Polymer xxx (2014) 1-10



Contents lists available at ScienceDirect

Polymer



journal homepage: www.elsevier.com/locate/polymer

Polymeric ionic liquids based on ether functionalized ammoniums and perfluorinated sulfonimides

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ARTICLE INFO

Article history: Received 16 November 2013 Received in revised form 11 March 2014 Accepted 22 March 2014 Available online xxx

Keywords: Polymeric ionic liquids Perfluorinated sulfonimide Ammonium

ABSTRACT

A new family of polymeric ionic liquids (PILs) based on alkyl and alkyl ether substituted ammoniums and perfluorinated sulfonimides (i.e., bis(fluorosulfonyl)imide (FSI⁻), and bis(trifluoromethanesulfonyl)imide (TFSI⁻)) have been synthesized by polymerization of the corresponding ionic liquid monomers (ILMs). Their structures and compositions have been characterized by ¹H and ¹⁹F NMR, FTIR and viscosity-average molecular weight (M_v). The physicochemical properties of both the ILMs and the PLs have been studied in terms of thermal stability, phase transition, and ionic conductivity. All the prepared ILMs and PILs reveal excellent thermal stabilities to greater than 250 °C. The PILs containing alkyl ether side unit show significant decrease in glass transition temperature (T_g), the values of T_g of the alkyl ether based-PILs are all significantly lower by 10–77 °C in magnitude than those of the corresponding alkyl based ones. The ionic conductivity of alkyl ether based-PILs in the best case increases up to 4.0×10^{-6} S cm⁻¹ at 30 °C, and reaches 7.6×10^{-5} S cm⁻¹ at 60 °C, and outperform their ammonium counterparts with alkyl side chain that were synthesized as references.

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1. Introduction

Polymeric ionic liquids (PILs) have been gaining a rapidly growing attention as promising materials for a wide range of applications [1-4], which is mainly motivated by the combination of both the advanced properties of conventional ionic liquids (ILs) and the flexibility and mechanical properties of polymers. Currently, there is a growing interest in PILs as safe electrolytes for the application in electrochemical devices, such as lithium-ion battery [5-10], solar-cells [11-13], fuel cells [14-17] and supercapacitors [18]. The properties of PILs can be tailored and modified by modification of their structures for special application [19-22].

Recently, the art of introducing an alkyl ether group (e.g. $CH_3OCH_2CH_2$ or CH_3OCH_2) into the side chains of onium has been widely used to realize low-melting, and high conductivity ILs [23–27], and this method was employed to improve the ionic conductivity of PILs by Döbbelin et al. [28]. It was found that pyrrolidinium-based PILs bearing alkyl ether group side chains exhibited lower T_g and the blend electrolytes of these PILs with IL

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http://dx.doi.org/10.1016/j.polymer.2014.03.041 0032-3861/© 2014 Elsevier Ltd. All rights reserved. and lithium salt showed high ionic conductivities. In a recent article, Koo and coworkers [29] described the synthesis of poly(vinylimidazolium) cations containing alkyl ether pendant groups, and found that the introduction of ethylene oxide pendant group on the imidazolium cation could improve the chain mobility of the PILs. All these encouraging results strongly suggest that the alkyl ether functionalized PILs would be promising component of the electrolyte materials for electrochemical devices.

In addition, the bis(trifluoromethanesulfonyl)imide (TFSI⁻) has been extensively studied as counterion of PILs, because of its highly delocalized charge distribution and plasticizing effect [5,19– 21,30,31]. While, previous study has shown that lithium salt and ILs with bis(fluorosulfonyl)imide (FSI-) anion have superior electrochemical properties [23,32-35], and we have found that FSI-based PILs showed lower glass transition temperature (T_g) and higher conductivity compared with TFSI⁻-based ones [36]. Thus far, little has been done on incorporating alkyl ether side chains into ammonium-based PILs with perfluorinated sulfonimides, and the structure-properties relationships of these PILs including the molecular weight, thermal stability, T_{g} and ionic conductivity have not fully explored yet. In the present work, we wish to report the synthesis and characterization of a new family of functionalized PILs based on the guaternary ammonium with alkyl and alkyl ether group side chains (Scheme 1 and Table 1), and two representative

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Scheme 1. Synthetic route for the the ionic liquid monomers (ILMs) and polymeric ionic liquids (PILs).

perfluorinated sulfonimide anions, FSI[–] and TFSI[–]. The structure effects on the physicochemical and electrochemical properties for these ionic liquid monomers (ILMs) and PILs are systematically studied.

2. Experimental

2.1. Materials

Commercially available reagents were obtained from Sinopharm Chemical Reagent Co. (China), Shanghai Chemical Reagent Co. (China), and Aladdin (China), and were analytical grade and used as received. *N*-[2-(2-(2-methoxyethoxy)ethoxy)ethyl]-*N*,*N*-dimethylamine and 2-bromoethyl methacrylate were prepared according to the references [37] and [38], respectively. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, battery grade, Rhodia), potassium bis(fluorosulfonyl)imide (KFSI, battery grade, Suzhou Fluolyte, China) were used as received. Azodiisobutyronitrile (AIBN, 98%, Shanghai Reagent, China) was recrystallized from methanol before use. All the procedures relative to handling moisture and oxygen sensitive reagents were performed under a dry argon atmosphere, or in a glove box (Mikrouna, H₂O and O₂ < 1 ppm).

2.2. Synthesis

2.2.1. Preparation and characterization of ionic liquid monomers 2.2.1.1. N-(n-Butyl)-N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]ammonium bis(fluorosulfonyl)imide ([$C_4N_{MA,11}$]FSI). The mixture of 2-(dimethylamino)ethyl methacrylate (DMAEMA, 10.0 g, 64 mmol) and a little excess of 1-bromobutane (9.7 g, 70 mmol) in acetone (20 mL) was stirred at room temperature for 12 h. Then, the acetone and unreacted 1-bromobutane were completely removed under

Table 1	
Abbreviation of the 10 ionic liquid monomers (ILMs).	

Abbreviation	R	Anion
[C ₄ N _{MA,11}]FSI	$n-C_4H_9$	FSI
[C ₃ ON _{MA,11}]FSI	CH ₂ CH ₂ OCH ₃	FSI
[C ₇ N _{MA,11}]FSI	$(CH_2)_6CH_3$	FSI
[C ₅ O ₂ N _{MA,11}]FSI	$(CH_2CH_2O)_2CH_3$	FSI
[C ₇ O ₃ N _{MA,11}]FSI	$(CH_2CH_2O)_3CH_3$	FSI
[C ₄ N _{MA,11}]TFSI	$n-C_4H_9$	TFSI
[C ₃ ON _{MA,11}]TFSI	CH ₂ CH ₂ OCH ₃	TFSI
[C ₇ N _{MA,11}]TFSI	$(CH_2)_6CH_3$	TFSI
[C ₅ O ₂ N _{MA,11}]TFSI	(CH ₂ CH ₂ O) ₂ CH ₃	TFSI
[C ₇ O ₃ N _{MA,11}]TFSI	(CH ₂ CH ₂ O) ₃ CH ₃	TFSI

reduced pressure, and the obtained solid was recrystallized from acetonitrile/ethyl acetate (1/2, v./v.), and dried under high vacuum at room temperature to afford the intermediate, N-(nbutyl)-N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]ammonium bromide ([C₄N_{MA,11}]Br), as a solid (16.8 g, 89% yield). Afterwards, the intermediate, [C₄N_{MA,11}]Br (5.0 g, 17 mmol), was dissolved in deionized water (60 mL), and a slightly excess of KFSI (4.2 g, 19 mmol) was added and stirred for 3 h at room temperature. The organic layer at the bottom was separated and washed with deionized water until no more bromide anion was detected by AgNO₃ solution. The liquid was rigorously dried under vacuum at room temperature for 24 h to afford pure product, N-(n-butyl)-N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]ammonium bis(fluorosulfonyl)imide ([C₄N_{MA.11}]FSI), as a colorless oil (6.0 g, 90% yield). ¹H NMR (399.76 MHz; DMSO- d_6 ; TMS; ppm): $\delta = 0.94$ (t, 3H), 1.30 (m, 2H), 1.66 (m, 2H), 1.92 (s, 3H), 3.31 (s, 2 × 3H), 3.36 (t, 2H), 3.70 (t, 2H), 4.53 (t, 2H), 5.77 (s, 1H), 6.09 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO- d_6 ; CCl₃F; ppm): $\delta = 53.5$. ESI-MS: m/z (%): 214 (100) [C₄N_{MA,11}]⁺, 180 (100) FSI⁻. Elemental analysis calcd (%) for C₁₂H₂₄F₂N₂O₆S₂: C, 36.54; H, 6.13; N, 7.10. Found (%): C, 36.61; H, 6.09; N, 7.08. IR (KBr, *v*_{max}, cm⁻¹): 3047 (s), 2968 (m), 1723 (s), 1636 (m), 1382 (s), 1320 (m), 1181 (s), 1106 (s), 951 (s), 832 (m).

