Cationic Polymerization of a Novel Oxetane-Bearing Ionic Liquid Structure and Properties of the Obtained Poly(ionic liquid)

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ABSTRACT: An ionic liquid, 1-ethyl-3-(3-ethyl-3-oxetanylmethyl)imidazolium bis(trifluoromethanesulfonyl)imide (OXImTFSI), was synthesized, and its cationic polymerization was examined. The heating of a mixture of 1-ethylimidazole and 3chloromethyl-3-ethyloxetane at 90 °C for 48 h yielded 1-ethyl-3-(3-ethyl-3-oxetanylmethyl)imidazolium chloride, which was transformed to a room-temperature ionic liquid, OXImTFSI, by ion exchange with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). This ionic liquid was polymerized using boron trifluoride ethyl ether complex as a catalyst to give polyOXImTFSI. Five percent weight loss temperature (T_{d5}) of polyOXImTFSI evaluated by thermal gravimetric analysis was 409 °C, indicating the high thermal stability. Glass transition temperature (T_g) of the polymer evaluated by differential scanning calorimetry was –19 °C, indicating the high flexibility of the material. Ionic conductivity of polyOXImTFSI was determined to be 1.86 × 10⁻⁸ S/cm at 23 °C, which was far lower than that of the OXImTFSI monomer (5.05 × 10⁻⁴ S/cm). © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2986–2990

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INTRODUCTION Ionic liquids, or room-temperature molten salts, have recently been attracting the attention of many researchers because of their unique properties such as extremely low vapor pressure, nonflammability, high thermal stability, specific solubility, and ionic conductivity.¹⁻³ These properties strongly depend on the combinations of cations and anions. Polymerized ionic liquids, so-called poly(ionic liquid)s, are a new class of polyelectrolytes.⁴⁻¹⁴ They may be useful as functional materials applicable to polymer electrolytes, sensors, actuators, CO₂ absorbents, and so forth. Several poly(ionic liquid)s have already been synthesized and characterized by some research groups. For example, linear poly(meth)acrylates,^{5-8,12-14} polystyrenes,^{10,11} and poly(vinyl ether)s15,16 having imidazolium pendant groups and networked polymethacrylates,¹⁷⁻¹⁹ polystyrenes,²⁰ or epoxides²¹ have been investigated so far. Recently, poly(ethylene oxide)s having imidazolium pendant groups have been synthesized and characterized.²² However, more materials should be studied and developed to further understand the nature of such poly(ionic liquid)s and to promote their applications to novel functional materials.

Oxetanes are four-membered cyclic ether compounds, which are well known as highly polymerizable compounds under acidic conditions, although they are rather stable under neutral or basic conditions.²³ Oxetane-based polymers are soft and flexible materials with high thermal and chemical stability. Their applications to solid electrolyte usages have been investigated.^{24,25}

In this study, we focused on the synthesis and polymerization of a new polymerizable ionic liquid, an imidazolium salt having a four-membered cyclic ether oxetanyl moiety on the imidazolium cation, and elucidated their fundamental properties such as thermal stability, phase transition behavior, and ionic conductivity in detail.

EXPERIMENTAL

Materials

3-Ethyl-3-oxetanemethanol, triphenylphosphine, tetrachloromethane, and 1-ethylimidazole were purchased from Tokyo Chemical Industry (Tokyo, Japan) and used as delivered. Bis(trifluoromethanesulfonyl)imide lithium salt (LiTFSI) was purchased from Wako Pure Chemical Industry (Osaka, Japan) and dried at 120 °C for 2 h *in vacuo*. Dichloromethane was distilled over CaH₂ before use. Boron trifluoride ethyl ether complex was purchased from Tokyo Chemical Industry and used after dilution to 0.5 mol/L solution with dry

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dichloromethane. Acetone- d_6 and dimethylsulfoxide- d_6 were purchased from Cambridge Isotope Laboratories (Cambridge, MA).

Preparation of 3-Chloromethyl-3-ethyloxetane

In a 500-mL round-bottomed flask equipped with a magnetic stirring bar, 3-ethyl-3-oxetanemethanol (13.7 mL, 120 mmol), triphenylphosphine (37.7 g, 144 mmol), and tetra-chloromethane (110 mL) were mixed. The mixture was stirred at 80 °C for 2 h. After cooling the mixture to room temperature, 220 mL of hexane was added to precipitate the triphenylphosphine oxide. After removal of the precipitates by filtration, the filtrate was concentrated under reduced pressure, and the residual oil was distilled to give the title compound (bp: 80–82 °C/30 mmHg, 11.4 g, 84.6 mmol) in 71% yield.

