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# Facile synthesis of polymerized ionic liquids with high thermal stability

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## ABSTRACT

Twelve main-chain-type polymerized ionic liquids that have alkylimidazolium cation units were prepared using simple synthetic processes. The polymers were prepared using the self-polymerization of a single monomer; no polymerization initiators were required. The thermal stability and solvent miscibility of these polymers were studied. Results show that the combined anions greatly influence the solubility and thermal stability of the polymers. Among these polymers, poly-alkylimidazolium bis(trifluoromethylsulfonyl)imide polymers exhibited the highest thermal stability (>400 °C), which makes them candidates for many applications.

Ionic liquids (ILs) are salts with relatively low melting points that are composed entirely of cations and anions. The term has been generally restricted to salts whose melting point is at or below 373 K. They also have negligible vapor pressure and relatively high thermal stability when compared to those of conventional molecular-type solvents. Their physical and chemical properties are easily tunable by synthetic means. In the recent decades, they have attracted a lot of research interests.[1–5] More recently, ionic liquids have been used in polymer science.[6] Polymerized ionic liquids (PILs) have some of the aforementioned advantages, and their immobilized structure usually improves their mechanical strength, which can eliminate possible liquid leakage. Therefore, PILs have potential applications in many emerging technological fields. Many ionic-liquid-type polymers have been produced via the radical polymerization of vinyl-containing ionic liquid monomers, such as vinylimidazolium-based ionic liquids. After the radical polymerization reaction, the imidazolium moieties form a side-chain (or comb)-type polymer. This type of polymer has been used in polymer electrolytes,[7] $CO_2$ absorption media,[8] stationary phases for gas chromatography,[9–11] and extraction fiber for solid-phase microextraction.[12] Synthetic vinyl-containing ionic liquids are extremely promising because their physical and chemical properties can be readily tuned by chemical functionalization. Nevertheless, the syntheses often require the addition of polymerization initiators and the polymerization parameters need to be carefully selected. The amount of initiators, the reaction time, and temperature greatly affect polymerization. Several steps are required to remove the initiator and by-products after the polymerization, making the process labor intensive and sometimes poorly reproducible. Recently, polymerization reactions that require no initiators have been developed. Suzuki et al. demonstrated a new ionic polymer electrolyte for dye-sensitized solar cells.[13] They used diiodoalkane and alkylene-bis(imidazole) as the monomers. The polymerization was carried out via the alkylimidazolium salt formation reaction, which requires no polymerization initiators. Yoshida et al. presented an oligomeric gelator synthesized via a quaternization reaction.[14] The reaction was carried out using commercially available 4-aminopyridine and 4-(chloromethyl)benzoyl chloride. An intermediate product containing nucleophilic and electrophilic parts at both termini was produced. The intermolecular quaternization reaction occurred immediately after the condensation reaction, forming the ionic oligomeric gelator. The ionic gelator was successfully used as a dispersant for single-walled carbon nanotubes. Both of the aforementioned processes are polymerization-initiator-free and can be applied for the in situ polymerization of main-chain-type co-polymers. However, in the synthesis of main-chain-type polymers, stoichiometric control is very sensitive to the molecular weight control. For the AB-type co-polymer, the reaction quenches in the absence of either monomer (A or B). The end groups of the polymer depend on the excess monomer. Therefore, the reaction parameters must be carefully selected.

In the present study, a process for the synthesis of PILs using a self-polymerization reaction is presented. Only a single monomer is used for self-polymerization. The proposed homopolymer-type PILs have several desirable features: (i) easy preparation procedure; (ii) tunable solubility; (iii) high thermal stability (~420 °C); (iv) polymerization-initiator-free. The synthesis of the proposed PILs was carried out in two or three steps: (1) synthesis of the monomer; (2) self-polymerization; and (3) metathesis of the anions (if different combinations of anions are required). The processes are outlined in Scheme 1. Briefly, (1) 0.046 mol (3.17 g) of