2.2.1.2. *N*-(*n*-Butyl)-*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl] ammonium bis(trifluoromethanesulfonyl) imide ([$C_4N_{MA,11}$]TFSI). This monomer was prepared from [$C_4N_{MA,11}$]Br and LiTFSI according to similar procedures as described above for [$C_4N_{MA,11}$]FSI. Yield: 90%, colorless oil. ¹H NMR (399.76 MHz; DMSO- d_6 ; TMS; ppm): $\delta = 0.94$ (t, 3H), 1.30 (m, 2H), 1.66 (m, 2H), 1.92 (s, 3H), 3.31 (s, 2 × 3H), 3.36 (t, 2H), 3.70 (t, 2H), 4.53 (t, 2H), 5.77 (s, 1H), 6.08 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO- d_6 ; CCl₃F; ppm): $\delta = -78.9$. ESI-MS: *m/z* (%): 214 (100) [$C_4N_{MA,11}$]⁺, 280 (100) TFSI⁻. Elemental analysis calcd (%) for $C_{14}H_{24}F_6N_2O_6S_2$: C, 34.01; H, 4.89; N, 5.67. Found (%): C, 34.14; H, 4.82; N, 5.86. IR (KBr, ν_{max} , cm⁻¹): 2970 (m), 1724 (s), 1637 (m), 1353 (s), 1296 (w), 1058 (s), 1140 (s), 1196 (s), 952 (w), 790 (m).

2.2.1.3. N,N-Dimethyl-N-[2-(methacryloyloxy)ethyl]-N-(2methoxyethyl)ammonium bis(fluorosulfonyl)imide ([C₃ON_{MA,11}]FSI). This monomer was prepared from N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-(2-methoxyethyl)ammonium iodide ([C₃ON_{MA,11}]I) and KFSI according to similar procedures as described above for [C₄N_{MA,11}]FSI. Yield: 90%, colorless oil. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): δ = 1.91 (s, 3H), 3.15 (s, 2 × 3H), 3.30 (s, 3H), 3.63 (t, 2H), 3.73–3.77 (m, 2 × 2H), 4.53 (t, 2H), 5.77 (s, 1H), 6.09 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): δ = 53.5. ESI-MS: *m*/*z* (%): 216 (100) [C₃ON_{MA,11}]⁺, 180 (100) FSI⁻. Elemental analysis calcd (%) for C₁₁H₂₂F₂N₂O₇S₂: C, 33.33; H, 5.59; N, 7.07. Found (%): C, 33.43; H, 5.52; N, 7.02. IR (KBr, ν_{max} , cm⁻¹): 3047 (s), 2936 (m), 1723 (s), 1635 (m), 1382 (s), 1182 (s), 1107 (s), 919 (w), 832 (m).

2.2.1.4. N,N-Dimethyl-N-[2-(methacryloyloxy)ethyl]-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl) imide ([$C_3ON_{MA,11}$]TFSI). This monomer was prepared from [$C_3ON_{MA,11}$]I and LiTFSI according to similar procedures as described above for [$C_4N_{MA,11}$]FSI. Yield: 90%, colorless oil. ¹H NMR (399.76 MHz; DMSO- d_6 ; TMS; ppm): $\delta = 1.92$ (s, 3H), 3.15 (s, 2 × 3H), 3.30 (s, 3H), 3.63 (t, 2H), 3.73–3.77 (m, 2 × 2H), 4.53 (t, 2H), 5.77 (s, 1H), 6.09 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO- d_6 ; CCl₃F; ppm): $\delta = -78.9$. ESI-MS: m/z (%): 216 (100) [$C_3ON_{MA,11}$]⁺, 280 (100) TFSI⁻. Elemental analysis calcd (%) for $C_{13}H_{22}F_6N_2O_7S_2$: C, 31.45; H, 4.47; N, 5.64. Found (%): C, 31.48; H, 4.42; N, 5.56. IR (KBr, ν_{max} , cm⁻¹): 2930 (m), 1723 (s), 1636 (m), 1473 (m), 1382 (s), 1215 (m), 1182 (s), 1107 (s), 957 (w), 832 (m), 751 (m).

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2.2.1.5. *N*,*N*-Dimethyl-*N*-(*n*-heptyl)-*N*-[2-(methacryloyloxy)ethyl] ammonium bis(fluorosulfonyl)imide ([$C_7N_{MA,11}$]FSI). This monomer was prepared from *N*,*N*-dimethyl-*N*-(*n*-heptyl)-*N*-[2-(methacryloyloxy)ethyl]ammonium bromide ([$C_7N_{MA,11}$]Br) and KFSI according to similar procedures as described above for [$C_4N_{MA,11}$]FSI. Yield: 88%, colorless oil. ¹H NMR (399.76 MHz; DMSO-*d*₆; TMS; ppm): δ = 0.88 (t, 3H), 1.22–1.34 (m, 4 × 2H), 1.68 (m, 2H), 1.92 (s, 3H), 3.09 (s, 2 × 3H), 3.36 (t, 2H), 3.69 (t, 2H), 4.53 (t, 2H), 5.77 (s, 1H), 6.08 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO-*d*₆; CCl₃F; ppm): δ = 53.5. ESI-MS: *m*/*z* (%): 256 (100) [$C_7N_{MA,11}$]⁺, 180 (100) FSI⁻. Elemental analysis calcd (%) for C₁₅H₃₀F₂N₂O₆S₂: C, 41.27; H, 6.93; N, 6.42. Found (%): C, 41.32; H, 6.85; N, 6.49. IR (KBr, *ν*_{max}, cm⁻¹): 3047 (s), 2931 (m), 1724 (s), 1640 (m), 1464 (m), 1382 (s), 1106 (s), 1296 (w), 1215 (m), 1181 (s), 919 (w), 832 (m).

2.2.1.6. *N*,*N*-Dimethyl-*N*-(*n*-heptyl)-*N*-[2-(methacryloyloxy)ethyl] ammonium bis(trifluoromethanesulfonyl) imide ([$C_7N_{MA,11}$]TFSI). This monomer was prepared from [$C_7N_{MA,11}$]Br and LiTFSI according to similar procedures as described above for [$C_4N_{MA,11}$]FSI. Yield: 85%, colorless oil. ¹H NMR (399.76 MHz; DMSO-*d*₆; TMS; ppm): δ = 0.88 (t, 3H), 1.23–1.35 (m, 4 × 2H), 1.68 (m, 2H), 1.92 (s, 3H), 3.09 (s, 2 × 3H), 3.36 (t, 2H), 3.69 (t, 2H), 4.53 (t, 2H), 5.77 (s, 1H), 6.08 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO-*d*₆; CCl₃F; ppm): δ = -78.9. ESI-MS: *m*/*z* (%): 256 (100) [$C_7N_{MA,11}$]⁺, 280 (100) TFSI⁻. Elemental analysis calcd (%) for C₁₇H₃₀F₆N₂O₆S₂: C, 38.05; H, 5.64; N, 5.22. Found (%): C, 38.07; H, 5.69; N, 5.29. IR (KBr, *v*_{max}, cm⁻¹): 3047 (s), 2931 (m), 1724 (s), 1635 (m), 1464 (m), 1382 (s), 1106 (s), 1296 (w), 1215 (m), 1181 (s), 919 (w), 832 (m).

2.2.1.7. N,N-Dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2*methoxyethoxy*)*ethyl*]*ammonium* bis(fluorosulfonyl)imide ([C₅O₂N_{MA.11}]FSI). This monomer was prepared from N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-methoxyethoxy)ethyl] ammonium iodide ($[C_5O_2N_{MA,11}]I$) and KFSI according to similar procedures as described above for [C₄N_{MA,11}]FSI. Yield: 80%, colorless oil. ¹H NMR (399.76 MHz; DMSO- d_6 ; TMS; ppm): $\delta = 1.92$ (s, 3H), 3.15 (s, 2×3 H), 3.26 (s, 3H), 3.47 (t, 2H), 3.59 (t, 2H), 3.64 (t, 2H), 3.76 (t. 2H), 3.86 (t. 2H), 4.54 (t. 2H), 5.76 (s. 1H), 6.09 (s. 1H), ¹⁹F NMR (376.05 MHz; DMSO- d_6 ; CCl₃F; ppm): $\delta = 53.5$. ESI-MS: m/z (%): 260 (100) [C₅O₂N_{MA.11}]⁺, 180 (100) FSI⁻. Elemental analysis calcd (%) for C₁₃H₂₆F₂N₂O₈S₂: C, 35.45; H, 5.95; N, 6.36. Found (%): C, 35.54; H, 5.92; N, 6.36. IR (KBr, *v*_{max}, cm⁻¹): 2930 (m), 1723 (s), 1635 (m), 1473 (m), 1382 (s), 1215 (m), 1182 (s), 1107 (s), 957 (w), 832 (m), 751 (m).

