Confinement of Ionic Liquid by Networked Polymers Based on Multifunctional Epoxy Resins

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ABSTRACT: Networked polymers confining an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMImTFSI), were prepared by curing a mixture of bisphenol A diglycidyl ether (BADGE) and tetrafunctional epoxy resins with tetraethylenepentamine (TEPA) in the presence of ionic liquid. It was found that addition of the tetrafunctional epoxy resins was inevitable for better ionic liquid confinement. The ionic liquid confinement, ionic conductivity, mechanical strength, and morphology of the materials strongly depended on the ionic liquid content. At a low ionic liquid content (<40 wt %), the material tightly confined the ionic liquid and showed little ionic conductivity with a high Young's modulus, while at a high ionic liquid content (>40 wt %), it did not confine the ionic liquid showing higher ionic conductivity with a low Young's modulus. At a high ionic liquid content (>40 wt %), microphase separation between the ionic liquid and the epoxy networked polymer was observed by scanning electron microscopy (SEM). A transition of the microphase separation from discrete sphere to continuous structure was also observed between 40 wt % and 50 wt % ionic liquid contents. This morphology transition caused a drastic change of the material properties around these ionic liquid contents.

Introduction

Ionic liquids, which are classified as molten salts around room temperature, have attracted much attention in recent years due to their unique properties such as high thermal and chemical stability, nonvolatility, and inflammability with high ionic conductivity.[1−3] Intense efforts have been made to apply them to green solvents, catalysts, or ion conducting matrixes for electrochemical devices.[4−13] Particularly, the combination of ionic liquids with cross-linked polymers exhibits various interesting properties which are useful for practical applications.[14−20] In most cases, however, the ionic liquid easily exudes from the polymer network, and one cannot maintain the properties of the material for long, which is quite unfavorable from the viewpoint of applications.

On the other hand, epoxy resins are important thermosetting networked materials that have been used in various fields for many years.[21] They have excellent physicochemical properties such as high thermal and chemical stability and good mechanical, electrical, and adhesive properties. Cured epoxy resins are often used steady fine structures of various inorganic or organic materials. We consider that highly cross-linked epoxy networked polymers can enclose and confine the ionic liquid well into the networked materials and provide new functions with the aid of the ionic liquid.

In this study, we synthesized ionic-liquid-containing networked polymers by curing epoxy resins in the presence of an ionic liquid. The chemicals used here to prepare the materials are depicted in Figure 1. Then the fundamental properties of the materials such as ionic liquid confinement, ion conductivity, mechanical stiffness, and morphology were examined. As a result, the highly networked epoxy resins obtained by curing a mixture of difunctional and tetrafunctional epoxy compounds with tetraethylenepentamine can effectively confine the ionic liquid in the networked materials below a certain ionic liquid content (<40 wt %). It was also found that the ion confinement, ionic conductivity, and Young's modulus drastically changed above this ionic liquid content, which was closely related to the material's morphology. To the best of our knowledge, no work has been reported on the ionic liquid confinement in such networked materials so far.

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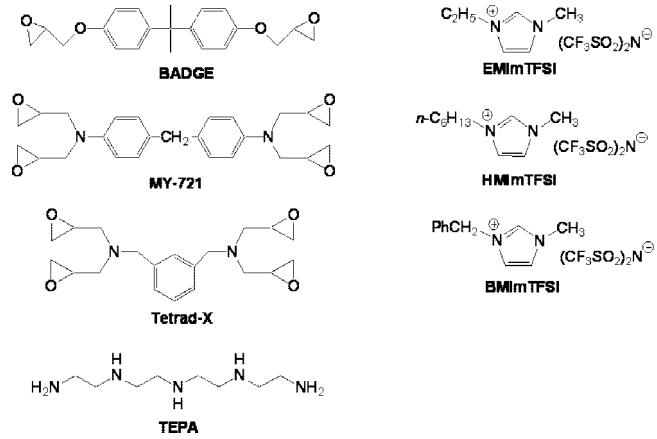

Figure 1. Chemical structures of the compounds used in this study.

