4580 *Macromolecules* **2009**, *42*, 4580–4584
DOI: 10.1021/ma900508q

Macromolecules
ARTICLE

Synthesis of Ion Conductive Networked Polymers Based on an Ionic Liquid Epoxide Having a Quaternary Ammonium Salt Structure

Kozo Matsumoto and Takeshi Endo*

Molecular Engineering Institute, Kinki University 11-6 Kayanomori, Iizuka, Fukuoka Prefecture 820-8555, Japan

Received March 10, 2009; Revised Manuscript Received May 14, 2009

ABSTRACT: Various epoxy-based networked polymers having trimethylammonium bis(trifluoromethanesulfonyl)imide groups on the network were synthesized by heating a mixture of diepoxide, glycidyl trimethylammonium bis(trifluoromethanesulfonyl)imide (GTMATFSI), and diamine curing reagent. Ethylene glycol diglycidyl ether (EGGE), poly(ethylene glycol) diglycidyl ether (PEGGE), and poly(propylene glycol) diglycidy ether (PPOGE) were used as diepoxides, and ethylene glycol bis(3-aminopropy) ether (EGBA), poly(ethylene glycol) diglycidyl ether bis(3-aminopropyl ether) (PEGBA), and polypropylene glycol bis(2-aminopropyl ether) (PPOBA) were used as diamine curing reagents. The obtained networked polymers having quaternary ammonium structure showed high thermal stability, low crystallinity, low glass transition temperature, and good ionic conductivity. In particular, the networked polymers consisting of poly (ethylene glycol) segments showed high ionic conductivity (>1.0×10^{-3} S/m) at room temperature.

Introduction

An ionic liquid is a molten salt with high thermal stability and good ionic conductivity at room temperature.[1−3] It is a promising candidate for novel high performance electrolytes for electrochemical devices such as lithium ion batteries and electronic double layer capacitors. A drawback for practical application is that fluidity of the ionic liquid causes liquid electrolyte leakage. To solve this problem, Watanabe et al. attempted ion gel formation by polymerization of methacrylate monomers with cross-linker in the presence of an ionic liquid.[4,5] Vioux et al. reported synthesis of an ionogel composed of an ionic liquid with silica-derived netoworks.[6] These materials have high ionic conductivity but the ions easily exude. We previously reported that highly rigid epoxy-based networked polymers can completely confine ionic liquid in the polymer network, but they showed no ionic conductivity.[7] Other workers attempted to polymerize ionic liquids. For example, Ohno and co-workers reported synthesis of various polymers composed of imidazolium-substituted methacrylates.[8−10] However, polymerization of ionic compounds often reduces the molecular motion and provide low ionic conductivity. To improve the ionic conductivity, they examined the introduction of polyethylene glycol (PEG) spacers between the ionic group and polymerizable group.[11]

Polyethylene glycols (PEGs) are known as excellent polymeric matrices for solid polymer electrolytes since PEGs contain ether coordination sites which assist the dissociation of salts, and also have flexible polymer chains which enhance the ionic transport.[12,13] In particular, PEGs having hyperbranched structures are favorable to achieve a high ionic conductivity at a low temperature, because they have low crystallinity and can provide a highly amorphous state.[14,15]

Networked polymers, which have three dimensionally cross-linked structures, possess excellent physicochemical properties such as mechanical strength, toughness, adhesive properties, and gel-forming abilities. It is quite easy to prepare networked polymers by curing multifunctional epoxy compounds with amines.[16] Various epoxides and amines having oligo(ethylene glycol) structures are now commercially available. In addition, such oligo(ethylene glycol)-derived networked polymers have ether coordinating sites and soft hyperbranched structures with low crystallinity.[17] Hence, we expect that ionic-networked polymers with good mechanical property and high ionic conductivity can be attained in this PEG-derived epoxy/anime curing system just by adding an ionic liquid epoxy monomer without the use of a complicated monomer preparation or troublesome polymerization procedures.

Here we synthesized some epoxy-based ionic-networked polymers[18] and examined their physical properties. We found that PEG-based networked polymers with a trimethylammonium bis (trifluoromethanesulfonyl)imide structure exhibited good thermal and mechanical stability with high ionic conductivity.

