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ORIGINAL PAPER

Synthesis and properties of methacrylate-based ionic networked polymers containing ionic liquids: comparison of ionic and nonionic networked polymers

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Abstract Ionic networked polymers containing ionic liquids were synthesized by radical copolymerization of 1-(2-methacryloyl)ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Met-IL) and difunctional or trifunctional methacrylate cross-linkers, ethylene glycol dimethacrylate (EGDMA), or trimethylolpropane trimethacrylate (TMPTMA) in the presence of an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI). For comparison, nonionic networked polymers containing the ionic liquid were prepared by radical copolymerization of methyl methacrylate (MMA) with EGDMA in the presence of EMImTFSI. Met-IL/EGDMA/EMImTFSI(50) showed higher ion conductivity and ionic liquid holding ability than the corresponding MMA/EGDMA/EMImTFSI(50), while Met-IL/TMPTMA/EMImTFSI(50) showed lower ionic conductivity with higher holding ability than MMA/EGDMA/EMImTFSI(50).

Keywords Ionic liquid · Radical polymerization · Cross-link · Networked polymer · Poly(ionic liquid) · Ionomer

Introduction

Ionic liquid, which is a thermally stable, nonvolatile, nonflammable, and ion-conductive molten salt, has recently been attracting much interest for use in environmentally friendly chemical reactions, separations, and electrochemical energy devices [1–6]. Although the ionic liquid is a fluid at room temperature, it

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would be more widely applicable if it could be treated as a quasi solid material. Incorporation of ionic liquids into networked polymers enables them to behave as quasi solid materials [7–17]. Watanabe and coworkers synthesized ion gels by polymerization of methyl methacrylate (MMA) with a difunctional methacrylic ester cross-linker, ethylene glycol dimethacrylate (EGDMA), in the presence of an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI) [9, 10]. They found that these materials showed relatively high ionic conductivity as quasi solid materials at a high ionic liquid content, which was comparable to that of bulk ionic conductivity.

In the practical usage of these gel-like materials, it is important to preserve the ionic liquid in the materials. In order to improve the holding ability of the ionic liquid in the networked polymers, we introduced ionic groups with a chemical structure similar to the ionic liquid in the polymer network. We expected these materials to hold the ionic liquid inside due to their high affinity to the ionic liquid and high osmotic pressure, and to alter the ionic conductivity by electrostatic interaction between the ionic liquids and ionic moieties on the polymer network.

Methacrylate monomers having an imidazolium salt structure in the pendant group can be copolymerized with nonionic methacrylate monomers [18, 19]. We recently reported that 1-(2-methacryloylethyl)-3-methylimidazolium bis(trifuluromethanesulfonyl)imide (Met-IL) can be readily copolymerized with methyl methacrylate using azobisisobutyronitrile (AIBN) as an initiator and an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI) as a solvent [19]. We prepared ionic liquid containing ionic networked polymers by copolymerization of Met-IL with difunctional or trifunctional methacrylates, ethylene glycol dimethacrylate (EGDMA) or trimethylolpropane trimethacrylate (TMPTMA) in the presence of EMImTFSI, and examined their ionic conductivities as well as their ionic liquid holding abilities. As a result, we found that the ionic liquid containing an ionic networked polymer (Met-IL/EGDMA/EMImTFSI) possessed apparently higher ionic conductivities with apparently higher holding abilities than the corresponding ionic liquid containing nonionic networked polymer (MMA/EGDMA/EMImTFSI). The effect of the ionic substituent in the network on the properties of the networked polymer materials that contained an ionic liquid is described.

Experimental

Materials

Methyl methacrylate (MMA), EGDMA, and TMPTMA were purchased from Wako Pure Chemical Industry and washed three times with 1 M NaOH aqueous solution, three times with distilled water, dried with anhydrous Na_2SO_4, and then distilled over CaH_2 before use. Met-IL[19] and EMImTFSI[9] were prepared by the reported procedures. AIBN was purchased from Wako Pure Chemical Industry and purified by recrystallization from methanol. The mold for synthesis of a networked polymer film was made of two glass plates (76 × 26 mm) with a thickness of 1.2–1.5 mm covered with PTFE tape (Permacel P422) and a PTFE spacer (0. 5 mm thickness) making a apace of 55 mm × 18 mm.