2.2.1.8. N,N-Dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2methoxyethoxy)ethyl]ammonium bis(trifluoromethanesulfonyl)imide ([$C_5O_2N_{MA,11}$]TFSI). This monomer was prepared from [$C_5O_2N_{MA,11}$]I and LiTFSI according to similar procedures as described above for [$C_4N_{MA,11}$]FSI. Yield: 80%, colorless oil. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): δ = 1.92 (s, 3H), 3.15 (s, 2 × 3H), 3.27 (s, 3H), 3.47 (t, 2H), 3.59 (t, 2H), 3.64 (t, 2H), 3.76 (t, 2H), 3.86 (s, 2H), 4.54 (t, 2H), 5.77 (s, 1H), 6.08 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): $\delta = -78.9$. ESI-MS: m/z (%): 260 (100) [C₅O₂N_{MA,11}]⁺, 280 (100) TFSI⁻. Elemental analysis calcd (%) for C₁₅H₂₆F₆N₂O₈S₂: C, 33.33; H, 4.85; N, 5.18. Found (%): C, 33.44; H, 4.82; N, 5.16. IR (KBr, ν_{max} , cm⁻¹): 2968 (m), 2934 (m), 1724 (s), 1637 (m), 1474 (m), 1354 (s), 1296 (w), 1058 (s), 1140 (s), 1197 (s), 955 (m), 790 (m).

2.2.1.9. N,N-Dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-(2*methoxyethoxy*)*ethoxy*)*ethyl*]*ammonium* bis(fluorosulfonyl)imide $([C_7O_3N_{MA,11}]FSI)$. The mixture of N-[2-(2-(2-methoxyethoxy)) ethoxy)ethyl]-N,N-dimethylamine (10.0 g, 52 mmol) and a little excess of 2-bromoethyl methacrylate (11.0 g, 57 mmol) in acetone (30 mL) was stirred at room temperature for 3 days. Then, the acetone and unreacted 2-bromoethyl methacrylate were completely removed under reduced pressure, and the obtained product was recrystallized from acetonitrile/ethyl acetate (1/2, v./ v.), and dried under high vacuum at room temperature to afford the intermediate, N,N-dimethyl -N-[2-(methacryloyloxy)ethyl]-N-[2-(2-(2-methoxy)ethoxy)ethyl]ammonium bromide ([C₇O₃N_{MA.11}]Br), as a solid (19.6 g, 89% yield). Finally, [C₇O₃N_{MA.11}] FSI was prepared from [C₇O₃N_{MA.11}]Br and KFSI according to similar procedures as described above for [C₄N_{MA,11}]FSI. Yield: 80%, colorless oil. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): $\delta = 1.91$ (s, 3H), 3.16 (s, 2 × 3H), 3.24 (s, 3H), 3.42 (t, 2H), 3.53 (t, 4H), 3.58 (t, 2H), 3.65 (t, 2H), 3.76 (t, 2H), 3.86 (s, 2H), 4.53 (t, 2H), 5.76 (s, 1H), 6.09 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): δ = 53.5. ESI-MS: *m*/*z* (%): 304 (100) [C₇O₃N_{MA,11}]⁺, 180 (100) FSI⁻. Elemental analysis calcd (%) for $C_{15}H_{30}F_2N_2O_9S_2$: C, 37.18; H, 6.24; N, 5.78. Found (%): C, 37.08; H, 6.27; N, 5.74. IR (KBr, ν_{max} , cm⁻¹): 3048 (s), 2888 (m), 1634 (m), 1724 (s), 1382 (s), 1297 (w), 1183 (s), 1106 (s), 958 (m), 832 (m).

2.2.1.10. N,N-Dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-(2-methoxyethoxy)ethoxy)ethyl]ammonium bis(trifluoromethanesulfonyl)imide ([$C_7O_3N_{MA,11}$]TFSI). This monomer was prepared from ([$C_7O_3N_{MA,11}$]Br) and LiTFSI according to similar procedures as described above for [$C_7O_3N_{MA,11}$]FSI. Yield: 80%, colorless oil. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): δ = 1.96 (s, 3H), 3.17 (s, 2 × 3H), 3.24 (s, 3H), 3.43 (t, 2H), 3.54 (t, 4H), 3.58 (t, 2H), 3.65 (t, 2H), 3.74 (t, 2H), 3.90 (s, 2H), 4.53 (t, 2H), 5.72 (s, 1H), 6.13 (s, 1H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): δ = -78.9. ESI-MS: *m/z* (%): 304 (100) [$C_7O_3N_{MA,11}$]⁺, 280 (100) TFSI⁻. Elemental analysis calcd (%) for C₁₇H₃₀F₆N₂O₉S₂: C, 34.93; H, 5.17; N, 4.79. Found (%): C, 34.97; H, 5.24; N, 4.78. IR (KBr, *v*_{max}, cm⁻¹): 3048 (s), 2888 (m), 1724 (s), 1636 (m), 1353 (s), 1297 (w), 1195 (s), 1058 (s), 958 (m), 849 (m).

2.2.2. Preparation and characterization of PILs

The PILs were synthesized by polymerizing the corresponding neat monomer in acetone or other solvent (Table 2) via a free

Table	2
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Characterization of j	polymeric ionic	liquids	(PILs) of	[C ₅ O ₂ N _{MA,1}	1]FSI at	different	preparative	conditions.
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Entry	I/m ^a (%)	M/s ^b	Solvent	$[\eta]^{c}$ (cm ³ g ⁻¹)	$M_{\rm v}{}^{\rm d}$ (10 ⁴ g mol ⁻¹)	Appearance
1	1	0.5	Dimethylformamide	_	_	Liquid
2	4	1	Acetone	10	1.8	Viscous liquid
3	2	1	Acetone	21	6	Sticky rubber
4	1	1	Acetone	67	39	Soft rubber
5	1	2	Dimethylformamide	87	59	Soft rubber
6	1	4	Dimethylformamide	-	-	Crosslinked

^a Molar ratio of the initiator to the monomer.

^b Volume ratio of the monomer to the solvent.
 ^c In MEK solution containing 10 mM KFSI at 30 °C.

^d Employing $[\eta] = KM_v^{\alpha}$ with parameters of $K = 2.3 \times 10^{-2}$ cm³ g⁻¹ and $\alpha = 0.62$ [39–41].

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radical process. In a typical reaction, [C₄N_{MA.11}]FSI (3.0 g, 7.6 mmol), AIBN (1.3 mg, i.e., [AIBN]/[vinyl unit] = 0.01 by mole) as initiator, and acetone (2 mL, i.e., V[acetone]/V[monomer] = 1/1) were mixed to form a homogeneous solution, and were heated to 70 °C for 10 h under argon atmosphere. Then, a small amount of acetone (ca. 5-10 mL) was added into the resulting inhomogeneous solutions until the solid dissolved completely. The product was isolated and purified by pouring the solution into a large excess of ether (100 mL), the solid obtained was then washed thoroughly with ether three times $(3 \times 50 \text{ mL})$ and dried rigorously under high vacuum at 70 °C for 24 h to afford the target polymer product, poly(N-(n-butyl)-N,N-dimethyl-N-[2-(methacryloyloxy)ethyl] ammonium) bis(fluorosulfonyl)imide (P[C₄N_{MA.11}]FSI), as a white powder (2.4 g, 80%). ¹H NMR (399.76 MHz; DMSO-*d*₆; TMS; ppm): $\delta = 0.89 - 1.15$ (board, 8H), 1.24 - 1.42 (board, 2H), 1.62 - 1.81 (board, 2H), 3.11–3.25 (board, 2H), 3.58–3.62 (board, 2 × 3H), 3.82–3.90 (board, 2H), 4.31-4.52 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO*d*₆; CCl₃F; ppm): δ = 53.5. IR (KBr, ν_{max} , cm⁻¹): 2934 (m), 1730 (s), 1382 (s), 1263 (w), 1217 (m), 1182 (s), 1108 (s), 957 (m), 831 (m), 749 (m). Intrinsic viscosity ([η]): [η] = 67.0 cm³ g⁻¹, viscosity-average molecular weight (M_v) : $M_v = 3.9 \times 10^5$ g mol⁻¹.