Experimental Section

Materials. Ethylene glycol diglycidyl ether (EGGE) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and distilled under reduced pressure. Poly(propylene glycol) diglycidyl ether (PPOGE, $M_n = 640$), poly(ethylene glycol) diglycidyl ether (PEGGE, $M_n = 526$), poly(propylene glycol) bis(2-aminopropyl) ether (PPOBA, M_n = 400), and poly(ethylene glycol) bis(3-aminopropyl) terminated (PEGBA, M_n = 1500), glycidyl trimethylammonium chorolide (GTMACl) aqueous solution were purchased from Aldrich (Milwaukee, WI), ethylene glycol bis-(2-aminoethyl ether) (BAE) was purchased from Tokyo Chemical Industry, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), glycidyl phenyl ether (PhGE), and *n*-octylamine were purchased from Wako Pure Chemical Industry (Osaka, Japan), and they were used as delivered. Dimethylsulfoxide-d_6 (DMSO-d_6) was purchased from Cambridge Isotope Laboratories, Inc. (Cambridge, MA).

Preparation of Glycidyl Trimethylammonium Bis(trifluoromethanesulfonyl)imide (GTMATFSI). To a 25 mL aqueous solution of LiTFSI (14.4 g, 50.0 mmol) was added GTMACl (containing 25 wt % water, 10.0 g, 49.5 mmol) at room temperature, and the mixture was stirred for 24 h. After transfer to a

---

*To whom correspondence should be addressed. Telephone: +81-948-22-7210. Fax: +81-948-22-7210. E-mail: tendo@mol-eng.fuk.kindai.ac.jp.

separating funnel, the mixture separated into two phases. The lower phase was collected and washed with 30 mL pure water three times, and dried in vacuo for 3 h to obtain the title compound as a colorless viscous liquid (14.3 g, 36.2 mmol) in 73% yield. IR (ATR) 740, 788, 867, 895, 926, 970, 1049, 1130, 1174, 1326, 1344, 1476 cm^{-1}. ^{1}H NMR δ (CD_3OH) 2.73 (dd, $J = 2.4$, 5.0 Hz, 1H), 3.01 (dd, $J = 4.6$, 5.0 Hz, 1H), 3.16 (dd, $J =$ 8.8 Hz, 13.8 Hz, 1H), 3.29 (s, 9H), 3.48−3.56 (m, 1H), 3.95 (dd, $J = 2.0$, 13.8 Hz, 1H) (for the ^{1}H NMR spectrum, see Figure 1S in the Supporting Information). ^{13}C NMR δ (CD_3OD) 46.34, 47.06, 22.52, 71.48. Anal. Calcd for $C_8H_{14}F_6N_2O_5S_2$: C, 24.24; H, 3.56; N, 7.07; S, 16.18. Found C, 24.16; H, 3.48; N, 6.93; S, 15.86.

Model Reaction of GTMATFSI with *n*-Octylamine. In a 25 mL round-bottomed flask under an argon atmosphere were charged GTMATFSI (396 mg, 1.00 mmol), *n*-octylamine (63.0 mg, 0.50 mmol), and a magnetic stirring bar, and the mixture was heated at 60 °C with stirring. After a designated period, a small portion of the mixture was taken, diluted with DMSO-d_6, and analyzed by ^{1}H NMR spectrometry. The conversion of GTMATFSI was estimated by the integral ratio of the epoxy proton signal at 2.90 ppm to the terminal methyl proton signal at 0.85 ppm of *n*-octyl groups (Figure 2S in the Supporting Information).

Model Reaction of PhGE with *n*-Octylamine. In a 25 mL round-bottomed flask under an argon atmosphere were charged PhGE (300 mg, 2.00 mmol), *n*-octylamine (129 mg, 1.00 mmol), and a magnetic stirring bar, and the mixture was heated at 60 °C with stirring. After a designated period, a small portion of the mixture was taken, diluted with DMSO-d_6, and analyzed by ^{1}H NMR spectrometer. The conversion of PhGE was estimated by the integral ratio of the epoxy proton signal at 2.90 ppm to the aromatic proton signal at 7.20−7.30 ppm in the PhGE moiety (Figure 3S in the Supporting Information).

Preparation of Epoxy-Based Networked Polymer Films. A mold (2 cm × 4 cm × 500 μm) for a film preparation was fabricated with two pieces of PTFE-tape-coated slide glass and PTFE spacer (500 μm thickness). A mixture of a diepoxy compound and diamine with or without GTMATFSI was put into the mold, and the mixture was heated at 100 °C for 8 h. Chemical structures for the epoxides and diamines used for the film preparation are depicted in Figure 1. The cured film was removed from the mold, and washed by immersing it in excess methanol for 2 h in three times, and dried by heating 100 °C for 3 h (see Tables 1S−5S in the Supporting Information for the amount of diepoxides, diamines, and GTMATFSI used in the film preparation, and the yield (wt %) of the films obtained after washing with methanol.).