Experimental Section

Materials. 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI)[16] and 1-benzyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMImTFSI)[22] were prepared according to the reported procedures. Bisphenol A diglycidyl ether (BADGE, 170 g/equiv) and tetraethylenepentamine (TEPA) were purchased from Tokyo Chemical Industry (Tokyo, Japan), 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (HMImTFSI) from Kanto Chemical (Tokyo, Japan), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) from Wako Pure Chemical Industry (Osaka, Japan), and used as delivered. *N*,*N*,*N*′,*N*′-Tetraglycidyl-diaminodiphenylmethane (Araldite MY721, 109−116 g/equiv) and *N*,*N*,*N*′,*N*′-tetraglycidyl-*m*-xylenediamine (Mitsubishi Gas Chemicals, Tetrad-X, 95−105 g/equiv) were a kind gift from JSR Co. (Tokyo, Japan).

Preparation of BADGE/TEPA/EMImTFSI Films. To a mixture of BADGE (680 mg, 2.0 mmol) and EMImTFSI (396−445 mg, 1.01−1.14 mmol), was added a designated amount of TEPA (89 mg, 0.47 mmol to 184 mg, 0.97 mmol) (Table 1). After stirring,

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Table 1. Synthesis of BADGE/TEPA/(34 wt %)EMImTFSI Films

run	BADGE (mg)	TEPA (mg)	EMImTFSI (mg)	2[BADGE]/ 7[TEPA]	EMImTFSI (wt %)
1	680	89	396	0.88	34
2	680	102	403	0.94	34
3	680	108	406	1.00	34
4	680	115	409	1.06	34
5	680	121	413	1.12	34
6	680	128	416	1.18	34
7	680	134	419	1.24	34
8	680	141	423	1.30	34
9	680	155	428	1.43	34
11	680	162	434	1.50	34
12	680	184	445	1.70	34

Table 2. Synthesis of BADGE/MY721/TEPA/EMImTFSI Films

run	BADGE (mg)	MY721 (mg)	TEPA (mg)	EMImTFSI (mg)	[BADGE]/ [MY-721]	EMImTFSI (wt %)
13	680	0	119	412	1/0	34
14	680	45	131	441	1/0.05	34
15	680	90	143	470	1/0.1	34
16	340	90	83	264	1/0.2	34
17	340	181	107	324	1/0.4	34
18	170	226	89	250	1/1.0	34
19	0	452	119	294	0/1	34
20	170	226	89	323	1/1.0	40
21	170	226	89	485	1/1.0	50

Table 3. Synthesis of BADGE/Tetrad-X/TEPA/EMImTFSI Films

run	BADGE (mg)	Tetrad-X (mg)	TEPA (mg)	EMImTFSI (mg)	[BADGE]/ [Tetrad-X]	EMImTFSI (wt %)
22	680	40	131	438	1/0.05	34
23	680	80	143	465	1/0.1	34
24	340	80	83	259	1/0.2	34
25	340	160	107	313	1/0.4	34
26	170	200	89	237	1/1.0	34
27	0	400	119	267	0/1	34
28	170	200	89	306	1/1.0	40
29	170	200	89	346	1/1.0	43
30	170	200	89	376	1/1.0	45
31	170	200	89	407	1/1.0	47
32	170	200	89	459	1/1.0	50

the mixture was put into polytetrafluoroethylene (PTFE) mold (55 mm × 18 mm × 0.5 mm) and kept at 70 °C for 5 h and 130 °C 10 h. Removal of the PTFE mold gave a white glassy films (BADGE/TEPA/(34 wt %)EMImTFSI) in runs 1−12.

Preparation of BADGE/MY721/TEPA/EMImTFSI Films. A designated amount of BADGE, MY721, TEPA (1.1 equivalent to total epoxy mole amount), and EMImTFSI (Table 2) were thoroughly mixed in a glass vial, and the mixture was poured into a PTFE mold (55 mm × 18 mm × 0.5 mm). The mixture was kept at 70 °C for 5 h, and 130 °C for 10 h. After cooling to room temperature, the mold was peeled off the sample, and white glassy films (BADGE/MY721/TEPA/(34 wt %)EMImTFSI) were obtained in runs 13−21.