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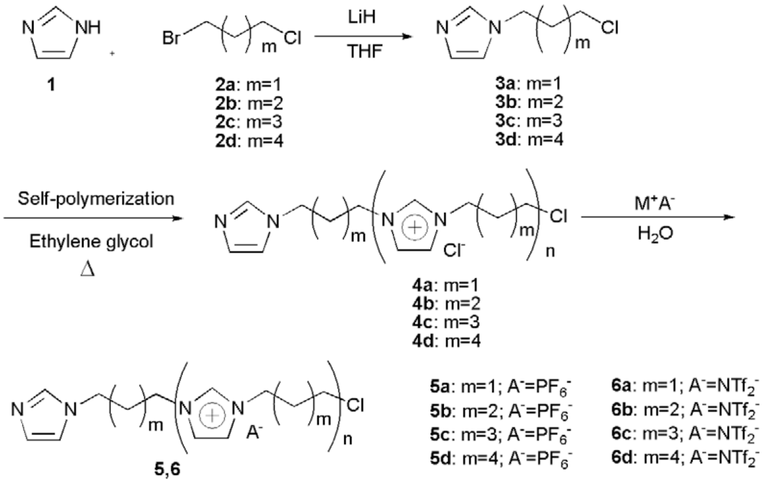

**Scheme 1.** Schematic illustrations of the synthesis procedures for the proposed PILs.

imidazole **1** was added into 10 mL of dry THF solution; 0.056 mol (0.45 g) of lithium hydride was dissolved in a 100-mL round-bottomed flask containing 10 mL of dry THF solution and a stir-bar at 0 °C. The imidazole solution was slowly mixed with LiH solution at 0 °C under nitrogen atmosphere. 0.027 mol (4.34 g) of 1-bromo-3-chloropropane **2a** were slowly added into the mixture for reaction, which was carried out under nitrogen atmosphere for 24 h at room temperature (25 ± 1 °C). Then, 10 mL of distilled water was added to terminate the reaction. The THF solvent was removed using an aspirator, and then the product was extracted several times using dichloromethane. After the removal of dichloromethane, the monomer 1-(3-chloropropyl)imidazole ($ImC_3Cl$, **3a)** was obtained as a transparent oily liquid. The yield of the monomer was around 94%. Monomers **3b**–**d** were prepared using the same procedure, but **2b**–**d** were applied as the starting materials, respectively. (2) Then, 0.02 mol (3 g) of **3a** was added into a 50-mL round-bottomed flask containing 2 mL of ethylene glycol solution, which was then heated in an oil bath at 90 °C for 12 h. The solution was cooled to room temperature after the reaction completed. Ten milliliters of methanol were poured into the round-bottomed flask to dissolve the product. The solution was added to 200 mL of acetone to cause precipitation. After the removal of acetone, the precipitate was washed using acetone three times, and then dried in a vacuum to obtain the polymer product as a white powder (polypropylimidazolium chloride, $PImC_3Cl$, **4a**). The yield of the polymers was around 88%. Polymers **4b**–**d** were prepared using the same procedure, but monomers **3b**–**d** were used for polymerization, respectively. (3) One gram of **4a** was dissolved in 50 mL of deionized water in a 250-mL round-bottomed flask. Then, 100 mL of 0.35 M potassium hexafluorophosphate was slowly added into stirred **4a** solution for metathesis. The reaction was carried out at room temperature for 12 h. The precipitate ($PImC_3PF_6$, **5a**) was first filtrated and washed using deionized water three times, and then dried at 50 °C in an oven for three days. The yield of the product was around 90%. Other $PF_6^-$-containing polymers (**5b**–**d)** were prepared using the same procedure. For $NTf_2^-$-containing PILs (**6a**–**d**), lithium bis-(trifluoromethylsulfonyl)imide was used as the metathesis reagent. The ion-exchanged products were then subjected to a silver nitrate test to make sure that there was no silver chloride precipitate. All four monomers (**3a**–**d**) were characterized using $^1H$ NMR, $^{13}C$ NMR, and HRMS-FAB. The $^1H$ NMR spectra (200 MHz) and $^{13}C$ NMR spectra (50 MHz) were recorded in deuterated chloroform; high resolution mass spectra (HRMS) were determined using a JEOL JMS-700 mass spectrometer in fast atom bombardment (FAB) mode. The spectra of the four monomers are listed in the notes.[15–18] The four chloride-containing polymers (**4a**–**d**) were characterized using $^1H$ NMR; the spectra were recorded in deuterated water and are listed in the notes.[19–22] The relative molecular weights of the PILs were measured using gel permeation chromatography (GPC) (equipped with a Jasco-880PU pump, Waters Styragel HR4E (Mw: 50–100,000) and a UV detector) with DMF as the eluent. The flow rate was 0.60 mL min$^{-1}$. The relative molecular weights were calculated using a series of poly-styrene standards as references. Due to solvent compatibility (see Table 1, **6a**–**d** are totally miscible with DMF), only the four $NTf_2^-$-containing polymers (**6a–d**) were tested. The relative