Characterization. Proton NMR spectra were recorded on Varian UNITY INOVA 400 in DMSO-d_6 with residual CH_3SOCH_3 as an internal standard. IR spectra were recorded on a Perkin-Elmer SPECTRUM ONE spectrometer equipped with a universal ATR sampling accessory. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument Inc. DSC-6200 using an aluminum pan under a 20 mL/min N_2 flow at the heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko Instrument Inc. TG-DTA 6200 using an alumina pan under a 50 mL/min N_2 flow at a heating rate of 10 °C/min. Ionic conductivity of the cured epoxy films was measured by HIOKI 3532-80 chemical impedance meter at 50 mV using a frequency range of 4 Hz to 1 MHz and analyzed by Nyquest plot (see Supporting Information, Figure 4S for a typical Nyquest plot). Stress−strain data were taken on a Seiko Instrument Inc. TMA 6200, measuring stress in the length of control mode at room temperature.

Results and Discussion

Model Reaction of GTMATFSI with Amine. To introduce ionic moiety in the polymer network, ionic liquid epoxide, we used GTMATFSI as an ionic monofunctional monomer, because it has high compatibility with various organic compounds such as diepoxides and dimanies, and it is easily prepared by a simple ion-exchange of the chloride in commercially available GTMACl to TFSI anion. Before the networked polymer synthesis, we examined a model reaction of GTMATFSI with $^1/_2$ mol amount of a normal amine. Figure 2 shows the time versus conversion of GTMATFSI in the reaction with *n*-octylamine as well as that of PhGE with the same amine.

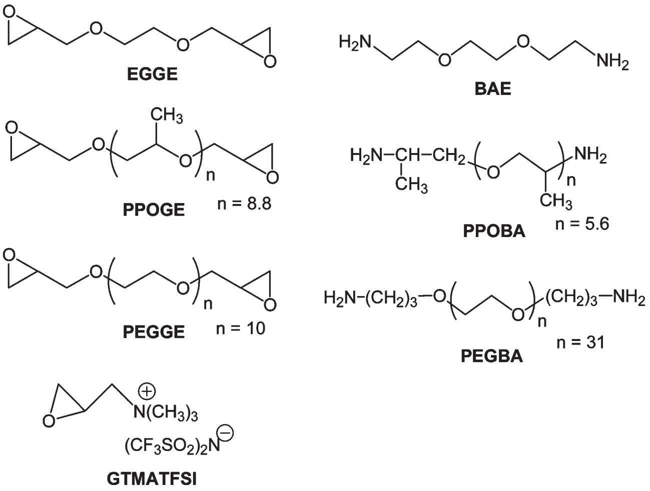


Figure 1. Chemical structures of compounds used in this study.

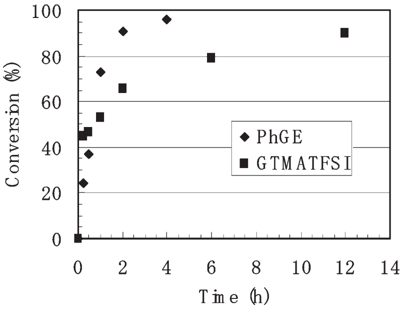
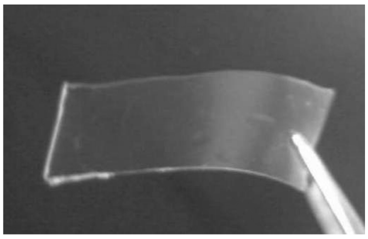


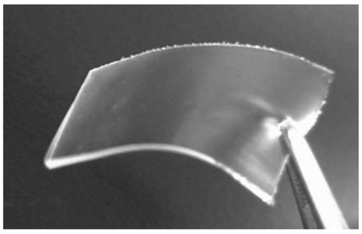
Figure 2. Time vs conversion curve for reaction of GTMATFSI and PhGE with *n*-octylamine.