2.2.2.1. Poly(N-(n-butyl)-N,N-dimethyl-N-[2-(methacryloyloxy)ethyl] ammonium) bis(trifluoromethanesulfonyl) imide ($P[C_4N_{MA,11}]TFSI$). Yield: 82%, white powder. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): $\delta = 0.88-1.16$ (board, 8H), 1.22–1.41 (board, 2H), 1.63–1.80 (board, 2H), 3.13–3.26 (board, 2H), 3.57–3.63 (board, 2 × 3H), 3.82–3.90 (board, 2H), 4.32–4.54 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): $\delta = -78.9$. IR (KBr, ν_{max} , cm⁻¹): 2959 (m), 1729 (s), 1479 (m), 1353 (s), 1296 (w), 1058 (s), 1139 (s), 1195 (s), 968 (w), 790 (m). [η] = 68.6 cm³ g⁻¹, $M_v = 4.0 \times 10^5$ g mol⁻¹.

2.2.2.2. Poly(N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-(2methoxyethyl)ammonium) bis(fluorosulfonyl)imide (P[C₃ON_{MA,11}] FSI). Yield: 76%, white powder. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): $\delta = 0.87-1.28$ (board, 5H), 3.12–3.21 (board, 3 × 3H), 3.31–3.39 (board, 2H), 3.60–3.67 (board, 2H), 3.82–3.90 (board, 2H), 4.31–4.52 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): $\delta = 53.5$. IR (KBr, ν_{max} , cm⁻¹): 2994 (m), 1729 (s), 1477 (m), 1382 (s), 1265 (w), 1217 (m), 1107 (s), 1181 (s), 920 (w), 955 (w), 832 (m), 751 (m). [η] = 44.0 cm³ g⁻¹, $M_v = 2.0 \times 10^5$ g mol⁻¹.

2.2.2.3. Poly(N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-(2methoxyethyl)ammonium) bis(trifluoromethanesulfonyl)imide (P [C₃ON_{MA,11}]TFSI). Yield: 80%, white powder. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): $\delta = 0.88-1.27$ (5H), 3.11–3.19 (board, 3 × 3H), 3.32–3.39 (board, 2H), 3.61–3.68 (board, 2H), 3.82–3.90 (board, 2H), 4.31–4.52 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSOd₆; CCl₃F; ppm): $\delta = -78.9$. IR (KBr, v_{max} , cm⁻¹): 2994 (m), 1729 (s), 1478 (m), 1353 (s), 1057 (s), 1297 (w), 1139 (s), 1193 (s), 954 (m), 790 (m). [η] = 47.0 cm³ g⁻¹, $M_V = 2.2 \times 10^5$ g mol⁻¹.

2.2.2.4. Poly(N,N-dimethyl-N-(n-heptyl)-N-[2-(methacryloyloxy) ethyl]ammonium) bis(fluorosulfonyl)imide (P[C₇N_{MA,11}]FSI). Yield: 75%, white powder. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): $\delta = 0.88-1.08$ (board, 8H), 1.12–1.32 (board, 8H), 1.70–1.83 (board, 2H), 3.04–3.14 (board, 2 × 3H), 3.34–3.45 (board, 2H), 3.52–3.61 (board, 2H), 4.30–4.53 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): $\delta = 53.5$. IR (KBr, ν_{max} , cm⁻¹): 2958 (m), 1729 (s), 1480 (m), 1382 (s), 1216 (m), 1181 (s), 1106 (s), 967 (w), 832 (m). [η] = 70.4 cm³ g⁻¹, M_V = 4.2 × 10⁵ g mol⁻¹.

2.2.2.5. Poly(N,N-dimethyl-N-(n-heptyl)-N-[2-(methacryloyloxy) ethyl]ammonium) bis(trifluoromethanesulfonyl) imide (P[C₇N_{MA,11}]

TFSI). Yield: 72%, white powder. ¹H NMR (399.76 MHz; DMSO-*d*₆; TMS; ppm): $\delta = 0.86-1.09$ (board, 8H), 1.10–1.31 (board, 4 × 2H), 1.72–1.81 (board, 2H), 3.05–3.13 (board, 2 × 3H), 3.32–3.41 (board, 2H), 3.55–3.62 (board, 2H), 4.31–4.52 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO-*d*₆; CCl₃F; ppm): $\delta = -78.9$. IR (KBr, ν_{max} , cm⁻¹): 2969 (m), 1729 (s), 1480 (m), 1353 (s), 1297 (w), 1058 (s), 1139 (s), 1194 (s), 957 (m), 791 (m). [η] = 55.9 cm³ g⁻¹, $M_{\rm V} = 2.9 \times 10^5$ g mol⁻¹.

2.2.2.6. Poly(N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-methoxyethoxy)ethyl]ammonium) bis(fluorosulfonyl)imide (P [$C_{502N_{MA,11}}$]FSI). Yield: 70%, soft rubber. ¹H NMR (399.76 MHz; DMSO- d_6 ; TMS; ppm): $\delta = 0.86-1.04$ (board, 5H), 3.12-3.17 (board, 3 × 3H), 3.44-3.52 (board, 2 × 3H), 3.52-3.61 (board, 2H), 3.86-3.92 (board, 2H), 4.32-4.36 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO- d_6 ; CCl₃F; ppm): $\delta = 53.5$. IR (KBr, ν_{max} , cm⁻¹): 2932 (m), 1729 (s), 1476 (m), 1382 (s), 1264 (w), 1217 (m), 1181 (s), 1107 (s), 959 (w), 832 (m). [η] = 66.6 cm³ g⁻¹, M_v = 3.8 × 10⁵ g mol⁻¹.

2.2.2.7. Poly(N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-methoxyethoxy)ethyl]ammonium) bis(trifluoromethanesulfonyl) imide ($P[C_5O_2N_{MA,11}]TFSI$). Yield: 68%, soft rubber. ¹H NMR (399.76 MHz; DMSO- d_6 ; TMS; ppm): $\delta = 0.86-1.00$ (board, 5H), 3.14–3.19 (board, 3 × 3H), 3.45–3.51 (board, 2 × 3H), 3.55–3.63 (board, 2H), 3.85–3.91 (board, 2H), 4.31–4.37 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO- d_6 ; CCl₃F; ppm): $\delta = -78.9$. IR (KBr, ν_{max} , cm⁻¹): 3049 (m), 1730 (s), 1482 (m), 1353 (s), 1058 (s), 1296 (w), 1139 (s), 1191 (s), 953 (m), 790 (m). [η] = 54.3 cm³ g⁻¹, $M_v = 2.8 \times 10^5$ g mol⁻¹.

2.2.2.8. Poly(N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-(2-methoxyethoxy)ethyl)ammonium) bis(fluorosulfonyl)imide (*P*[C₇O₃N_{MA,11}]FSI). Yield: 62%, sticky rubber. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): δ = 0.91–1.12 (board, 5H), 3.14–3.25 (board, 9H), 3.51–3.54 (board, 2H), 3.60–3.73 (board, 10H), 3.85–3.91 (board, 2H), 4.31–4.37 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): δ = 53.5. IR (KBr, ν_{max} , cm⁻¹): 2888 (m), 1728 (s), 1474 (m), 1382 (s), 1216(m), 1181 (s), 1106 (s), 831 (m). [η] = 42.2 cm³ g⁻¹, $M_{\rm V}$ = 1.8 × 10⁵ g mol⁻¹.

2.2.2.9. Poly(N,N-dimethyl-N-[2-(methacryloyloxy)ethyl]-N-[2-(2-(2-methoxyethoxy)ethoxy)ethyl]ammonium) bis(tri-fluoromethanesulfonyl)imide (P[C₇O₃N_{MA,11}]TFSI). Yield: 60%, sticky rubber. ¹H NMR (399.76 MHz; DMSO-d₆; TMS; ppm): δ = 0.90–1.14 (board, 5H), 3.11–3.22 (board, 9H), 3.54–3.56 (board, 2H), 3.58–3.64 (board, 10H), 3.84–3.92 (board, 2H), 4.33–4.39 (board, 2H). ¹⁹F NMR (376.05 MHz; DMSO-d₆; CCl₃F; ppm): δ = -78.9. IR (KBr, ν_{max} , cm⁻¹): 2918 (m), 1728 (s), 1474 (m), 1352 (s), 1190 (s), 1138 (s), 831 (m). [η] = 38.1 cm³ g⁻¹, M_V = 1.6 × 10⁵ g mol⁻¹.