Preparation of 1-Ethyl-3-(3-ethyl-3-oxetanylmethyl) imidazolium Chloride

In a 50-mL round-bottomed flask equipped with a magnetic stirring bar, 3-chloromethyl-3-ethyloxetane (773 mg, 5.00 mmol) and 1-ethylimidazole (481 mg, 5.00 mmol) were mixed, and the mixture was heated at 90 °C for 48 h. A portion of the mixture was taken to check the conversion by ¹H NMR spectroscopy. The mixture was diluted with 2 mL of dichloromethane, and the solution was poured into an excess amount of diethyl ether to precipitate the ionic products. The precipitated liquid was collected and purified by reprecipitation. The residual oil was dried at 70 °C *in vacuo* for 3 h to give the title compound (880 mg, 3.51 mmol) in 70.2% yield as a brown liquid.

IR (ATR): 973, 1160, 1450, 1460, 1560, 2870, 2930, 2960, 3050 cm⁻¹. ¹H NMR δ (DMSO-*d*₆): 0.87 (t, *J* = 7.5 Hz, 3H), 1.37 (t, *J* = 7.4 Hz, 3H), 1.48 (q, *J* = 7.5 Hz, 2H), 4.21 (q, *J* = 7.4 Hz, 2H), 4.24 (d, *J* = 6.0 Hz, 2H), 4.43 (d, *J* = 6.0 Hz, 2H), 4.45 (s, 2H), 7.89 (s, 1H), 7.94 (s, 1H), 9.71 (s, 1H). ¹³C NMR δ (DMSO-*d*₆): 7.88, 15.17, 26.17, 42.91, 44.28, 52.25, 76.24, 122.17, 123.39, 136.69.

Preparation of 1-Ethyl-3-(3-ethyl-3-oxetanylmethyl) imidazolium Bis(trifluoromethanesulfonyl)imide

In a 50-mL round-bottomed flask equipped with a magnetic stirring bar, 1-ethyl-3-(3-ethyl-3-oxetanylmethyl)imidazolium chloride (OXImCl; 693 mg, 2.77 mmol), distilled water (3 mL), and LiTFSI (953 mg, 3.32 mmol) were mixed, and the mixture was stirred at room temperature for 12 h. A viscous liquid was precipitated, and the precipitate was collected and washed four times with distilled water (3 mL). The residual viscous liquid was dried at 70 °C *in vacuo* for 3 h to give the title compound (1310 mg, 2.64 mmol) in 95.5% yield as a liquid.

IR (ATR): 738, 790, 977, 1050, 1130, 1180, 1330, 1340, 2890, 2970, 3150 cm⁻¹. ¹H NMR δ (acetone- d_6): 1.06 (t, J = 7.5 Hz, 3H), 1.63 (t, J = 7.2 Hz, 3H), 1.76 (q, J = 7.5 Hz, 2H), 4.45 (d, J = 6.4 Hz, 2H), 4.48 (q, J = 7.2 Hz, 2H), 4.59 (d, J = 6.4 Hz, 2H), 4.73 (s, 2H), 7.88 (s, 1H), 7.91 (s, 1H), 9.25 (s, 1H). ¹³C NMR δ (acetone- d_6): 8.09, 15.42, 27.17, 44.33,

45.98, 53.77, 77.31, 120.93 (q, *J*_{CF} = 309 Hz), 123.36, 124.54, 137.03.

Polymerization of 1-Ethyl-3-(3-ethyl-3-oxetanylmethyl) imidazolium Bis(trifluoromethanesulfonyl)imide

In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, three-way stopcock, rubber septa, and a rubber balloon filled with nitrogen, 1-ethyl-3-(3-ethyl-3-oxetanylmethyl)imidazolium bis(trifluoromethanesulfonyl)imide (OXImTFSI; 495 mg, 1.05 mmol) was charged, and the flask was filled with nitrogen. Then, a dichloromethane solution of BF₃ ethyl ether complex (0. 5 mol/L, 0.21 mL, 0.105 mmol) was added, and the mixture was stirred at room temperature. The viscosity of the mixture gradually increased. After stirring for 2 h, a methanol solution of triethylamine (1 mol/L, 0.5 mL, 0.5 mmol) was added to terminate the polymerization. The resulting mixture was diluted with a small amount of acetone and was poured into an excess amount of dichloromethane. Precipitated oil was washed twice with dichloromethane, and the residue was heated at 80 °C for 2 h with stirring in vacuo to give polyOXImTFSI (350 mg, 0.707 mmol/monomer unit) in 67.3% yield.