Addition of GTMATFSI to the amine had almost completed after heating the mixture at 60 °C for 12 h. It is worth noting that GTMATFSI was consumed faster than PhGE below 50% conversion, but the rate of GTMATFSI consumption became slower than that of PhGE over 50% conversion. This result suggests that the addition of the first GTMATFSI to the amine proceeds rapidly but the second GTMATFSI addition proceeds slowly compared to PhGE. The electrostatic repulsion between the GTMATFSI-added amine and the second GTMATFSI may reduce the rate of the second addition. This suggests that during the curing of GTMATFSI and nonionic diepoxide mixture with diamine, diamine/GTMATFSI adduct forms first, and then the adduct gradually reacts with diepoxide to generate networked polymer.

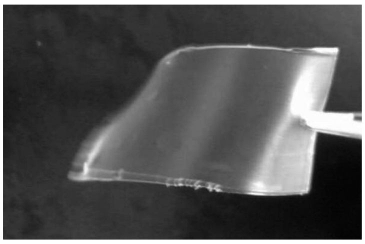
Synthesis of Networked Polymer Samples. Film samples of epoxy-based networked polymer were prepared by curing a mixture of epoxides and an amine in a PTFE mold. Introducing an ionic moiety to the network was readily achieved by using GTMATFSI. We used three diepoxides and three diamines to prepare networked polymers with various chemical structures. Figure 1 shows the chemical structures. A stoichiometric amount of amine was added to the epoxides in



EGGE/GTMATFSI-0.5/PEGBA



PPOGE/GTMATFSI-0.5/PEGBA



PEGGE/GTMATFSI-0.5/PEGBA

Figure 3. Photographs of networked polymers prepared with GTMATFSI.

all cases. (The amount of epoxides and amines used for the sample preparation and the yield of the films are summarized in Tables 1S−5S in the Supporting Information.) All the samples obtained here were soft, rubber-like, and homogeneous transparent films. Figure 3 shows photographs of the typical cationic-networked polymer films prepared by using PEGBA as a curing diamine.

Figure 4 shows the FTIR spectrum of the obtained EGGE/GTMATFSI-0.5/BAE films after repeated washing with methanol. For comparison, the spectra of EGGE/BAE and GTMATFSI are also shown in the figure. Absorption of the glycidyl group is usually observed around 910 cm^{-1}, but such absorption could not be observed in the EGGE/GTMATFSI-0.5/EGBA sample, indicating that almost no epoxy groups remained in the cured material. In addition, the absorption at 1350 cm^{-1} and 1170 cm^{-1} in the PEGGE/GTMATFSI-0.5/PEGBA sample can be assigned to the sulfonylimide (SO_2-N-SO_2) structure, and the absorption at 1130 cm^{-1} can be assigned to the CF_3 group respectively, which clearly indicated the formation of networked polymer having ammonium TFSI groups.

Thermal Analysis of Networked Polymers. Thermal decompositions of the obtained samples were analyzed by TGA. The 5% weight loss temperatures (T_{d5}) are summarized in Table 1. Epoxy-based networked polymers without cationic moiety showed very high thermal stability ($T_{d5} > 300$ °C). Introduction of the trimethylammonium structure in the networks lowered the decomposition temperature around 30 °C, but this drop of the decomposition temperature was rather small, and all the samples kept the T_{d5} above 270 °C, indicating that they are thermally stable enough.

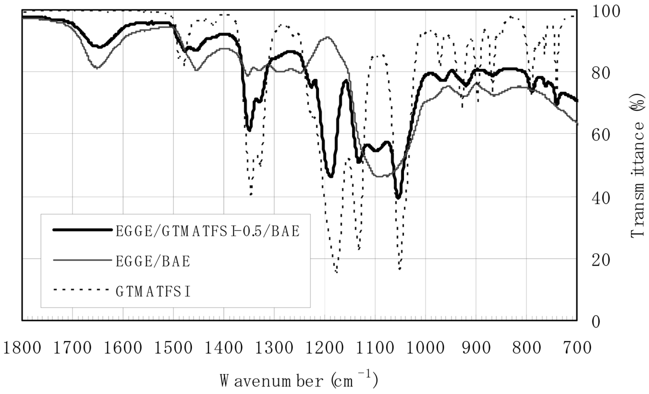


Figure 4. IR spectra of EGGE/GTMATFSI-0.5/BAE, EGGE/BAE, and GTMATFSI.