**Table 1**
Solvent compatibility test

| Polymer | $H_2O$ | DMSO | MeOH | Acetone | EA | THF | DCM | Toluene | Hexane | DMF |
|---|---|---|---|---|---|---|---|---|---|---|
| **4a** | + | + | + | – | – | – | – | – | – | – |
| **5a** | – | + | – | ± | – | – | – | – | – | ± |
| **6a** | – | + | ± | + | – | – | – | – | – | + |
| **4b** | + | + | + | – | – | – | – | – | – | – |
| **5b** | – | + | – | + | – | – | – | – | – | ± |
| **6b** | – | + | ± | + | – | – | – | – | – | + |
| **4c** | + | + | + | – | – | – | – | – | – | – |
| **5c** | – | + | – | + | – | – | – | – | – | ± |
| **6c** | – | + | + | + | – | – | – | – | – | + |
| **4d** | + | + | + | – | – | – | – | – | – | – |
| **5d** | – | + | – | + | – | – | – | – | – | ± |
| **6d** | – | + | + | + | – | – | – | – | – | + |

+: Miscible; ±: soluble on heating; –: immiscible; testing temperature: 25 ± 1 °C

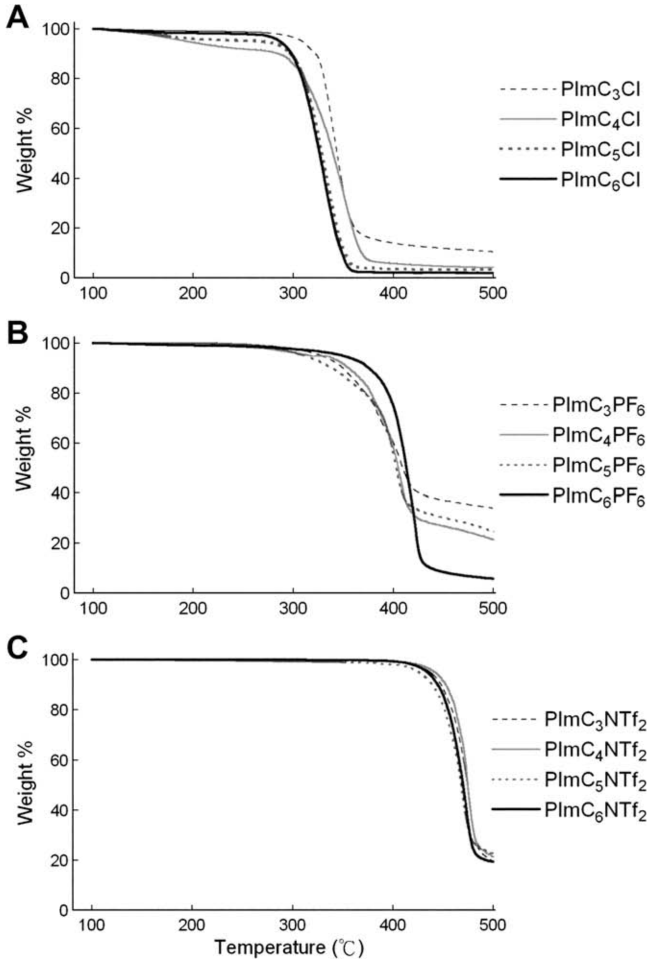

**Fig. 1.** Thermal gravimetric analysis of the 12 PILs. (a) $Cl^-$-containing PILs, **4a–d**; (b) $PF_6^-$-containing PILs, **5a–d**; (c) $NTf_2^-$-containing PILs, **6a–d**. Temperature program: 100–500 °C at a heating rate of 10 °C $min^{-1}$; $N_2$ flow: 20 mL $min^{-1}$.

molecular weights of **6a–d** are listed in note.[23] They are in the range of 50,000–90,000 g $mol^{-1}$.