IR (ATR): 738, 790, 1050, 1090, 1130, 1180, 1330, 1350, 2880, 2970, 3150 cm⁻¹. ¹H NMR δ (DMSO-*d*₆): 0.75–0.9 (m, 3H), 1.20–1.50 (m, 2H), 1.46 (t, *J* = 7.4 Hz, 3H), 3.00–3.45 (m, 4H), 4.05–4.30 (m, 4H), 7.45 (s, 1H), 7.87 (s, 1H), 8.92 (s, 1H). ¹³C NMR δ (DMSO-*d*₆): 7.30, 15.10, 22,90, 42.74, 44.44, 51.82, 70.70, 119.48 (q, *J*_{CF} = 319 Hz), 122.07, 123.89, 136.34.

Measurements

¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a JEOL JME-ECS 400 NMR spectrometer in $CDCl_3$ or $DMSO-d_6$. Chemical shifts were determined using the residual protons as the internal standard. IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer equipped with a Smart iTR Sampling Accessory. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument DSC-6200 using an aluminum pan under a 20 mL/min N₂ flow at a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko Instrument TG-DTA 6200 using an aluminum pan under a 50 mL/min N₂ flow at a heating rate of 10 $^{\circ}$ C/min. The ionic conductivities of the ionic liquid monomer and polymers were both measured by HIOKI 3532-80 chemical impedance meter at 50 mV in a frequency range of 4 Hz to 100 KHz using a two-electrode battery evaluation stainless coin cell (2E-CELL-SUS; Eager Corporation) with a PTFE guide and PTFE spacers (200 µm).

RESULTS AND DISCUSSION

Synthesis of Ionic Liquid Monomer OXImTFSI

A new ionic liquid monomer OXImTFSI, which has a cationically polymerizable oxetanyl group on the cationic part, was synthesized in three steps starting from a commercially available 3-ethyl-3-oxetanemethanol (Scheme 1). First of all, 3-ethyl-3-oxetanemethanol was transformed to





SCHEME 1 Synthetic route for OXImTFSI.

3-chloromethyl-3-ethyloxetane by treatment with triphenylphosphine in tetrachloromethane (Appel reaction), which was further transformed to imidazolium chloride salt (OXImCl) by heating at 90 °C with 1-ethylimidazole. Then, anion exchange of chloride to TFSI was carried out by mixing OXImCl with LiTFSI in an aqueous solution. Liquid–liquid phase separation occurred, and the lower liquid layer was collected, washed four times with water, and dried *in vacuo* at 70 °C to give the desired ionic liquid monomer, OXImTFSI. The absence of AgCl precipitates after addition of the obtained OXImTFSI to an aqueous AgNO₃ solution indicated the absence of chloride contamination.

Figure 1(a) shows the ¹H NMR spectrum of the obtained OXImTFSI. All the signals are assignable to OXImTFSI, which are depicted in the figure. Particularly, four protons on the oxetane ring were observed separately in two parts at 4.45 and 4.59 ppm. Figure 2(a) shows the IR spectrum of



FIGURE 2 IR spectra of OXImTFSI and polyOXImTFSI.

OXImTFSI. Absorption of the oxetane ring C—O—C asymmetric stretching was observed at 977 cm⁻¹. Absorption of the sulfonamide group S=O stretching was observed at 1330 and 1340 cm⁻¹. Additionally, in the ¹³C NMR spectrum, CF₃ carbon was observed at 111.64 ppm as a quartet peak with $J_{CF} = 309$ Hz (see "Experimental" section). These data are evidence of the formation of OXImTFSI.

The ionic conductivity was evaluated by impedance measurements. Temperature dependence of the ionic conductivity of OXImTFSI is plotted in Figure 3. The conductivity at 23 °C was found to be 5.05×10^{-4} S/cm, which was slightly lower than that (8.4 $\times 10^{-3}$ S/cm) of a simple imidazolium TFSI ionic liquid, 1-ethyl-3-methylimidazolium TFSI salt, reported previously. This is probably because of the higher viscosity



FIGURE 1 ¹H NMR spectra of (a) OXImTFSI in acetone-*d*₆ and (b) polyOXImTFSI in DMSO-*d*₆.

