly(ether sulfone) requires sufficient dehydration time (2.5–8.5 h), high reaction temperature (250–300 °C) and organic solvents with high boiling point (TMS, DMAc or Diphenyl sulfone). In our work, 1-isopropyl-3-methylimidazolium hexafluorophosphate (i-pmim PF₆)/MImBS was chosen as a model medium to study the polymerization process (Scheme 1). The chemical structure of PES was confirmed by FTIR and ¹H-NMR, in which all peaks were well-assigned (Fig. S1).



Scheme 1 Synthetic route for PES in IL/ZI and structures of IL and ZI

Composition of Reaction Medium

ZI, which tethers both cation and anion, tends to have higher melting points (up to 200 °C) than traditional imidazolium-based ILs. It has been reported that due to increasing hydrogen-bond accepting ability, addition of ZI is confirmed to elevate β value, which is a determining factor for the solubility of monomers^[17]. However, the viscosity of ZI is relatively high which hinders the elimination of by-products during the synthesis of PES. So composition of reaction medium was studied firstly in order to find the optimal ratio. Table 1 provided the inherent viscosities (η_{inh}) of PESs in IL/ZI, in which mass ratio of IL to ZI was different. The highest η_{inh} was obtained when the mass ratio of IL to ZI was 5:5 (Table 1, Entry 3). Furthermore, we investigated dissolving ability of IL after mixing with ZI. For this purpose, the solubility of Bisphenol-S in pure IL or IL/ZI was evaluated at 100–130 °C, and results are shown in Table 2. In pure IL, Bisphenol-S was almost insoluble up to 130 °C (Table 2, Entry 1). Oppositely, even a small amount of ZI can significantly enhance the solubility of Bisphenol-S in IL. As can be seen from Table 2, entry 3 with the highest solubility was obtained in the mixture containing 50 wt% ZI. Due to high viscosity and high melting point of ZI, mixtures with high content of ZI induce lower solubility (Table 2, Entries 4, 5). It is implied that the improved solubility of monomer results in the formation of high molecular weight PES. Therefore, the polymerization was monitored in IL/ZI with 5:5 mass ratio.

Table 1. Influence of the mass ratio of IL to ZI on the synthesis of PES

Entry ^a	Mass ratio of IL to ZI	η_{inh} ^b (dL·g ⁻¹)	Yield (%)
1	3:7	0.18	58.4
2	4:6	0.23	90.8
3	5:5	0.30	95.2
4	6:4	0.28	87.7
5	8:2	0.24	92.3
6	9:1	0.14	60.0
7	10:0	0.10	55.4

^a General polymerization conditions: equimolar of Bisphenol-S and DFDPS, 30% mole excess of K₂CO₃, 60 wt% IL/ZI content, dehydrate at 150 °C for 0.5 h, and then polymerized at 150 °C for another 2 h. Polymers were washed by hot water and then subjected to soxhlet extraction with ethanol.

^b Solutions of 0.1 g polymer in 10.0 mL DMF at 25 °C

Table 2. Solubility of Bisphenol-S in IL or IL/ZI

Entry ^a	Mass ratio of IL to ZI	Solubility at different temperatures (g)		
		110 °C	120 °C	130 °C
1	10:0	0.045	0.061	0.072
2	7:3	0.363	0.399	0.458
3	5:5	0.265	0.413	0.507
4	3:7	–	–	0.232
5	0:10	–	–	–

^a The total amount of IL or IL/ZI was 0.6 g.

Phenoxide Formation

It is well known that the existence of water generated during phenoxide formation may induce side reactions such as the cleavage of polymer chains and hydrolysis of halogen-containing monomers in organic solvent at elevated temperatures, consequently disturbing the stoichiometry of monomers. So it is necessary to exclude water before polymerization stage, which normally requires sufficient dehydration time of 2.5–8.5 h^[9]. In our work, a great deal of gas bubbles was surprisingly observed after K₂CO₃ was added, which indicated that the rate of salt forming reaction was accelerated, and it is noteworthy that no agglomeration was found after toluene was added. They are distinctive features of this novel protocol. Because of these unique phenomena, we studied the effect of dehydration time on properties of PES and evaluated water content collected in Dean-Stark trap during formation of phenoxide by using molecular sieves (Table 3)^[36]. As indicated in Table 3, a large amount of water was removed rapidly within 30 min and no water droplet was refluxed in Dean-Stark trap after 90 min. The