2.3. Instrumentation

¹H (399.65 MHz), and ¹⁹F (376.05 MHz) NMR spectra were recorded on a Bruker AV400 spectrometer, and dimethyl sulfoxide- d_6 (DMSO- d_6) was used as solvent. Chemical shift values are reported in ppm relative to TMS for ¹H, and to external references, CCl₃F, for ¹⁹F. Electrospray ionization mass spectra (ESI-MS) were measured on a PerkinElmer ELAN DRC–e spectrometer. Element analyses (C, H, and N) were performed on an Elementar Vario Micro Cube elemental analyzer. Fourier transform infrared spectra (FTIR) were recorded on a Bruker Equinox 55 spectrometer at a resolution of 2 cm⁻¹, and the scan number equals to 32 (KBr pellets).

The intrinsic viscosity ([η]) of the prepared PILs was measured using an Ubbelohde-type viscometer at 30 °C in methyl ethyl ketone (MEK), which contained 10 mM KFSI for suppression of

polyelectrolyte effect [37–39]. The values of viscosity-average molecular weight (M_v) of the prepared PILs were calculated according to Mark–Houwink–Sakurada equation, [η] = KM_v^{α} , wherein $K = 2.3 \times 10^{-2}$ cm³ g⁻¹ and $\alpha = 0.62$, were determined by using a polystyrene/MEK solution at 30 °C [39–41]. Polystyrene was used as an internal standard.

The calorimetric measurement was performed on a differential scanning calorimeter (Netzsch 200 F3). The prepared ILMs or PILs (see Section 2.2) sample with average weight of ca. 5 mg was hermetically sealed in an aluminum pan in a glove box (H₂O and O₂ < 1 ppm). The as-prepared sample was initially cooled from room temperature (20–25 °C) to –150 °C and was allow to stand for 5 min, and then heated to 150 °C at a rate of 10 °C min⁻¹ under nitrogen flow. The glass transition temperature (T_g , onset of the heat capacity change) was detected at the heating scan.

Thermal gravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA system. Samples of average weight of 5–10 mg were placed in a platinum pan and heated at 10 °C min⁻¹ from room temperature to 600 °C under a flow of nitrogen. The temperature at which 5% weight lost was defined as the decomposition temperature (T_d).

The water content of ILMs was detected by Karl-Fischer titration (Metrohm KF 831).

The density (ρ , in g cm⁻³) of ILMs was the mean of three measurement values, which were determined by measuring the weight of three separate samples of 1.0 mL at 25 °C.

The viscosity (η , in cP) of ILMs was measured on a programmable viscometer (Brookfield, DV-III+) in a homemade box filled with Ar, and the temperature was accurately controlled at 25 \pm 0.1 °C with a Brookfield TC-502 oil bath.

The ionic conductivities (σ , in S cm⁻¹) were measured by using ac impedance spectroscopic technique. The ac impedance spectra were measured on an Autolab PGSTAT302N impedance analyzer (Eco Chemie, Netherlands) in the frequency range from 0.1 to 10⁶ Hz over a temperature range from 10 to 60 °C at an interval of 5 °C. The temperature was accurately controlled to ± 0.1 °C with a JULABO F12 oil bath. At each temperature of measurement, the cells were allowed to equilibrate for at least 30 min for good contact. The conductivity of ILMs was measured in a sealed platinum black disk conductivity cell (cell constant: 9.96 cm⁻¹). The cell was calibrated with 0.1 M KCl aqueous solution before and after each measurement. The conductivity of PILs was performed on symmetric twoelectrode stainless steel (SS) | polymer electrolyte | SS cells. The polymer electrolyte was sandwiched between a pair of stainless steel blocking electrodes and a Teflon spacer was used to maintain the proper diameter (5 mm in diameter) and sample thickness (200 µm thick). Before measurement, the sandwiched cell was heated at 60 °C for 4 h for obtaining good contact, and then were allowed to stand at room temperature overnight. The ionic conductivity was derived from the value of resistance (R, in Ω) of the bulk electrolyte obtained in the complex impedance diagram, according to the equation: $\sigma = L/(RS)$, where L (cm) is the thickness of membrane of the polymer electrolyte, and $S(cm^2)$ is the area of the membrane.

3. Results and discussion

3.1. Synthesis of ILMs and PILs

The preparation for the ILMs in the present study is shown in Scheme 1 and Table 1, where each subscript in the abbreviation denotes a side chain group of the ammonium cation (i.e. CH₃, 2-(methacryloyloxy)ethyl groups in the cations are subscripted as 1, MA, respectively), while C_m and C_mO_n in the abbreviations mean the changed side chains (i.e., C_m is alkyl, $C_m = n$ - C_mH_{2m+1} , m = 4 and

7; C_mO_n is alkyl ether, $C_3O = CH_2CH_2OCH_3$, $C_5O_2 = (CH_2CH_2O)_2CH_3$, and $C_7O_3 = (CH_2CH_2O)_3CH_3$). The ten ILMs comprised of the five cations and two anions in Scheme 1 were prepared by a metathesis reaction of the corresponding ammonium salt with a slight excess of KFSI or LiTFSI (1.05 equiv.) in water at room temperature.

All these 10 new ammonium ILMs are hydrophobic and colorless liquids at room temperature. Their structures and compositions were confirmed by ¹H and ¹⁹F NMR, and elemental analyses (see Section 2.2).

Fig. 1 shows ¹H NMR spectra of the representative IL monomer $[C_5O_2N_{MA,11}]FSI$, and its polymer, $P[C_5O_2N_{MA,11}]FSI$. $[C_5O_2N_{MA,11}]FSI$ monomer shows proton signals at 6.06 and 5.79 ppm corresponding to the vinyl group $(CH_2=CH(CH_3)-C)$. After the polymerization of the monomer, the double bond peaks disappeared, while new proton signals representing single bond peaks appeared between 0.86 and 1.00 ppm $(CH_2-CH(CH_3)-C)$, which suggests that $[C_5O_2N_{MA,11}]FSI$ was polymerized successfully. Additionally, the disappearance of double bond stretching frequencies at around 1640 cm⁻¹ in the FTIR spectrum also strongly supports the successful polymerization.

It has been shown that the physicochemical and electrochemical properties of PILs (e.g., solubility, film-forming ability and conductivity) are greatly affected by their molecular weights [41]. Herein, the free radical polymerization of $[C_5O_2N_{MA,11}]FSI$ was studied in detail and the optimal conditions for the preparation of good physicochemical properties polyelectrolytes were elaborated. AIBN was used as a standard well known initiator for free radical polymerization processes. To exclude the inhibition by air oxygen, the reaction was carried out in degasified sealed ampoule.

The influence factors such as the nature of the solvent and its quantity, the reaction time and the concentration of the monomer on the yield and inherent viscosity of the $P[C_5O_2N_{MA,11}]FSI$ were summarized in Table 2.

Fig. 2 shows the influence of the molecular weight on the conductivity and appearance of the P[C₅O₂N_{MA,11}]FSI. The result indicates that the size of the polyelectrolyte chain strongly influences the conductivity of the obtained PIL. The conductivities change in the range of nearly three orders of magnitude (from 10^{-4} to 10^{-7} S cm⁻¹ at 30 °C). Starting from the pure monomer, [C₅O₂N_{MA,11}]FSI, with the conductivity of 3.7×10^{-4} S cm⁻¹ at 30 °C, the conductivity curve sharply decreases with the increase of



Fig. 1. ¹H NMR spectra of the ionic liquid monomer, $[C_5O_2N_{MA,11}]FSI$ (a), and its polymer, $P[C_5O_2N_{MA,11}]FSI$ (b).

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Fig. 2. The conductivities (at 30 °C) and appearance of the polymeric ionic liquids (PILs), $P[C_5O_2N_{MA,11}]FSI$, with different inherent viscosity (in MEK solution at 30 °C).

molecular weight until the conductivity becomes 3.8×10^{-7} S cm⁻¹ while the molecular weight of PIL approaches 6.0×10^5 g mol⁻¹. In addition, the appearance of the P[C5O2NMA.11]FSI changes from viscous liquid (inset of Fig. 2a) to sticky rubber (inset of Fig. 2b) and then to soft rubber (inset of Fig. 2c) with the increase of molecular weight. However, with further increasing the molecular weight, P [C₅O₂N_{MA,11}]FSI is cross-linked (inset of Fig. 2d, which shows the swelling behavior of the P[C₅O₂N_{MA.11}]FSI in acetone) and insoluble in various solvents, such as tetrahvdrofuran (THF), acetone, dimethylformamide (DMF), methanol and dimethylsulfoxide (DMSO). This would be attributed to the oxygen radicals generated by high concentration of alkyl ether group during the polymerization, initiate the crosslinking, and thus results in the gelation of the P [C₅O₂N_{MA.11}]FSI [42]. The obtained result leads to the conclusion that molecular weight is crucial to the ionic conductivity and filmforming ability of PILs. In this case, P[C₅O₂N_{MA.11}]FSI with a medium molecular weight $(3.8 \times 10^5 \text{ g mol}^{-1}, \text{ Table 2, entry 4})$ shows a relative good balance between ionic conductivity and film-forming ability.