Preparation of BADGE/Tetrad-X/TEPA/EMImTFSI Films. Designated amounts of BADGE, Tetrad-X, TEPA (1.1 equivalent to total epoxy mole amount), and EMImTFSI (Table 3) were thoroughly mixed in a glass vial, and the mixture was poured into a PTFE mold (55 mm × 18 mm × 0.5 mm). The mixture was kept at 70 °C for 5 h, and 130 °C for 10 h. After cooling to room temperature, the mold was peeled off the sample, and white glassy films (BADGE/Tetrad-X/TEPA/(34 wt %)EMImTFSI) were obtained in runs 22−32.

Preparation of BADGE/Tetrad-X/TEPA/HMImTFSI Film. To a mixture of BADGE (170 mg, 0.5 mmol), Tetrad-X (200 mg, 0.5 mmol), and HMImTFSI (237 mg, 0.53 mmol) was added TEPA (89 mg, 0.47 mmol). After stirring, the mixture was put into a PTFE mold (55 mm × 18 mm × 0.5 mm) and kept at 70 °C for 5 h and at 130 °C for 10 h. Removal of the PTFE mold gave a white translucent glassy film (run 33, BADGE/TEPA/Tetrad-X/(34 wt %)HMImTFSI).

Preparation of BADGE/Tetrad-X/TEPA/BMImTFSI Film. To a mixture of BADGE (170 mg, 0.5 mmol), Tetrad-X (200 mg, 0.5 mmol), and BMImTFSI (237 mg, 052 mmol) was added TEPA (89 mg, 0.47 mmol). After stirring, the mixture was put into a PTFE mold (55 mm × 18 mm × 0.5 mm) and heated 70 °C for 5 h and 130 °C 10 h. Removal of the PTFE mold gave a yellow transparent

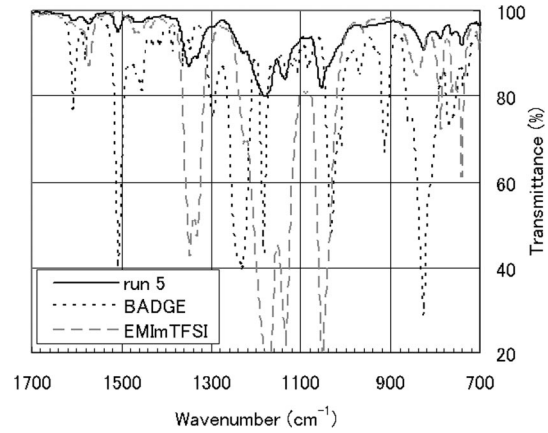

Figure 2. IR spectra of BADGE/TEPA/(34 wt %)EMImTFSI (run 5), BADGE, and EMImTFSI.

Table 4. Thermal Properties for the Cured Epoxy Resins with or without EMImTFSI

sample	T_g (°C)	T_{d5} (°C)
BADGE/TEPA	134	337
BADGE/MY721-1.00/TEPA	151	329
BADGE/Tetrad-X-1.00/TEPA	138	319
BADGE/TEPA/(34 wt %)EMImTFSI (run 5)	119	325
BADGE/MY721-1.00/TEPA/(34 wt %)EMImTFSI (run 18)	142	314
BADGE/Tetrad-X-1.00/TEPA/(34 wt %)EMImTFSI (run 26)	128	299

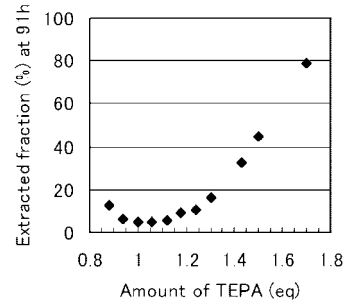

Figure 3. The EMImTFSI fraction extracted with methanol at 91 h as a function of the amount of TEPA used in the film preparation (runs 1−12).