highest molecular weight was obtained when the dehydration time is 30 min (Table 3). The evaluated weight of water exceeded theoretical value about 3.1 mg attributed to the trace water of starting materials. Thus we presumed that phenoxide formation reaction was complete. The η_{inh} of PESs decreased with increasing dehydration time. This may be attributed to the existent toluene which reduced the monomer concentration and solubility of potassium phenate in IL/ZI. Moreover, the flowing nitrogen was used to remove water instead of toluene, and PES with $\eta_{\text{inh}} = 0.26 \text{ dL}\cdot\text{g}^{-1}$ was obtained. This provides us a green protocol without any volatile organic solvent during the whole polymerization process.

Table 3. Influence of dehydration properties on the synthesis of PES

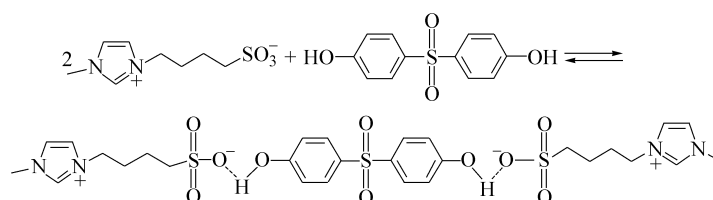
Dehydration time (min)	Dehydration amount ^a (mg)	Dehydration rate ^b (%)	η_{inh} ^c ($\text{dL}\cdot\text{g}^{-1}$)	Yield (%)
0	—	—	0.26	83.1
15	12.9	45.6	0.27	86.2
30	7.1	25.1	0.30	95.2
45	4.5	16.0	0.27	92.3
60	3.8	13.3	0.24	86.2
90	—	—	0.23	92.3

^a The weight difference between pure molecular sieves and those after absorbing water;

^b Dehydration rate was calculated as the ratio of the water content to the total water content;

^c Solution of 0.1 g polymer in 10.0 mL DMF at 25 °C

In view of the dehydration time shortened to 30 min, we inferred that sulfonic-type IL with high acidity was generated due to the reaction between Bisphenol-S and MImBS at elevated temperatures (Scheme 2). In order to validate this assumption, thermal stability of Bisphenol-S, MImBS and their mixture (1:2, by mole) was studied by TGA (Fig. 1). As can be seen from Fig. 1, the mixture showed a distinctly higher thermal decomposition temperature than both Bisphenol-S and MImBS, which is similar to brønsted acidic ionic liquids^[37, 38]. This supposition was further supported by melting behavior of the mixture of Bisphenol-S and MImBS (1:2, by mole) at elevated temperatures, as shown in Fig. 2. It is known that the melting points of both starting materials are all above 200 °C. In our experiment, Bisphenol-S and MImBS were grinded well at room temperature. With increasing temperature, the appearance of the mixture changed from white solid into viscous liquid at 150 °C, and a homogeneously colorless transparent liquid was obtained at 170 °C. Notably, no phase separation happened in this mixed solution by cooling down to room temperature, and the mixture was still homogeneous and stable after a few months. Furthermore, FTIR was applied to investigate the interaction between Bisphenol-S and MImBS. Figure 3 illustrated the FTIR spectra of Bisphenol-S, MImBS at room temperature, and mixture of Bisphenol-S and MImBS at room temperature (Fig. 3, curve c) and elevated temperature (heated to 170 °C and cool down to room temperature as the mentioned above), respectively (Fig. 3, curve d). The absorption peaks at 1280, 1222, 1140 and 1102 cm^{-1} were assigned to asymmetric and symmetric stretch of S=O group. The band at 3431 cm^{-1} , characteristics of water attributed to moisture absorbed by ZI very easily, is clearly observed in Fig. 3(b). It was observed from Fig. 3 (curves c, d) that the broad and asymmetric featured peak at 3409 cm^{-1} for Bisphenol-S shifted to 3422 cm^{-1} significantly due to O—H vibrations, which indicated that sulphonic-type complex between Bisphenol-S and MImBS was formed^[39].