Many reports on ILs and/or PILs have indicated that the solubility can be changed by changing the combination of cations and anions, the latter of which seems to have a greater influence.[9–11] Twelve prepared PILs (**4**, **5**, **6** series) were subjected to solvent compatibility tests. Table 1 summarizes the solvent compatibility of the PILs in various solvents. The chloride-containing PILs (**4** series) are water soluble. However, when the anions were replaced by $PF_6^-$ or $NTf_2^-$ (**5** and **6** series, respectively), the PILs became more hydrophobic. The alkyl-chain length also influences solvent compatibility. **6a** and **6b** are insoluble in methanol (at 25 ± 1 °C) despite containing hydrophobic anions. However, they became soluble when the alkyl-chain length was increased (e.g., **6c** and **6d**). According to Table 1, none of the prepared PILs are soluble in less polar organic solvents. Previous studies suggest that some side-chain-type PILs can be dissolved in some less polar solvents such as tetrahydrofuran (THF) and dichloromethane(DCM).[11] This could be attributed to the fact that for side-chain-type polymers, the alky chains are exposed out of the polymer base, which leads to better interaction with an organic solvent. In contrast, for main-chain-type PILs, both hydrophobic alky-chains and ionic moieties are in-line. Therefore, the contributions of the hydrophobic interactions from the alky-chains are suppressed.

It is believed that the anions have a great influence on thermal stability and solubility. The 12 PILs were subjected to thermal stability tests. The tests were carried out using a thermal gravimetric analyzer (TGA-50, Shimadzu, Japan); the results are shown in Fig. 1. The thermal stability of the 12 PILs can be divided into three groups. Chloride-containing PILs, $PF_6^-$-containing PILs, and $NTf_2^-$-containing PILs have significant weight loss at around 280––350 °C (Fig. 1a), 320–400 °C (Fig. 1b), and 420–460 °C (Fig. 1c), respectively. There seems to be no significant effect on the alkyl-chain lengths. The differences between PILs containing the same anions are minor. The results suggest that the thermal stability of the PILs is mostly anion dependent. Of note, $NTf_2^-$-containing PILs exhibited a very high thermal stability. Under nitrogen atmosphere, almost no weight loss was observed at temperatures below 400 °C. The melting points of **5a–d** and **6a–d** were also measured; they are listed in the notes.[24] Chloride-containing PILs (**4a–d**) were not tested because they are too hygroscopic. The results suggest that melting point decreases with increasing alkyl-chain length and larger anion size. This could be due to the asymmetry of the ionic structure decreasing the lattice energy. Of note, **6d** was successfully applied to be a high-thermal-stable stationary phase for gas chromatography.[25] The column can be applied to separate very low-volatile organic compounds (such as coronene, bp 525 °C), because the stationary phase can resist high temperature (maximum programmable oven temperature ~400 °C).

In conclusion, a facile procedure for the synthesis of the main-chain-type ionic liquid homopolymers was reported. No polymerization initiators are required; only a single monomer is used for each polymerization. The solubility and thermal stability can be easily tuned by adjusting the combination of anions and/or cations. Results suggest that the anions have a major influence on the polarity and thermal stability of the proposed PILs. $NTf_2^-$-containing PILs show very high thermal stability (~420 °C), which makes them suitable for a variety of applications.