Table 1. Results of Thermal Analysis of the Epoxy-Based Networked Polymers

sample	T_g (°C)	T_{d5} (°C)
EGGE/BAE	−41	307
EGGE/GTMATFSI-0.5/BAE	−37	273
EGGE/PPOBA	−25	305
EGGE/GTMATFSI-0.5/PPOBA	−26	279
EGGE/PEGBA	−55	320
EGGE/GTMATFSI-0.5/PEGBA	−62	295
PPOGE/BAE	−44	301
PPOGE/GTMATFSI-0.5/BAE	−38	273
PPOGE/PPOBA	−46	313
PPOGE/GTMATFSI-0.5/PPOBA	−40	279
PPOGE/PEGBA	−59	314
PPOGE/GTMATFSI-0.5/PEGBA	−60	293
PEGGE/BAE	−53	309
PEGGE/GTMATFSI-0.5/BAE	−52	276
PEGGE/PPOBA	−52	326
PEGGE/GTMATFSI-0.5/PPOBA	−50	285
PEGGE/PEGBA	−62	321
PEGGE/GTMATFSI-0.5/PEGBA	−62	298

Figure 5 shows the results of DSC analysis of PEGBA, PEGGE/PEGBA, and PEGGE/PhGE-1.0/PEGBA. PEGBA is a highly crystalline polymer and showed its melting transition (T_m) at 49 °C. By comparing the enthalpy of fusion (163 J/g) with the literature value (197 J/g) for 100% crystalline PEO,[19] we estimated the crystallinity of the PEGBA to be 83%. In contrast to this, the T_m of the PEGGE/PEGBA was observed at −2 °C and its PEGBA crystallinity was estimated to be 16%. This fact implies that network formation significantly lowered the T_m and reduced the crystallinity. Introduction of PhGE to the networked system slightly increased the melting temperature ($T_m = 15$ °C) and the PEGBA crystallinity (25%), since PhGE is a diluting reagent and lowed the network density, but the T_m is still lower than room temperature. Use of GTMATFSI instead of PhGE again lowered the T_m to 1 °C and the PEGBA crystallinity was only 11%, though GTMATFSI is also a diluting reagent. This is presumably because GTMATFSI has a bulky ionic group to hinder the crystallization. The low crystallinity of this networked material prepared with an ionic liquid component is considered to be quite advantageous for various electrochemical applications. The glass transition temperature (T_g) of the networked polymers was observed around −60 °C, which is far below the room temperature and was hardly affected by the use of diluting reagents. T_gs of other samples are also listed in Table 1.

Ionic Conductivity of Networked Polymers. Table 2 summarizes the ionic conductivity of the networked polymers prepared with various diepoxides and diamines with

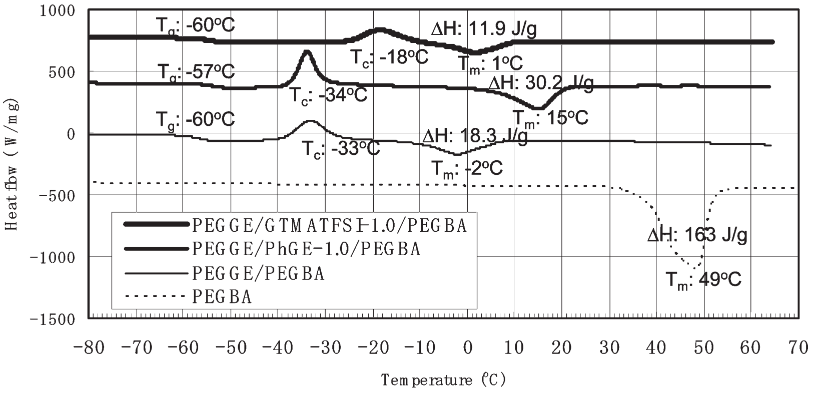


Figure 5. DSC chats of heating scans for PEGBA, PEGGE/PEGBA, PEGGE/PhGE-1.0/PEGBA, and PEGGE/GTMATFSI-1.0/PEGBA. PEGGE/PhGE-1.0/PEGBA was prepared by curing a mixture of PEGGE (174 mg, 0.33 mmol) and PhGE (50 mg, 0.33 mmol) with PEGBA (371 mg, 0.248 mmol). Samples were annealed at 60 °C for 5 min and rapidly cooled to −100 °C. Heating rate: 10 °C/min.

