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ORIGINAL PAPER

Preparation of networked polymer electrolytes by copolymerization of a methacrylate with an imidazolium salt structure and an ethyleneglycol dimethacrylate in the presence of lithium bis(trifluoromethanesulfonyl)imide

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Abstract A cationic networked polymer solid electrolyte (Met-IL/EGDMA/LiTFSI) synthesized by copolymerization of 1-(2-methacryloyl)ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Met-IL) and ethylene glycol dimethacrylate (EGDMA) in the presence of lithium bis(trifluromethanesulfonyl)imide (LiTFSI) showed higher ionic conductivity (1.0×10^{-2} S/m) than the corresponding non-ionic networked polymer solid electrolyte (MMA/EGDMA/LiTFSI) ($<1.0 \times 10^{-3}$ S/m) prepared by copolymerization of methyl methacrylate (MMA) and EGDMA in the presence of LiTFSI. A gel polymer electrolyte composed of the cationic networked polymer Met-IL/EGDMA and propylene carbonate (PC) solution of LiTFSI prepared by copolymerization of Met-IL and EGDMA in a PC solution of LiTFSI showed much higher ionic conductivity (3.0×10^{-1} S/m) than the solid polymer electrolyte.

Keywords Solid polymer electrolyte · Gel electrolyte · Radical polymerization · Networked polymer · Poly(ionic liquid)

Introduction

Polymer electrolytes are key materials for development of various electrochemical devices such as rechargeable lithium or lithium ion batteries, super capacitors, fuel cells, electrochromic cells, and sensors [1–3]. Moreover, the electrochemical energy-producing and energy-storing devices are environmentally friendly energy sources. Solid-type polymer electrolytes may be ideal for many electrochemical applications, but they have lower ionic conductivity compared with conventional liquid type

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electrolytes. This problem may be solved by usage of so-called gel polymer electrolytes. For example, polymer electrolytes with poly(ethylene oxide) (PEO) [4, 5], poly(acrylonitrile) (PAN) [6, 7], poly(methyl methacrylate) (PMMA) [8–11], and poly(vinylidene difluoride) (PVdF) [12–15] as a base polymer have been widely studied. However, even these gelled polymer systems need to be improved.

We recently found that polymer electrolytes composed of an ionic liquid and cross-linked polymethacrylates having an imidazolium salt structure as a pendant group possess higher ionic conductivity holding the ionic liquid better in the materials than the corresponding non-ionic networked polymer [16]. These results stimulated us to examine the lithium salt added polymer electrolytes consisting of cationic networked polymers. Here, we prepared solid and gel polymer electrolytes by copolymerization of an ionic liquid monomer, 1-(2-methacryloylethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Met-IL), and a difunctional cross-linker (EGDMA) in the presence of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or propylene carbonate (PC) solution of LiTFSI, and examined their ionic conductivity. We found that the solid electrolytes composed of the ionic networked polymer showed higher ionic conductivity than the non-ionic networked polymer, and also the gel electrolyte composed of Met-IL/EGDMA networked polymer and PC solution of LiTFSI exhibited much higher ionic conductivity.

Experimental

Materials

MMA and EGDMA 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 [16] was prepared by the reported procedures. Azobisisobutyronitrile (AIBN) was purchased from Wako Pure Chemical Industry and purified by recrystallization from methanol. PC was purchased from Tokyo Chemical Industry (Tokyo, Japan) and distilled over CaH_2 before used. LiTFSI was purchased from Wako Pure Chemical Industry and dried in vacuo at 120 °C for 3 h before use. The mold for synthesis of the networked polymer films consisted of two glass plates (76 × 26 mm) with a thickness of 1.2–1.5 mm each covered with PTFE tape (Permacel P422) and a PTFE spacer (0.5 mm thickness) making a space of 55 mm × 18 mm.