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15. *Spectral data of 1-(3-chloropropyl)imidazole* (*ImC$_3$Cl*, **3a**): $^1$H NMR spectra (200 MHz, $CDCl_3$): $\delta$ 7.46 (s, 1H), 7.03 (s, 1H), 6.89 (s, 1H), 4.12 (t, $J$ = 6.4 Hz, 2H), 3.43 (t, $J$ = 5.8 Hz, 2H), 2.22–2.10 (m, 2H); $^{13}$C NMR spectra (50 MHz, $CDCl_3$): $\delta$ 137.5, 130.0, 119.0, 43.6, 41.2, 33.6; HRMS-FAB: $m/z$ [M+H]$^+$ calcd for $C_6H_{10}N_2Cl$: 145.0533; found: 145.0531.
16. *Spectral data of 1-(4-chlorobutyl)imidazole* (*ImC$_4$Cl*, **3b**): $^1$H NMR spectra (200 MHz, $CDCl_3$): $\delta$ 7.44 (s, 1H), 7.04 (s, 1H), 6.89 (s, 1H), 3.96 (t, $J$ = 6.7 Hz, 2H), 3.51 (t, $J$ = 6.0 Hz, 2H), 2.00–1.87 (m, 2H), 1.80–1.67 (m, 2H); $^{13}$C NMR spectra (50 MHz, $CDCl_3$): $\delta$ 137.2, 130.0, 118.9, 46.5, 44.3, 29.5, 28.6; HRMS-FAB: $m/z$ [M+H]$^+$ calcd for $C_7H_{12}N_2Cl$: 159.0689; found: 159.0689.
17. *Spectral data of 1-(3-chloropentyl)imidazole* (*ImC$_5$Cl*, **3c**): $^1$H NMR spectra (200 MHz, $CDCl_3$): $\delta$ 7.43 (s, 1H), 7.02 (s, 1H), 6.88 (s, 1H), 3.92 (t, $J$ = 7.0 Hz,

2H), 3.49 (t, $J$ = 6.6 Hz, 2H), 1.85–1.70 (m, 4H), 1.49–1.37 (m, 2H); $^{13}$C NMR spectra (50 MHz, $CDCl_3$): $\delta$ 137.2, 130.0, 119.0, 47.0, 44.7, 32.1, 30.6, 24.1; HRMS-FAB: $m/z$ $[M+H]^+$ calcd for $C_8H_{14}N_2Cl$: 173.0846; found: 173.0848.

18. *Spectral data of 1-(3-chlorohexyl)imidazole* (*ImC$_6$Cl*, **3d**): $^1$H NMR spectra (200 MHz, $CDCl_3$): $\delta$ 7.42 (s, 1H), 7.02 (s, 1H), 6.87 (s, 1H), 3.90 (t, $J$ = 7.0 Hz, 2H), 3.48 (t, $J$ = 6.6 Hz, 2H), 1.84–1.56 (m, 4H), 1.52–1.20 (m, 4H); $^{13}$C NMR spectra (50 MHz, $CDCl_3$): $\delta$ 137.2, 130.0, 119.0, 47.0, 45.0, 32.4, 31.1, 26.5, 26.0; HRMS-FAB: $m/z$ $[M+H]^+$ calcd for $C_9H_{16}N_2Cl$: 187.1002; found: 187.1000.
19. *Spectral data of PImC$_3$Cl*, **4a**: $^1$H NMR spectra (200 MHz, $D_2O$): $\delta$ 9.02 (1H), 7.63 (2H), 4.40 (4H), 2.59 (2H).
20. *Spectral data of PimC$_4$Cl*, **4b**: $^1$H NMR spectra (200 MHz, $D_2O$): $\delta$ 8.92 (1H), 7.59 (2H), 4.33 (4H), 2.00 (4H).
21. *Spectral data of PimC$_5$Cl*, **4c**: $^1$H NMR spectra (200 MHz, $D_2O$): $\delta$ 8.87 (1H), 7.55 (2H), 4.25 (4H), 1.98 (4H), 1.40 (2H).
22. *Spectral data of PimC$_6$Cl*, **4d**: $^1$H NMR spectra (200 MHz, $D_2O$): $\delta$ 8.80 (1H), 7.50 (2H), 4.20 (4H), 1.88 (4H), 1.36 (4H).
23. *Relative molecular weights obtained from GPC*: *PImC$_3$ NTf$_2$*, **6a**: 94,500; *PImC$_4$ NTf$_2$*, **6b**: 49,800; *PImC$_5$ NTf$_2$*, **6c**: 47,300; *PImC$_6$ NTf$_2$*, **6d**: 51,300.
24. *Melting point tests*: *PImC$_3$ PF$_6$*, **5a**: 266 °C; *PImC$_4$ PF$_6$*, **5b**: 249 °C; *PImC$_5$ PF$_6$*, **5c**: 138 °C; *PImC$_6$ PF$_6$*, **5d**: 93 °C; *PImC$_3$ NTf$_2$*, **6a**: 117 °C; *PImC$_4$ NTf$_2$*, **6b**: 95 °C; *PImC$_5$ NTf$_2$*, **6c**: 79 °C; *PImC$_6$ NTf$_2$*, **6d**: 65 °C.
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