Scheme 2 The interaction between MImBS and Bisphenol-S at elevated temperatures

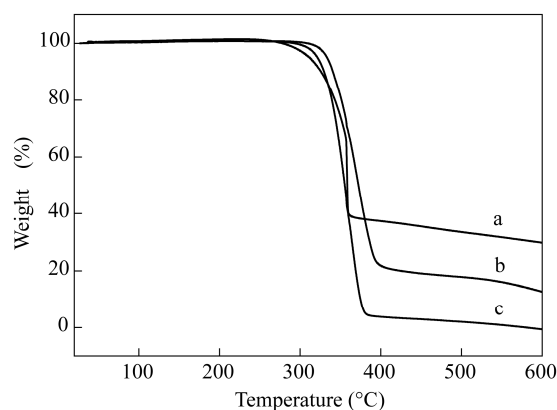


Fig. 1 TGA curves of Bisphenol-S (a), MImBS (c) and their mixture (1:2, molar ratio) (b)



Fig. 2 Photographs of the appearance of Bisphenol-S mixing with MImBS

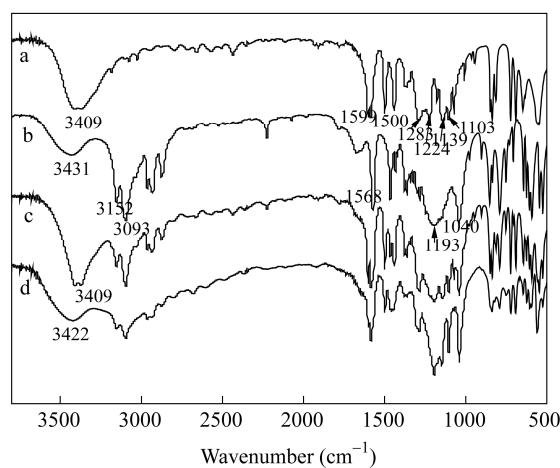


Fig. 3 IR spectra of Bisphenol-S (a), MImBS (b) at room temperature, their mixture (1:2, molar ratio) at room temperature (c) and elevated temperatures (d), respectively

Polymerization Conditions

In order to search optimum polymerization conditions, the influence of reaction temperature on η_{inh} of PESs was examined firstly by using i-pmim PF₆/MImBS as solvent. The η_{inh} of PESs are plotted in Fig. 4 as function of

reaction temperature. As indicated in Fig. 4, the η_{inh} showed a maximum at 160 °C. In addition, η_{inh} at 150 °C was slightly lower than that at 160 °C. With the increase of reaction temperature, η_{inh} decreased continuously and the color of PESs became dark, which is probably ascribed to decomposition of PESs and IL/ZI mixture or side reactions such as cyclization at high temperature^[40]. After phenoxide formation reaction was completed, a homogeneously transparent liquid was formed. As a consequence, the polymerization temperature is much lower than conventional ones (220–300 °C), which is attributed to the high solubility of Bisphenol-S dipotassium salt in IL/ZI. This is one of unique advantages during synthesis of PES in our study.

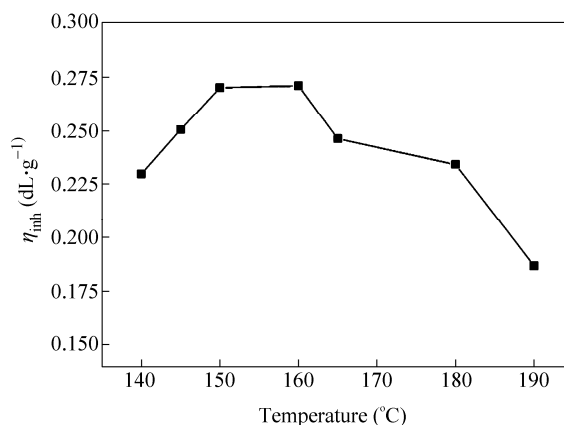


Fig. 4 Influence of polymerization temperature on inherent viscosity of PESs

We further investigated the influences of the amount of IL/ZI and K_2CO_3 , reaction time on the polymerization using i-pmim PF_6 /MImBS as solvent. Results are shown in Table 4. We all know that a lower monomer concentration is an unfavorable factor for polycondensation. While lower contents of solvent with high viscosity will hinder the water removal. It is apparent from Table 4 that η_{inh} of PESs showed a maximum when the amount of IL/ZI was 60% of conventional ones. The effect of amount of K_2CO_3 was also studied. It has been reported that an excess of anhydrous K_2CO_3 will not induce the hydrolytic side reaction of DFDPS^[11]. In order to form theoretical amount of phenoxide, a modest excess of anhydrous K_2CO_3 was added. The results showed that η_{inh} of PESs reached a plateau level as 30%–50% mole excess of anhydrous K_2CO_3 was used. Therefore, we monitored the polymerization in the presence of 30% mole excess of anhydrous K_2CO_3 at 150 °C. As increasing reaction time from 0.5 h to 2 h, η_{inh} of PESs became larger. However, when we continued to prolong the reaction time, η_{inh} of PES no longer increased. From the above investigation, we can get the conclusion that the optimum polymerization condition for synthesis of PES in IL/ZI was 60 wt% IL/ZI at 150 °C for 2 h in the presence of 30% mole excess of anhydrous K_2CO_3 .