The other PILs were prepared via free radical polymerization according to the optimized condition (Table 2, entry 4) for the preparation of $P[C_5O_2N_{MA,11}]$ FSI. Fig. 3 shows the appearance of the FSI⁻-based PILs films prepared by casting the solutions of PILs in acetone onto the Teflon dish. Depending on the structure of the PILs, the obtained films differ by their appearance and film-forming abilities. $P[C_4N_{MA,11}]$ FSI and $P[C_3ON_{MA,11}]$ FSI with shorter side chain length provide films which are brittle at room temperature, and P $[C_7O_3N_{MA,11}]$ FSI with the longest side chain length generates sticky film, while $P[C_7N_{MA,11}]$ FSI and $P[C_5O_2N_{MA,11}]$ FSI are possessing tight elastic films, and the latter one is more flexible. This result reveals that the enlargement of the space of polymer backbone by longer side chain length (especially alkyl ether side chain) of ammonium-based PILs can greatly improve the mechanical properties. Such

tendency in the film-forming behavior of PILs is in agreement with our DSC results (see Section 3.3).

3.2. Thermal stability

Fig. 4 depicts the TGA traces for the FSI⁻- and TFSI⁻-based monomers. All the monomers can be stable up to 250 °C. The thermal stabilities of the FSI⁻-based monomers are obviously lower than that of the TFSI⁻-based ones, as already observed in previous studies [27,35]. This could be attributed to the poor thermal stability of FSO₂-group towards pyrolysis [35]. In addition, the values of T_d of these methoxyethyl substituted ammonium ILMs are lower than those of the hydrocarbon alkyl substituted ammonium ones. This is consistent with the reported results that having an ether function into the onium of the ILs generally causes a decrease in thermal stability [24,25].

Fig. 5 exhibits the TGA traces for the FSI⁻- and TFSI⁻-based polymers. The thermal stabilities of the PILs significantly increase for both the FSI⁻- and TFSI⁻-based polymers, compared with the corresponding ILMs. For example, P[C₄N_{MA,11}]FSI (297 °C) vs. [C₄N_{MA,11}]FSI (267 °C), and P[C₄N_{MA,11}]TFSI (339 °C) vs. [C₄N_{MA,11}]TFSI (322 °C). This is might be caused by the increased ion—ion interactions after polymerization. The values of T_d of the FSI⁻- and TFSI⁻-based PILs are in the range of 268—300 °C and 326—351 °C, respectively, which are well acceptable for a wide range of electrochemical applications.

3.3. Phase transition

Fig. 6 shows the DSC traces of the FSI⁻ and TFSI⁻-based monomers. As seen in Fig. 6, all the prepared monomers exhibit glass-forming characteristics without crystallization/melting events. It is very interesting that the T_g values are lower for the FSI⁻-based ILMs than for the TFSI⁻-based ones (e.g., $[C_4N_{MA,11}]FSI$ ($-72 \degree C$) vs. $[C_4N_{MA,11}]TFSI$ ($-66 \degree C$) and $[C_3ON_{MA,11}]FSI$ ($-71 \degree C$) vs. $[C_3ON_{MA,11}]TFSI$ ($-66 \degree C$) and $[C_3ON_{MA,11}]FSI$ ($-71 \degree C$) vs. $[C_3ON_{MA,11}]TFSI$ ($-68 \degree C$)). This can be attributed to larger Van der Waals interactions in the latter due to the larger volume of TFSI⁻. For the same anion, the values of T_g of the ILMs containing the alkyl ether chains increase progressively with increasing the length of the alkyl ether chains, e.g., $[C_3ON_{MA,11}]FSI$ ($-71 \degree C$) vs. $[C_5O_2N_{MA,11}]$ FSI ($-61 \degree C$) and $[C_3ON_{MA,11}]TFSI$ ($-68 \degree C$) vs. $[C_5O_2N_{MA,11}]TFSI$ ($-59 \degree C$), as expected by the increased van der Waals interactions.

Fig. 7 displays the DSC traces of the FSI⁻ - and TFSI⁻-based PILs. Upon the monomers being polymerized, the corresponding polymers show much high glass transitions, e.g., $P[C_3ON_{MA,11}]FSI (51 °C)$ vs. $[C_3ON_{MA,11}]FSI (-71 °C)$; $P[C_3ON_{MA,11}]TFSI (61 °C)$ vs. $[C_3ON_{MA,11}]TFSI (-68 °C)$, which is essentially due to the sharp decrease in the segmental motion of ions in solid state. In addition, only a glass transition occurred in the range of -35 to 66 °C, while without melting, was observed for all these PILs. This phase behavior indicates that all these polymers do not crystallize, and have a high degree of amorphous phase, which would be helpful for improving the ionic conductivities.



Fig. 3. Photographs of the FSI⁻-based polymeric ionic liquids (PILs): (a) P[C₄N_{MA,11}]FSI, (b) P[C₃ON_{MA,11}]FSI, (c) P[C₇O₃N_{MA,11}]FSI, (d) P[C₅O₂N_{MA,11}]FSI, and (e) P[C₇O₃N_{MA,11}]FSI.

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Fig. 4. The TGA traces of the FSI⁻⁻ (a) and TFSI⁻⁻-based (b) ionic liquid monomers (ILMs).

Fig. 8 shows the dependence of $T_{\rm g}$ on the structure of PILs. Comparison of the values of T_g of the alkyl ether chains-based PILs with those of the isoelectronic alkyl chains-based ones clearly shows the impact of flexibility of alkyl ether group (e.g., P $[C_3ON_{MA,11}]FSI~(51\ ^\circ C)$ vs. $P[C_4N_{MA,11}]FSI~(59\ ^\circ C)$ and $P[C_3ON_{MA,11}]$ TFSI (61 °C) vs. $P[C_4N_{MA,11}]$ TFSI (66 °C)). For a given anion, the T_g values of the alkyl ether chains-based PILs dramatically decrease with the side chain length increase from one to two alkyl ether groups (-CH₂CH₂O-), i.e., $T_g = -33$ °C for P[C₅O₂N_{MA,11}]FSI vs. $T_g = 51$ °C for P[C₃ON_{MA,11}]FSI and $T_g = -15$ °C for P[C₅O₂N_{MA,11}]TFSI vs. $T_g = 61 \degree C$ for P[C₃ON_{MA.11}]TFSI, indicating the reduced restriction of mobility of polymer chain by grafting with alkyl ether chains [28,29]. However, with the further increase of the side chain length to three alkyl ether groups, the values of T_{g} of the alkyl ether chainsbased PILs have no substantial changes (e.g., $T_g = -35$ °C for P $[C_7O_3N_{MA,11}]$ FSI vs. $T_g = -33 \degree C$ for P $[C_5O_2N_{MA,11}]$ FSI). This might be due to the polarity of the alkyl ether group, which dominates over its flexibility, and introducing a long length of polar alkyl ether group into the ammonium cations turns to increase ion-ion and van der Waals interactions in the PILs, thus raising T_g.

On the other hand, one may note that the FSI⁻-based PILs show much lower T_g than the corresponding TFSI⁻-based PILs, e.g., $T_g = -33 \degree C$ for P[C₅O₂N_{MA,11}]FSI vs. $T_g = -15 \degree C$ for P[C₅O₂N_{MA,11}]



Fig. 5. The TGA traces of the FSI $^-$ (a) and TFSI $^-$ -based (b) polymeric ionic liquids (PILs).

TFSI. This can be attributed to much better plasticizing effect of FSI[–] vs. TFSI[–], as already observed in our recent study [36].

3.4. Conductivity

Some of the physicochemical properties of the prepared ILMs including density (*d*), dynamic viscosity (η) and ionic conductivity (σ) are presented in Table 3.