Table 2. Ionic Conductivity at Room Temperature of Various Networked Polymers Prepares with GTMATFSI

samples	GTMATFSI content (wt%)	ionic conductivity (S/m)
EGGE/GTMATFSI-0.5/BAE	43	$< 1.0 \times 10^{-5}$
EGGE/GTMATFSI-0.5/PPOBA	32	$< 1.0 \times 10^{-5}$
EGGE/GTMATFSI-0.5/PEGBA	15	1.5×10^{-3}
PPOGE/GTMATFSI-0.5/BAE	21	$< 1.0 \times 10^{-5}$
PPOGE/GTMATFSI-0.5/PPOBA	18	1.4×10^{-5}
PPOGE/GTMATFSI-0.5/PEGBA	11	1.2×10^{-3}
PEGGE/GTMATFSI-0.5/BAE	24	2.2×10^{-4}
PEGGE/GTMATFSI-0.5/PPOBA	20	2.3×10^{-4}

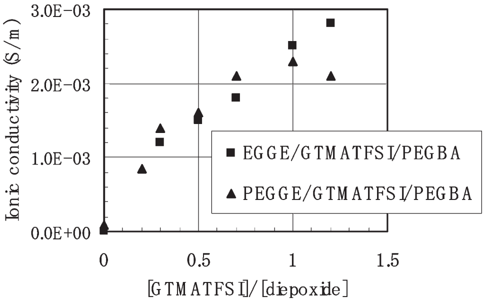


Figure 6. GTMATFSI content dependence on the ionic conductivity of EGGE/GTMATFSI/PEGBA and PEGGE/GTMATFSI/PEGBA.

GTMATFSI at room temperature. Samples having a PEG structure showed ionic conductivity, while samples having only a poly(prolylele glycol) (PPO) structure or monomeric ethylene glycol (EO) structure did not show measurable ionic conductivity. We assume that the PEG structure plays an important role in ionic conduction as well as in increasing the flexibility of the network backbone. In particular, samples prepared with PEGBA exhibited quite high ionic conductivity.

Figure 6 shows the GTMATFSI content dependence of the ionic conductivity of EGGE/GTMATFSI/PEGBA and PEGGE/GTMATFSI/PEGBA, respectively. The ionic conductivity generally increased with the increase of the GTMATFSI content. The ion concentration in the networked polymer increases and the cross-linking degree of the network decreases with the increase in the GTMATFSI content, both of which increased the ionic conductivity. EGGE/GTMATFSI-1.2/PEGBA showed ionic conductivity of 2.8×10^{-3} S/m. This value is markedly high for a networked polymer in a dry condition at room temperature, since the present system is considered to be a single ion conducting system where only the TFSI anions can move around but cations can not. Ohno and co-workers reported that the ionic conductivity of the acryalte-based networked polymer having imidazolium TFSI groups with very low network density (0.5 mol % cross-linker was used.) was 1.1×10^{-2} S/m at 30 °C.[10]

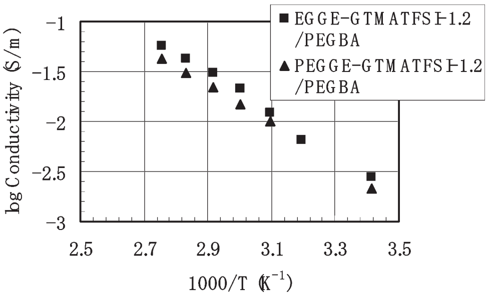


Figure 7. Temperature dependence of the ionic conductivity in EGGE/GTMATFSI-1.2/PEGBA and PEGGE/GTMATFSI-1.2/PEGBA.

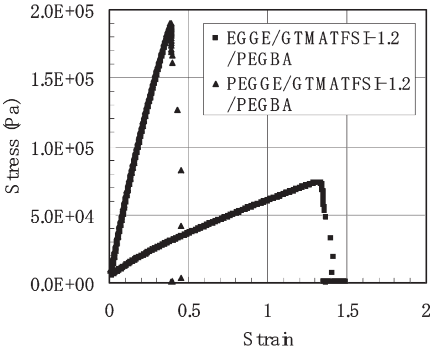


Figure 8. Stress−strain curves for EGGE/GTMATFSI-1.2/PEGBA and PEGGE/GTMATFSI-1.2/PEGBA at room temperature.

Figure 7 shows temperature dependence of the ionic conductivity in EGGE/GTMATFSI-1.0/PEGBA and PEGGE/GTMATFSI-1.0/PEGBA. The ionic conductivity increased with the increase of temperature, and reached 5.8×10^{-2} S/m for EGGE-GTMATFSI-1.2/PEGBA and 4.1×10^{-2} S/m for PEGGE/GTMATFSI-1.2/PEGBA at 90 °C, which is also quite high for a solid polymeric material.