Preparation of Met-IL/EGDMA film

A portion of a mixture of Met-IL (1.00 g, 2.1 mmol), EGDMA (280 mg, 1.4 mmol), and AIBN (8.0 mg, 0.049 mmol) was poured into a mold. The mold was placed in a 2-L glass chamber and the chamber was purged with nitrogen. A Met-IL/EGDMA film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Preparation of Met-IL/EGDMA/EMImTFSI(50) film

A portion of a mixture of Met-IL (1.00 g, 2.1 mmol), EGDMA (280 mg, 1.4 mmol), EMImTFSI (1.28 g, 3.3 mmol), and AIBN (8.0 mg, 0.049 mmol) was poured into a mold. The mold was placed in a 2-L glass chamber and the chamber was purged with nitrogen. A Met-IL/EGDMA/EMImTFSI(50) film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Preparation of MMA/EGDMA film

A portion of a mixture of MMA (600 mg, 6.0 mmol), EGDMA (790 mg, 4.0 mmol), and AIBN (23 mg, 0.14 mmol) was poured into a mold. The mold was placed in a 2-L glass chamber and the chamber was purged with nitrogen. A MMA/EGDMA/EMImTFSI(50) film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Preparation of MMA/EGDMA/EMImTFSI(50) film

A portion of a mixture of MMA (2.10 g, 21 mmol), EGDMA (2.77 g, 14 mmol), EMImTFSI (4.87 g, 13 mmol), and AIBN (80 mg, 0.49 mmol) was poured into a mold. The mold was placed in a 2-L glass chamber and the chamber was purged with nitrogen. A MMA/EGDMA/EMImTFSI(50) film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Preparation of Met-IL/TMPTMA/EMImTFSI(50) film

A portion of a mixture of Met-IL (1.00 g, 2.1 mmol), TMPTMA (440 mg, 1.4 mmol), EMImTFSI (1.44 g, 3.7 mmol), and AIBN (10 mg, 0.063 mmol) was poured into a mold. The mold was placed in a 2-L glass chamber and the chamber was purged with nitrogen. A Met-IL/TMPTMA/EMImTFSI(50) film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Solvent extraction of ionic liquid from the films

A small piece of the networked polymer film (ca. 15 mm × 7 mm) was weighed and immersed in acetone (40 mL) in a vial with a screw cap. The vial was shaken vigorously, and the ionic conductivity of the solution at the designated time was measured with a Mettler Toledo Seven Easy conductivity meter S30. The amount of extracted ionic liquid was estimated, using a calibration curve drawn by measuring known concentrations of ionic liquid solutions.

Characterization

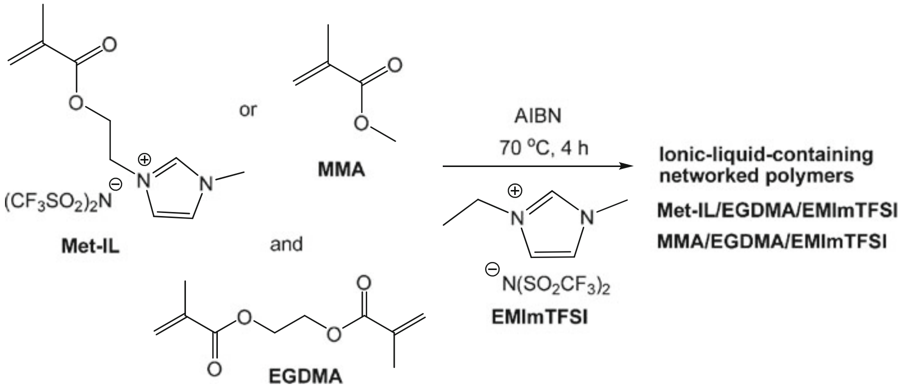
IR spectra were recorded on a Perkin Elmer SPECTRUM ONE spectrometer equipped with a universal ATR Sampling Accessory. The ionic conductivity of the networked polymers was measured with a HIOKI 3532-80 chemical impedance meter at 50 mV using a frequency range of 4 Hz to 1 MHz.