Under the identical optimum conditions, the polymerization was also carried out in various ionic liquids (Table 5). A comparison of the data of bmim PF_6 with bbim PF_6 (Table 5, Entries 4 and 9) revealed that best results were obtained in ILs with asymmetrical structure. With increasing aryl substitution length ($n > 6$), the yields and η_{inh} of the resulting polymers decreased. This can be explained by decreased polarity and poor solubility of ILs with longer alkyl chains. The use of hydrophilic ILs, such as i-pmim Br and bmim Br did not result in high η_{inh} of PES (Table 5, Entries 10 and 11). It is clear from Table 5 that inherent viscosities of PES in the range from 0.10 dL·g⁻¹ to 0.31 dL·g⁻¹, and i-pmim PF_6 and bmim PF_6 seem to be the suitable solvents for synthesis of PES (Table 5, Entries 3 and 4).

For comparison, we also performed the polymerization using sulfolane (TMS) as the reaction medium under the reaction conditions similar to those in IL/ZI. Photos of polymerization process were displayed in Fig. 5. It can be clearly seen from Fig. 5 that anhydrous K_2CO_3 deposited at the bottom of flask and the salt-forming reaction were carried out smoothly and unfortunately no significant bubbles were observed. In addition, agglomeration appeared due to the addition of toluene which significantly reduced the solubility of phenoxide in TMS. After dehydrated at 150 °C for 0.5 h, the reaction mixture was composed of a suspension of Bisphenol-S

dipotassium salt and excess K_2CO_3 . As a consequence, no polymer was obtained which was attributed to short dehydration time and low reaction temperature. Oppositely, when the same experiment was conducted in IL/ZI, a great deal of gas bubbles was surprisingly observed after K_2CO_3 was added and no agglomeration appeared. And a homogeneous liquid was obtained which indicated that Bisphenol-S dipotassium salt exhibits high solubility in IL/ZI. Consequently, high molecular weight PES was prepared. These significantly different phenomena demonstrated the advantage of IL/ZI as reaction medium as compared to organic solvent.

Table 4. Influence of IL/ZI amount, K_2CO_3 amount and polymerization on the synthesis of PES ^a

Amount of IL/ZI (%)	Mole excess of K_2CO_3 (%)	Reaction time (h)	η_{inh}^c (dL·g ⁻¹)	Yield (%)
40	30	2	0.16	72.3
50	30	2	0.23	89.6
60	30	2	0.30	95.2
65	30	2	0.29	92.4
70	30	2	0.24	72.3
75	30	2	0.21	86.2
60	0	2	0.23	63.1
60	50	2	0.29	93.8
60	30	0.5	0.11	75.4
60	30	1.5	0.26	90.7
60	30	3	0.30	93.8

^a General polymerization conditions: equimolar of Bisphenol-S and DFFPS, IL:ZI (5:5, by weight), dehydrate at 150 °C for 0.5 h and polymerized at 150 °C

Table 5. Influence of IL/ZI amount, K_2CO_3 amount and polymerization on the synthesis of PES ^a

Entry ^a	Ionic liquid			η_{inh}^b (dL·g ⁻¹)	Yield (%)
	R ₁	R ₂	Y ⁻		
1	CH ₃	C ₂ H ₅	PF ₆	0.21	87.7
2	CH ₃	C ₃ H ₇	PF ₆	0.23	89.2
3	CH ₃	<i>i</i> -C ₃ H ₇	PF ₆	0.30	95.2
4	CH ₃	C ₄ H ₉	PF ₆	0.31	89.2
5	CH ₃	<i>i</i> -C ₄ H ₉	PF ₆	0.24	83.1
6	CH ₃	C ₆ H ₁₃	PF ₆	0.22	81.6
7	CH ₃	C ₈ H ₁₇	PF ₆	0.13	80.2
8	CH ₃	C ₁₀ H ₂₁	PF ₆	0.10	78.2
9	CH ₃	C ₄ H ₉	PF ₆	0.18	91.6
10	CH ₃	<i>i</i> -C ₃ H ₇	Br	0.23	92.3
11	CH ₃	C ₄ H ₉	Br	0.22	86.2
12 ^c	TMS			—	—
13 ^d	TMS			0.35	—