Mechanical Strength of the Networked Polymer Films. Mechanical properties of the networked polymer films were examined by stress−strain analysis of the samples. Figure 8 shows the stress−strain curves for EGGE/GTMATFSI-1.2/PEGBA and PEGBA/GTMATFSI-1.2/PEGBA. Mechanical properties obtained from the curves are summarized in

Table 3. Mechanical Properties for the Networked Polymer Films

sample	Young's modulus (KPa)	tensile strength (KPa)	breaking elongation
EGGE/GTMATFSI-1.2 /PEGBA	75	74	1.34
PEGGE/GTMATFSI-1.2 /PEGBA	580	190	0.38

Table 3. The networked polymer films have enough mechanical strength and toughness to be self-standing films. They can be easily treated by tweezers without special techniques.

Conclusions

Epoxy-based networked polymer films having trimethylammonium TFSI were easily synthesized by curing mixtures of a diepoxide and glycidyl trimethylammonium TFSI salt with a diamine. The networked polymers were thermally stable and highly flexible with low crystallinity. Samples having a PEG structure showed ionic conductivity, and particularly samples prepared with PEGBA exhibited remarkably high ionic conductivity. These networked polymers are mechanically strong and tough enough to produce self-standing thin films. These polymers will be useful materials for application to ionic conductive membranes in electrochemical devices. Further elucidation of chemical and physical properties which are important for the application needs to be explored in future work.

Supporting Information Available: Tables S1−S5, giving data on the preparation of the polymers, and Figures S1−S4, showing NMR spectra and a Nyquest plot. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2084.
(2) Xu, W.; Angell, C. A. *Science* **2003**, *302*, 422–425.
(3) Ohno, H., Ed. *Electrochemical Aspects of Ionic Liquids*; John Wiley & Sons: Hoboken, NJ, 2005.
(4) Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M. *J. Am. Chem. Soc.* **2005**, *127*, 4976–4983.
(5) Seki, S.; Susan, M. A. B. H.; Kaneko, T.; Tokuda, H.; Noda, A.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 3886–3892.
(6) Néouze, M.-A.; Bideau, J. L.; Gaveau, P.; Bellayer, S.; Vioux, A. *Chem. Mater.* **2006**, *18*, 3931–3936.
(7) Matsumoto, K.; Endo, T. *Macromolecules* **2008**, *41*, 6981–6986.
(8) Ogihara, W.; Washiro, S.; Nakajima, H.; Ohno, H. *Electrochim. Acta* **2006**, *51*, 2614–2649.
(9) Nakajima, H.; Ohno, H. *Polymer* **2005**, *46*, 11499–11504.
(10) Washiro, S.; Yoshizawa, M.; Nakajima, H.; Ohno, H. *Polymer* **2004**, *45*, 1577–1582.
(11) Yoshizawa, M.; Ohno, H *Electrochim. Acta* **2001**, *46*, 1723–1728.
(12) Grau, F. M. *Solid Polymer Electrolytes*; VCH Publishers: New York, 1991.
(13) Meyer, W. H. *Adv. Mater.* **1998**, *10*, 439–448.
(14) Hawker, C. J.; Chu, F.; Pomery, P. J.; Hill, D. J. T. *Macromolecules* **1996**, *29*, 3831–3838.
(15) Nishimoto, A.; Agehara, K.; Furuya, N.; Watanabe, T.; Watanabe, M. *Macromolecules* **1999**, *32*, 1541–1548.
(16) Pham, H. Q.; Marks, M. J. In *Encyclopedia of Polymer Science and Technology*, 3rd ed.; Kroschwitz, J. I., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2003; Vol. 9, pp 678−804.
(17) Laine, R. M.; Kim, S. G.; Rush, J.; Tamaki, R.; Wong, E.; Mollan, M.; Sun, H.-J.; Lodaya, M. *Macromolecules* **2004**, *37*, 4525–4532.
(18) Polymeric materials, which are derived from bisepoxides and monomeric epoxides with quaternary ammonium salt part, have been reported. Kiryu, T. JP2007−9124.
(19) Ishikiriyama, K.; Wunderlich, B. *J. Polym. Sci., B: Polym. Phys.* **1997**, *35*, 1877–1886.