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FIGURE 3 Temperature dependence of ionic conductivity of OXImTFSI and polyOXImTFSI.

of OXImTFSI, which may be attributed to the bulky 3-ethyl-3-oxetanyl substitutent on the imidazolium cation.

Polymerization of OXImTFSI

OXImTFSI was polymerized by using boron trifluoride ether complex as a cationic polymerization catalyst (Scheme 2). By precipitation of the polymeric products diluted in dichloromethane, a rubbery material was obtained in 67% yield.

Figure 1(b) shows the ¹H NMR spectrum of the obtained polymer. All the signals are assignable to polyOXImTFSI. Particularly, methylene protons in the polymer main chain were observed at 3.00-3.40 ppm, whereas the corresponding oxetane protons in the monomer observed at 4.45 and 4.59 ppm disappeared. Figure 2(b) shows the IR spectra of the obtained polymer. Absorption of the oxetane ring C-O-C asymmetric stretching observed at 977 cm⁻¹ disappeared, whereas linear C-O-C asymmetric stretching in the polymer main chain was observed at 1090 cm⁻¹. Absorption of the sulfonamide group S=0 stretching was also observed at 1330 and 1340 cm⁻¹. Additionally, in the ¹³C NMR spectrum, CF_3 carbon was observed at 119.48 ppm as a quartet peak with $I_{CF} = 319$ Hz (see "Experimental" section). These data are evidence of the formation of polyOXImTFSI. We have not determined the molecular weight of the obtained polymer so far. GPC measurements using DMF containing 10 mM LiBr as an eluent were carried out, but no polymer peaks were detected, which may be due to the favorable interaction between the polymer and the polystyrene gels of the GPC column.









FIGURE 4 TGA curve of polyOXImTFSI (heating rate: 10 $^{\circ}$ C/min, under N₂ flow).

Properties of PolyOXImTFSI

The obtained polyOXImTFSI was soluble in polar organic solvent such as methanol, acetone, DMF, and DMSO, but insoluble in nonpolar solvent such as toluene, chloroform, dichloromethane, diethyl ether, and THF. It was also insoluble in water. Thermal stability of polyOXImTFSI was examined by TGA. Figure 4 shows the TGA curve obtained under a nitrogen flow. Almost no weight loss was observed below 350 °C, and 5 wt % decomposition temperature (T_{d5}) of polyOXImTFSI was 409 °C. Previously, we reported that T_{d5} of ImTFSI-containing methacrylate-based poly(ionic liquid) was 372 °C. Comparing these values, it is evident that polyOXImTFSI possesses markedly high thermal stability. It is probably because the polyoxetane main chains are thermally more stable than the polymethacrylate main chains.

The thermal phase transition behavior of polyOXImTFSI was examined by DSC measurement. Figure 5 shows the DSC first heating scan taken under a nitrogen flow after quenching the polymer to -100 °C. Glass transition temperature (T_g) was observed at -19 °C, which is much lower if it is compared with T_g (178 °C) of methacrylate-based poly(ionic liquid) having imidazolium TFSI salt pendant groups reported previously. This low T_g value clearly indicates that



FIGURE 5 DSC heating scan of polyOXImTFSI (heating rate: 10 °C/min, under N₂ flow).

polyOBMSB possesses a highly soft and flexible nature, which may be advantageous as an ion conducting material.

Ionic conductivity of the polymer was measured, and the ionic conductivity of the polyOBMSB was plotted against temperature in Figure 3 along with that of the OBMSB monomer. Although the ionic conductivity significantly decreased (three orders of magnitude) after polymerization, it still showed ionic conductivity (1.89 \times 10⁻⁸ S/cm at 20 °C) to the same extent as a dry bulk polymer, and it increased with the increase of the temperature. This ion conduction may be due to the thermal segmental motion of the flexible polyOXImTFSI chains.

CONCLUSIONS

A novel ionic liquid monomer having an oxetanyl group (OXImTFSI) was synthesized and polymerized by cationic ring-opening polymerization. The obtained poly(OXImTFSI) showed high thermal stability, low glass transition temperature, and ionic conductivity. As the polyoxetane backbone seems to be thermally, chemically, and electrochemically stable, this polymer is expected to be useful as a new functional material, which may be applicable as novel polymer electrolytes in electrochemical devices. Further studies on the film preparation, crosslinking, and mechanical and electrochemical properties of this polymer are currently in progress.

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