Preparation of Met-IL/EGDMA film

A portion of a mixture consisting of Met-IL (1.0 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 put in a 2-L glass chamber, and the chamber was purged with nitrogen. A soft transparent 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/LiTFSI film

A portion of a mixture consisting of Met-IL (1.0 mg, 2.1 mmol), EGDMA (280 mg, 1.4 mmol), LiTFSI (290 mg, 1.0 mmol), and AIBN (8.0 mg, 0.049 mmol) was poured into a mold. The mold was put in a 2-L glass chamber, and the chamber was purged with nitrogen. A soft transparent Met-IL/EGDMA/LiTFSI film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Preparation of Met-IL/EGDMA/LiTFSI/PC film

A portion of a mixture consisting of Met-IL (1.00 mg, 2.1 mmol), EGDMA (280 mg, 1.4 mmol), AIBN (8.0 mg, 0.049 mmol), LiTFSI (290 mg, 1.0 mmol), and PC (1 mL) was poured into a mold. The mold was put in a 2-L glass chamber, and the chamber was purged with nitrogen. A soft semitransparent Met-IL/EGDMA/LiTFSI/PC 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 consisting of MMA (210 mg, 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 put in a 2-L glass chamber, and the chamber was purged with nitrogen. A hard transparent MMA/EGDMA film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Preparation of MMA/EGDMA/LiTFSI film

A portion of a mixture of MMA (210 mg, 2.1 mmol), EGDMA (280 mg, 1.4 mmol), LiTFSI (290 mg, 1.0 mmol), and AIBN (8.0 mg, 0.049 mmol) was poured into a mold. The mold was put in a 2-L glass chamber, and the chamber was purged with nitrogen. A hard transparent MMA/EGDMA/LiTFSI film sample (55 mm × 15 mm × 0.5 mm) was obtained after 4 h at 70 °C.

Characterization

IR spectra were recorded on a Perkin Elmer SPECTRUM ONE spectrometer equipped with a universal ATR Sampling Accessory. 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

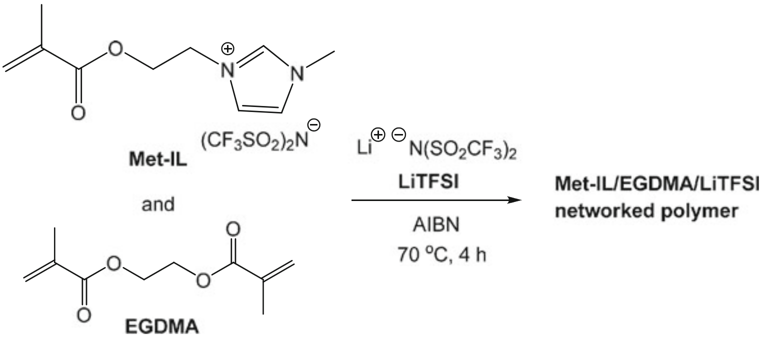
Preparation of LiTFSI added networked polymers

Our previous research suggested that cationic networked polymers can be easily prepared by radical copolymerization of an ionic liquid methacrylate monomer, Met-IL, with a difunctional methacrylate crosslinker, EGDMA. In fact, a glassy and transparent film of Met-IL/EGDMA (60/40) was obtained by bulk polymerization of the mixture of Met-IL and EGDMA in a PTFE mold at 70 °C using AIBN as an initiator. However, the networked polymer showed relatively low ionic conductivity (1.0×10^{-3} S/m). This is probably because anions in the networked polymer could not move freely due to the counter ion fixation and the rigid polymer backbone.

In contrast, the ionic conductivity of the networked polymer was significantly improved by the addition of lithium salt. We prepared a glassy and transparent film of lithium salt added cationic networked polymer by radical copolymerization of a mixture of Met-IL and EGDMA in the presence of LiTFSI as shown in Scheme 1. The ionic conductivity was significantly improved (1.0×10^{-2} S/m) by the addition of lithium salt to the cationic Met-IL/EGDMA networked system. The ionic conductivity was much higher than that of the corresponding lithium salt added non-ionic networked polymer, MMA/EGDMA/LiTFSI ($<1.0 \times 10^{-3}$ S/m) under a dry condition. This high ionic conductivity in the solid polymer electrolytes may indicate that ionic groups on the polymer network have act strongly to dissociate the cluster of added ions and that some of the added ions can move in the ionic networked polymer even in the glassy polymer network. Table 1 shows the ionic conductivity of each networked polymer in the dry condition.