The specific conductivity of the 10 ILMs in Table 3 (Entries 1–10) is mainly governed by the viscosity, molecular weight, density, and ion size [24,25,43,44]. Fig. 9 shows the ionic conductivity of these ten ILMs at 25 °C, which ranges from 0.16 to 0.71 mS cm⁻¹ (see Table 3). For a common cation, the TFSI⁻-based ILMs are less conductive than the FSI⁻-based ones (e.g., 0.31 mS cm⁻¹ for [C₄N_{MA,11}]TFSI vs. 0.55 mS cm⁻¹ for [C₄N_{MA,11}]FSI at 25 °C), as expected from their higher viscosity and higher molecular weight [24,25]. For a given anion, the conductivities at 25 °C decrease with increasing the length of the alkyl ether chains (e.g., Table 3 entry 4 vs. 2 and 9 vs. 7).

Fig. 10 shows equivalent conductivity (Λ) vs. reciprocal of viscosity (η^{-1}) at 25 °C in common logarithm form for the ten ILMs in Table 3, where $\Lambda = \sigma M/\rho$, M, σ , and ρ are the formula weight, specific conductivity, and density of the ILMs, respectively. As seen in Fig. 10, all the plots for the ILMs are located into a non-ionic region

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Fig. 6. DSC traces for the FSI-- (a) and TFSI--based (b) ionic liquid monomers (ILMs).

below the "ideal" Walden line, which suggests that the ILMs are not fully ionized [23,43,44]. A relatively larger deviation of the plots from the "ideal" Walden line was observed for the ILMs with $[C_7O_3N_{MA,11}]^+$ (nos. 5 and 10 in Fig. 10) than for the ILMs with $[C_5O_2N_{MA,11}]^+$ (nos. 4 and 9 in Fig. 10), indicating that the former is less ionic than the latter. This may be explained by the increased van der Waals interactions, due to the increase of the length of the alkyl ether chain, thus a higher dissociation energy in the former ILMs.

Generally, the ionic conductivity of polymer electrolytes is mainly governed by the concentration of charge carrier, and the polymer backbone and/or segmental mobility, and the latter factor is generally coupled with the T_g [45]. Fig. 11 shows the ionic conductivity at 30 °C vs. T_g for FSI[–] and TFSI[–]-based PILs. As seen in Fig. 11,with a constant anion, the ionic conductivities of the PILs increase with the decease of T_g in the order of P[C₄N_{MA,11}]X < P [C₃ON_{MA,11}]X < P[C₇N_{MA,11}]X < P[C₅O₂N_{MA,11}]X < P[C₇O₃N_{MA,11}]X (X = FSI and TFSI). This trend in conductivity is also observed in other PILs [21,22] and strongly indicates that the segmental mobility of PILs is the dominating impact in determining the conductivities. On the other hand, with a constant cation, the



Fig. 7. DSC traces for the FSI-- (a) and TFSI--based (b) polymeric ionic liquids (PILs).



Fig. 8. Glass transition temperature of various polymeric ionic liquids (PILs).

conductivities of FSI⁻-based PILs are higher than those of TFSI⁻-based ones, e.g., 2.6×10^{-6} S cm⁻¹ for P[C₅O₂N_{MA,11}]FSI (no. 4 in Fig 11) vs. 1.2×10^{-6} S cm⁻¹ for P[C₅O₂N_{MA,11}]TFSI (no. 9 in Fig 11) at 30 °C), this would be ascribed to the lower T_g and small anion size (i.e., 95 Å³ (FSI⁻) vs. 147 Å³ (TFSI⁻) [35]) for the corresponding FSI⁻-based PILs. Note is that the maximum ionic conductivity at 30 °C is 4.0×10^{-6} S cm⁻¹ for P[C₇O₃N_{MA,11}]FSI (no. 5 in Fig 11), which is higher than other poly(ammonium)-based PILs reported in literature, e.g., the conductivity at 30 °C is 1.7×10^{-7} S cm⁻¹ for the copolymer of poly(ammonium)-based PILs with poly(ethylene glycol)dimethacrylate (PEGDM) [41].

Fig. 12 depicts the Arrhenius plots of ionic conductivity for these ten PILs. Clearly, all these PILs show significantly decrease in ionic conductivity compared with corresponding ILMs, e.g., 2.6×10^{-6} S cm⁻¹ for P[C₅O₂N_{MA,11}]FSI (no. 4 in Fig 11) vs. 5.5×10^{-4} S cm⁻¹ for [C₅O₂N_{MA,11}]FSI at 30 °C, due to the decrease in the segmental motion of ions after polymerization. As can be seen from Fig. 12, the ionic conductivities increase with increasing the temperature for each PILs, and a notable change in ionic conductivity is observed around 20–40 °C for P[C₇N_{MA,11}]FSI and P [C₇N_{MA,11}]TFSI, due to their glass transitions (see Fig. 8) [36,46]. While, this change in conductivity is absent for P[C₄N_{MA,11}]X and P [C₃ON_{MA,11}]X (X = FSI and TFSI), which would arise from relatively high T_g values (see Fig. 8) and different kinetic rate of glass transition.

Table 3

Density, viscosity, and specific conductivity of various ionic liquid monomers (ILMs) at 25 $^\circ C$ (water content: <100 ppm).

Entry	Samples	<i>M</i> w ^a	d ^b	η^{c}	σ^{d}
		$(g mol^{-1})$	(g cm ⁻³)	(cP)	$(mS cm^{-1})$
1	[C ₄ N _{MA.11}]FSI	395	1.32	252	0.55
2	[C ₃ ON _{MA,11}]FSI	396	1.34	209	0.71
3	[C7NMA,11]FSI	437	1.22	493	0.28
4	[C5O2NMA,11]FSI	441	1.31	297	0.44
5	[C ₇ O ₃ N _{MA,11}]FSI	485	1.29	371	0.30
6	[C ₄ N _{MA,11}]TFSI	495	1.36	391	0.31
7	[C ₃ ON _{MA,11}]TFSI	496	1.41	319	0.45
8	[C ₇ N _{MA,11}]TFSI	537	1.30	659	0.16
9	[C ₅ O ₂ N _{MA,11}]TFSI	541	1.38	442	0.27
10	[C ₇ O ₃ N _{MA,11}]TFSI	585	1.36	557	0.18

^a Molecular weight.

^b Density at 25 °C.

^c Viscosity at 25 °C.

 $^{\rm d}\,$ Ionic conductivity at 25 $^\circ\text{C}.$

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Fig. 9. Ionic conductivity of various ionic liquid monomers (ILMs) at 25 °C.



Fig. 10. Plots of molar conductivity (Λ) against the reciprocal of viscosity (η^{-1}) at 25 °C in logarithm form, wherein the number is exactly consistent with the entry number in Table 3.



Fig. 11. Ionic conductivity at 30 $^\circ C$ vs. T_g for the FSI⁻- and TFSI⁻-based polymeric ionic liquids (PILs).

On the other hand, the Arrhenius plots of ionic conductivity for P $[C_5O_2N_{MA,11}]X$ and $P[C_7O_3N_{MA,11}]X$ (X = FSI and TFSI) exhibit positively curved profiles in the measured temperature range of 10-60 °C (Fig. 12). Therefore, we correlate the ionic conductivities of these four PILs with the empirical Vogel-Tammann-Fulcher (VTF) equation (Eq. (1)) [47–49]:

$$\sigma(T) = \frac{A}{\sqrt{T}} \exp\left[\frac{-B}{T - T_0}\right]$$
(1)

wherein A and B are constants, of which the former is a preexponential factor proportional to $T^{-1/2}$, and B is related to the critical free volume for ion transport. T_0 is the ideal glass transition temperature, at which free volume disappears. Fig. 13 shows VTF plots of conductivities for P[C5O2NMA.11]X and P[C7O3NMA.11]X (X = FSI and TFSI) in the temperature range of 10–60 °C, which was obtained by best fitting the experimental data to Eq. (1), and the values for all the parameters in Eq. (1) are presented in Table 4.



Fig. 12. Arrhenius plots of ionic conductivity for the FSI-- (a) and TFSI--based (b) polymeric ionic liquids (PILs).

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Fig. 13. VTF plots of ionic conductivity for the polymeric ionic liquids (PILs) $P[C_5O_2-N_{MA,11}]X$ and $P[C_7O_3N_{MA,11}]X$ (X = FSI and TFSI).

 Table 4

 The best-fitting parameters of VTF equation for the conductivity of the selected PILs.

Samples	A (S cm ⁻¹ K ^{1/2})	<i>B</i> (K)	T_0 (K)	R^2	$T_{\rm g}^{\rm a}$ (K)
P[C ₅ O ₂ N _{MA,11}]FSI	57	1489	198	0.998	240
P[C7O3NMA,11]FSI	2.6	1074	192	0.996	238
P[C ₅ O ₂ N _{MA,11}]TFSI	48	1387	211	0.999	258
P[C7O3NMA,11]TFSI	1.6	1078	204	0.998	251

 $^{\rm a}\,$ Glass transition temperature determined by DSC in absolute temperature unit (K).