Results and discussion

Preparation of networked polymers containing ionic liquid

As shown in Scheme 1, ionic or nonionic networked polymers that contained an ionic liquid were prepared by copolymerization of Met-IL or MMA with difunctional EGDMA as cross-linkers using AIBN as an initiator and EMImTFSI as a solvent. The initial feed ratios are summarized in Table 1. Figure 1 shows a photograph of the ionic networked polymer film containing 50 wt% EMImTFSI obtained by this method. The sample was a semi-transparent, tough, and flexible self-standing film.

Figure 2 shows the expanded IR spectra of the Met-IL monomer and ionic/nonionic networked polymers prepared in EMImTFSI. The absorption at 1640 cm^{-1} of the C=C stretching band observed in the monomer completely disappeared in both ionic and nonionic monomers after polymerization, indicating that the conversion of the monomers in these polymerization systems was complete.



Scheme 1 Preparation of networked polymers containing ionic liquid

Table 1 Synthesis and properties of networked polymer films

Sample	Monofunctional monomer/ cross-linker	Content of EMImTFSI (wt%)	Extraction (%)	Ionic conductivity (S/m)
MMA/EGDMA	60/40	0	–	–
MMA/EGDMA/ EMImTFSI(50)	60/40	50	100 (15 min)	2.0×10^{-2}
Met-IL/EGDMA	60/40	0	–	1.0×10^{-3}
Met-IL/EGDMA/ EMImTFSI(50)	60/40	50	100 (60 min)	1.0×10^{-1}
Met-IL/TMPTMA/ EMImTFSI(50)	60/40	50	54 (48 h)	1.0×10^{-3}

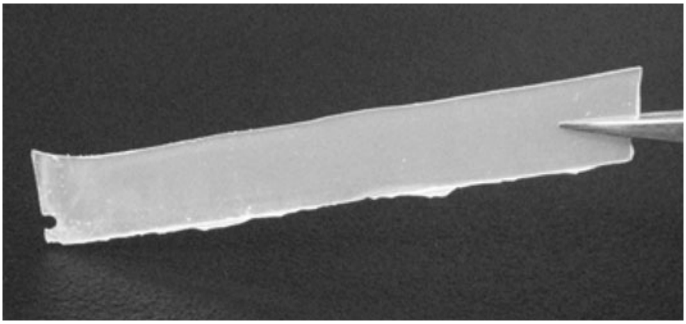


Fig. 1 A photograph of Met-IL/EGDMA/EMImTFSI(50) film

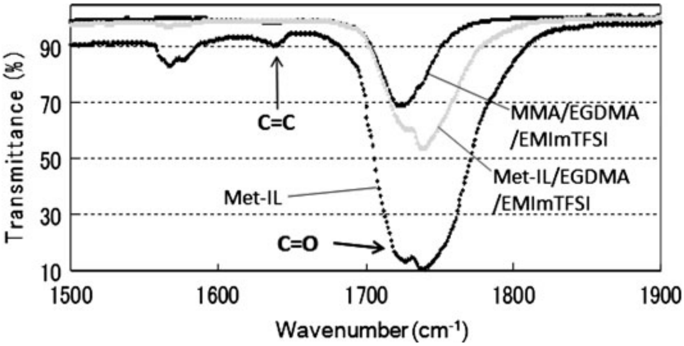
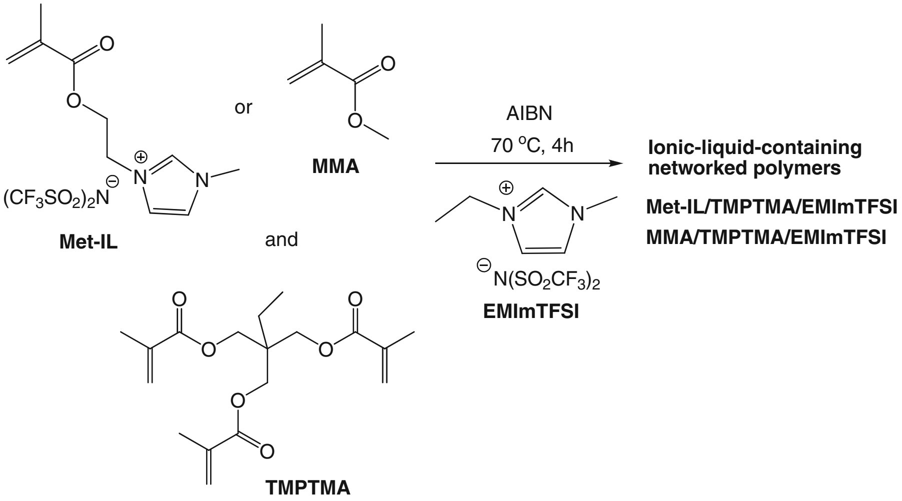