Properties of networked polymers swollen with LiTFSI/PC

Nevertheless, the ionic conductivity of the solid state Met-IL/EGDMA/LiTFSI was not high enough for use in a battery device. In order to increase the ionic conductivity, we prepared gel-type polymer electrolytes by using a polar organic solvent. A soft and flexible semi-transparent gel-like film was obtained by radical copolymerization of a mixture of Met-IL and EGDMA in a PC solution of LiTFSI (1.0 mol/L) at 70 °C using AIBN as an initiator (Scheme 2). This networked polymer gel showed ionic conductivity of 3.0×10^{-1} S/m. Since polymeric electrolytes can be applied to a battery if their ionic conductivity is higher than 1.0×10^{-1} S/m, this material is expected to be useful for such applications, although other factors should be evaluated.

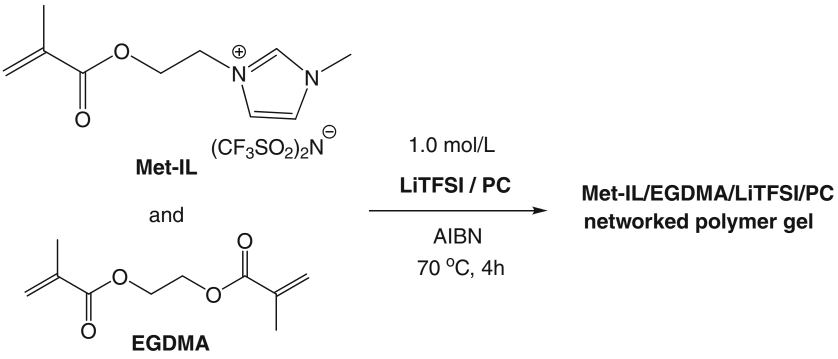


Scheme 1 Preparation of networked polymer in the presence of LiTFSI

Table 1 Synthesis and properties of networked polymer films

Run	Sample	[monofunctional monomer]/ [cross-linker]/[LiTFSI]	Ionic conductivity (S/m)
1	MMA/EGDMA/LiTFSI	2.1/1.4/1.0	$<1.0 \times 10^{-3}$
2	Met-IL/EGDMA	2.1/1.4/0	2.0×10^{-3}
3	Met-IL/EGDMA/LiTFSI	2.1/1.4/1.0	1.0×10^{-2}
4	Met-IL/EGDMA/LiTFSI/PC	2.1/1.4/1.0	3.0×10^{-1}

In run 4, concentration of PC solution of LiTFSI: 1.0 M



Scheme 2 Preparation of networked polymer gel electrolyte

Conclusions

An ionic networked polymer solid electrolyte (Met-IL/EGDMA/LiTFSI), prepared by copolymerization of Met-IL and EGDMA in the presence of LiTFSI, showed higher ionic conductivity than the corresponding non-ionic networked polymer solid electrolyte (MMA/EGDMA/LiTFSI) prepared by copolymerization of MMA and EGDMA in the presence of LiTFSI. The reason for the higher ionic conductivity in the cationic networked polymer is not clear, but we suppose that the ionic groups in the polymer network play an important role in the dissociation of ionic clusters. A gel-type electrolyte composed of the ionic networked polymer Met-IL/EGDMA prepared by copolymerization of Met-IL and EGDMA in a PC solution of LiTFSI showed much higher ionic conductivity than the solid-type electrolyte. Further evaluation of the applicability of this gel-type polymer electrolyte for energy-storing devices such as lithium ion batteries is currently in progress.

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