Indeed, excellently linear relationships (correlation coefficient $R^2 > 0.995$) are also obtained between two parameters, $\ln(\sigma T^{1/2})$ and $1000/(T-T_0)$, for these four PILs. This result indicates the σ -T dependence of these four PILs shows a typical VTF behavior and the ionic motion is coupled with the segmental motion of the polymer chain [50]. As seen in Table 4, the values of T_g obtained from the DSC measurements are all higher by a magnitude of 40–50 °C than those of the corresponding T_0 derived from Eq. (1). This is consistent with the reported results, where the values of T_0 are typically ~50 K below the measured T_g of the polymer [38,50,51].

4. Conclusions

A new family of functionalized ionic liquid monomers and their corresponding PILs based on alkyl and alkyl ether substituted ammoniums and perfluorinated sulfonimides (i.e., bis(fluorosulfonyl) imide (FSI⁻), and bis(trifluoromethanesulfonyl)imide (TFSI⁻), are prepared and characterized. All these ILMs and PILs show good thermal stability up to >250 °C. The values of T_g of the alkyl ether chains-based PILs greatly decrease with the increase of the side chain length to two alkyl ether units (-CH₂CH₂O-), while no notable changes in T_{g} can be observed with increasing the side chain length further, due to the increased ion-ion interactions. The ionic conductivity is greatly improved after introducing alkyl ether group, and the maximum ionic conductivities at 30 °C for FSI⁻ and TFSI⁻-based PILs are 4.0×10^{-6} S cm⁻¹ and 2.2×10^{-6} S cm⁻¹, respectively. The σ -T dependence of P[C₅O₂N_{MA,11}]X and P $[C_7O_3N_{MA 11}]X$ (X = FSI and TFSI) shows a typical VTF behavior and the ionic motion is coupled with the segmental motion of the polymer chain. The good physicochemical properties of the

presented PILs make them potential candidates for electrochemical applications.

Acknowledgments

We thank the National Natural Science Foundation of China (No. 51173054) for the financial support.

References

- [1] Lu JM, Yan F, Texter J. Prog Polym Sci 2009;34:431-48.
- [2] Yuan JY, Antonietti M. Polymer 2011;52:1469-82.
- [3] Mecerreyes D. Prog Polym Sci 2011;36:1629–48.
- [4] Yuan JY, Mecerreyes D, Antonietti M. Prog Polym Sci 2013;38:1009–36.
- [5] Washiro S, Yoshizawa M, Nakajima H, Ohno H. Polymer 2004;45:1577–82.
- [6] Nakajima H, Ohno H. Polymer 2005;46:11499–504.
- [7] Appetecchi GB, Kim GT, Montanino M, Carewska M, Marcilla R, Mecerreyes D, et al. J Power Sources 2010;195:3668–75.
- [8] Shaplov AS, Lozinskaya EI, Losada R, Wandrey C, Zdvizhkov AT, Korlyukov AA, et al. Polym Advan Technol 2011;22:448–57.
- [9] Shaplov AS, Vlasov PS, Armand M, Lozinskaya EI, Ponkratov DO, Malyshkina IA, et al. Polym Chem 2011;2:2609–18.
- [10] Shaplov AS, Vlasov PS, Lozinskaya EI, Ponkratov DO, Malyshkina IA, Vidal F, et al. Macromolecules 2011;44:9792–803.
- [11] Azaceta E, Marcilla R, Sanchez-Diaz A, Palomares E, Mecerreyes D. Electrochim Acta 2010;56:42–6.
- [12] Wang GQ, Wang L, Zhuo SP, Fang SB, Lin Y. Chem Commun 2011;47:2700-2.
 [13] Chen XJ, Li Q, Zhao J, Qiu LH, Zhang YG, Sun BQ, et al. J Power Sources
- 2012;207:216–21.
- [14] Neves LA, Coelhoso IM, Crespo JG. J Memb Sci 2010;360:363-70.
- [15] Lin BC, Qiu LH, Lu JM, Yan F. Chem Mater 2010;22:6718–25.
- [16] Ye YS, Elabd YA. Macromolecules 2011;44:8494–503.
- [17] Ye YS, Sharick S, Davis EM, Winey KI, Elabd YA. ACS Macro Lett 2013;2:575-80.
- [18] Kim TY, Lee HW, Stoller M, Dreyer DR, Bielawski CW, Ruoff RS, et al. ACS Nano 2011;5:436-42.
- [19] Hirao M, Ohno H. Electrochim Acta 2000;45:1291-4.
- [20] Ogihara W, Sun J, Forsyth M, MacFarlane DR, Yoshizawa M, Ohno H. Electrochim Acta 2004;49:1797–801.
- [21] Ohno H, Yoshizawa M, Ogihara W. Electrochim Acta 2004;50:255–61.
- [22] Ogihara W, Washiro S, Nakajima H, Ohno H. Electrochim Acta 2006;51:2614-9.
- [23] Xu W, Cooper EI, Angell CA. J Phys Chem B 2003;107:6170-8.
- [24] Zhou ZB, Matsumoto H, Tatsumi K. Chem Eur J 2004;10:6581-91.
- [25] Zhou ZB, Matsumoto H, Tatsumi K. Chem Eur J 2005;11:752-66.
- [26] Tsunashima K, Sugiya M. Electrochem Commun 2007;9:2353-8.
- [27] Han HB, Liu K, Feng SW, Zhou SS, Feng WF, Nie J, et al. Electrochim Acta 2010;55:7134–44.
- [28] Döbbelin M, Azcune I, Bedu M, Luzuriaga AR, Genua A, Jovanovski V, et al. Chem Mater 2012;24:1583–90.
- [29] Lee JH, Lee JS, Lee JW, Hong SM, Koo CM. Eur Polym J 2013;49:1017-22.
- [30] Li MT, Yang L, Fang SH, Dong SM. J Memb Sci 2011;366:245–50.
- [31] Ohno H, Ito K. Chem Lett 1998;27:751-2.
- [32] Zaghib K, Charest P, Guerfi A, Shim J, Perrier M, Striebel K. J Power Sources 2004;134:124–9.
- [33] Matsumoto H, Sakaebe H, Tatsumi K, Kikuta M, Ishiko E, Kono M. J Power Sources 2006;160:1308–13.
- [34] Han HB, Nie J, Liu K, Li WK, Feng WF, Armand M, et al. Electrochim Acta 2010;55:1221–6.
- [35] Han HB, Zhou SS, Zhang DJ, Feng SW, Li LF, Liu K, et al. J Power Sources 2011;196:3623–32.
- [36] Zhang H, Feng WF, Zhou ZB, Nie J. Solid State Ionics 2014;256:61-7.
- [37] Kerstin B, Manuela I. European patent EP1520849, 2005.
- [38] Ye YS, Elabd YA. Polymer 2011;52:1309–17.
- [39] Nakamura K, Saiwaki T, Fukao K. Macromolecules 2010;43:6092-8.
- [40] Nakamura K, Saiwaki T, Fukao K, Inoue T. Macromolecules 2011;44:7719–26.
 [41] Shaplov AS, Lozinskaya EI, Ponkratov DO, Malyshkina IA, Vidal F, Aubert PH,
- et al. Electrochim Acta 2011;57:74–90. [42] Tillet G, Boutevin B, Ameduri B. Prog Polym Sci 2011;36:191–217.
- [42] Full CT, Gong SZ, Liu CY, Zheng LP, Feng WF, Nie J, et al. Electrochim Acta
- 2013;94:229–37. [44] Liu CY, Xu F, Feng SW, Zheng LP, Zhang H, Feng WF, et al. Electrochim Acta 2013;99:262–72.
- [45] Feng SW, Shi DY, Liu F, Zheng LP, Nie J, Feng WF, et al. Electrochim Acta 2013;93:254–63.
- [46] Lupu A, Baltog I, Gluck P. J Polym Sci 1974;12:2399–407.
- [47] Vogel H. Physiol Zool 1921;22:645-6.
- [48] Fulcher GS. J Am Ceram Soc 1923;8:339-55.
- [49] Cohen MH, Turnbull D. J Chem Phys 1959;31:1164-9.
- [50] Seki S, Susan MABH, Kaneko T, Tokuda H, Noda A, Watanabe M. J Phys Chem B 2005;109:3886–92.
- [51] Lascaud S, Vallke A, Besner S, Prud'homme J, Armand M. Macromolecules 1994;27:7469–77.