Fig. 2 IR spectra of Met-IL, Met-IL/EGDMA/EMImTFSI(50) after extraction of the ionic liquid with acetone, and MMA/EGDMA/EMImTFSI(50) after extraction of the ionic liquid with acetone

An EMImTFSI-containing ionic networked polymer was synthesized by a similar method using TMPTMA as a trifunctional cross-linker as shown in Scheme 2. The initial feed ratio is given in Table 1, which was the same as that for



Scheme 2 Preparation of networked polymers containing ionic liquid using TMPTMA

Met-IL/EGDMA/EMImTFSI(50). The semi-transparent flexible film of Met-IL/TMPTMA/EMImTFSI(50) synthesized had an appearance similar to that of Met-IL/EGDMA/EMImTFSI(50).

Properties of networked polymers containing ionic liquid

Table 1 shows the ionic conductivity of each film sample. The ionic conductivity of the ionic networked polymer, Met-IL/EGDMA/EMImTFSI(50), was one order higher than that of the corresponding nonionic networked polymer, MMA/EGDMA/EMImTFSI(50), which may be due to the electrostatic effect of the ionic network to enhance the dissociation of ionic liquid clusters. However, another ionic networked polymer with higher cross-link density, Met-IL/TMPTMA/EMImTFSI(50), showed much lower ionic conductivity than the nonionic networked polymer, MMA/EGDMA/EMImTFSI(50). This is probably because most ions are completely confined in the polymer network of Met-IL/TMPTMA.

The ionic liquid holding ability of the networked material was evaluated by measuring the rate of the ionic liquid extraction with acetone. The amount of extracted ionic liquid was evaluated by comparing the ionic conductivity of the extraction solution to those of a known EMImTFSI concentration in acetone. As shown in Table 1, Met-IL/EGDMA/EMImTFSI(50) had an extraction rate apparently lower than that of MMA/EGDMA/EMImTFSI(50), indicating that the holding ability of the ionic liquid in an ionic networked polymer is higher than that in a nonionic networked polymer. On the other hand, the extraction rate of Met-IL/TMPTMA/EMImTFSI(50) was much lower than both MMA/EGDMA/EMImTFSI(50) and Met-IL/EGDMA/EMImTFSI(50), and it held about a half of the incorporated ionic liquid even after a 48-h extraction. This exceptionally high holding capacity is probably caused by a different effect, which may be the fixation of ionic liquid by the highly cross-linked polymer networks. The significantly lower ionic conductivity of the Met-IL/TMPTMA/EMImTFSI(50) film supports this explanation.

Conclusions

Ionic liquid containing ionic and nonionic networked polymers were prepared and their ionic conductivity and ionic liquid holding capacity were examined. The ionic networked polymer, Met-IL/EGDMA/EMImFTSI(50), exhibited higher ionic conductivity with higher ionic liquid holding capacity than the corresponding nonionic networked polymer, MMA/EGDMA/EMImTFSI(50). Although the reason for this phenomenon is not yet fully understood, the electrostatic interaction between the ionic groups on the network and the ions existing in the materials may play an important role. On the other hand, the ionic networked polymer with higher cross-linking density, Met-IL/TMPTMA/EMImFSI(50), showed little ionic conductivity while the ionic liquid holding capacity was much higher, which may be due to the fixation of ionic liquid by dense polymer networks. The present findings suggest that highly precise design of the polymer networks is important in the development of high performance functional materials consisting of networked polymers and ionic liquids.

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