^a General polymerization conditions: equimolar of Bisphenol-S and DFFPS, 30% mole excess of K_2CO_3 , the mass ratio of IL to ZI is 5:5, the content of IL/ZI was 60 wt%, dehydrate at 150 °C for 0.5 h and then polymerized for further 2 h; ^b Solutions of 0.1 g polymer in 10.0 mL DMF at 25 °C; ^c TMS instead of IL/ZI was used as reaction medium under the same reaction conditions; ^d Ref. [41], polymerized at 290 °C for 2 h

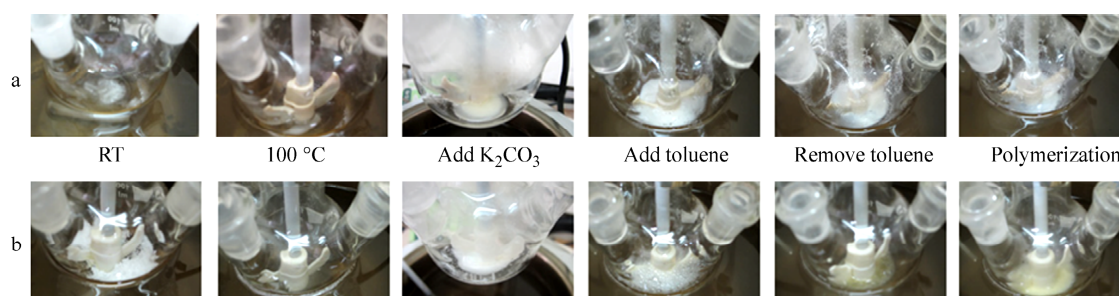


Fig. 5 Photographs of the polymerization process using TMS (a) and IL/ZI (b) as reaction medium, respectively

Recovery and Reuse of Ionic Liquid

From the viewpoint of environmental protection and economics benefits, recovery and reuse of IL are absolutely required after polymerization. In our study, the obtained PES can be separated from IL by soxhlet extraction. After that, the residual IL in the filtrate was easily recovered by drying it in a vacuum oven. The recycled i-pmim PF₆ after one reaction cycle was analyzed by ¹H-NMR and FTIR, and compared with that of freshly prepared one (Fig. S2). It is clear that there was no obvious change of the chemical shifts of i-pmim PF₆ and very little remaining monomer was observed after PES was synthesized. The peak at 830 cm⁻¹ ascribed to the P—F bond of PF₆⁻ in FTIR spectra still existed, which indicated that this ionic liquid underwent virtually no decomposition throughout the reaction. PES with slightly low molecular weight ($\eta_{inh} = 0.24 \text{ dL}\cdot\text{g}^{-1}$) was obtained in the recycled i-pmim PF₆. So we believed that the recovered IL is able to be reused in new polymerization cycle.

CONCLUSIONS

This work has demonstrated the first example of using ionic liquid with addition of ZI for efficient synthesis of PESs ($\eta_{inh} = 0.10\text{--}0.31 \text{ dL}\cdot\text{g}^{-1}$). It has shown that ZI can significantly improve the solubility of Bisphenol-S in IL, and the highest η_{inh} of PES was obtained in the mixture containing 50 wt% ZI. Furthermore, sulphonic-type IL with high acidity was proven to be unexpectedly formed from reaction between Bisphenol-S and ZI at elevated temperatures, resulting in remarkable reduction of dehydration time from 2.5–8.5 h to 0.5 h. On the other hand, high solubility of bisphenate in IL/ZI makes the reaction temperature (150 °C) much lower than conventional ones (220–300 °C). The method we proposed here possessed clear advantages for the synthesis of PES as compared to that in organic solvent. We believe that use of IL/ZI as reaction media makes the preparation of PES not only faster but also “greener”, and the proposed method in principle can be applied to other high performance polymers *via* nucleophilic aromatic substitution reaction.

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