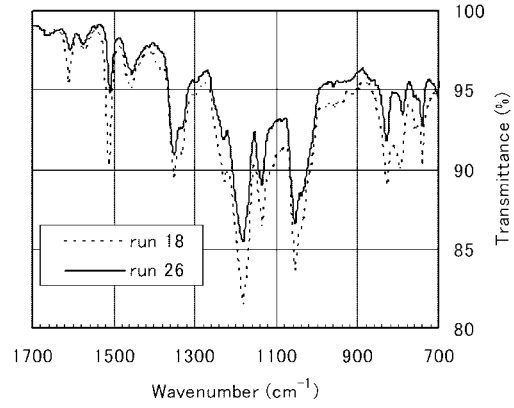

Figure 4. IR spectra of BADGE/MY721/TEPA/(34 wt %)EMImTFSI (run 18) and BADGE/Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 26).

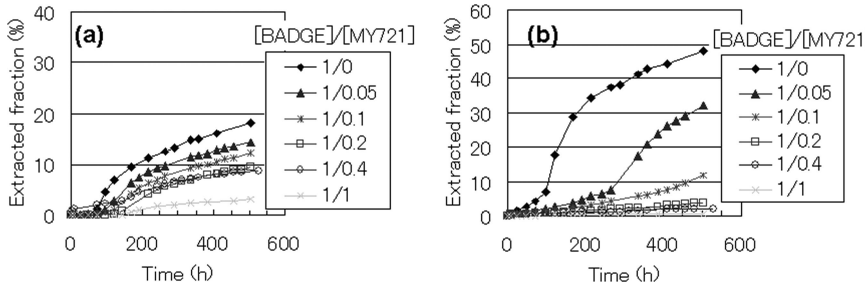

Figure 5. Time dependence of the extracted EMImTFSI fraction from BADGE/MY721/TEPA/(34 wt %)EMImTFSI (runs 13−18) with (a) methanol or (b) acetone.

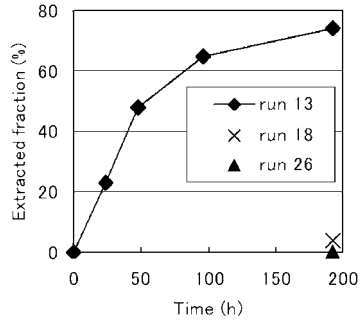

Figure 6. Soxhlet extraction of EMImTFSI from BADGE/TEPA/(34 wt %)EMImTFSI (run 13), BADGE/MY721/TEPA/(34 wt %)EMImTFSI (run 18), and BADGE/Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 26). The extraction solvent: acetone.

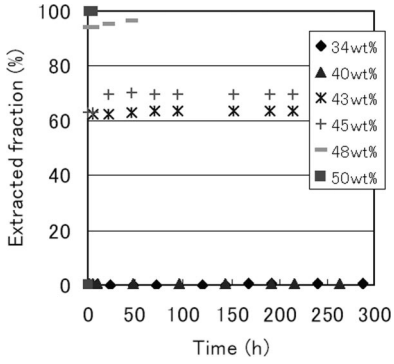

Figure 7. Time dependence of the extracted EMImTFSI fraction from BADGE/Tetrad-X/TEPA hybrids having various EMImTFSI contents (run 26 and runs 28−32). The extraction solvent: acetone.

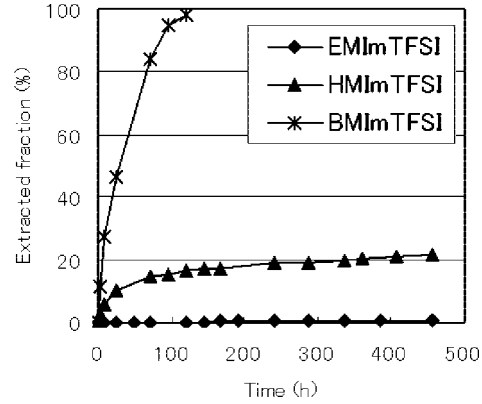

Figure 8. Time dependence of the extracted ionic liquid fraction from films of BADGE/Tetrad-X/TEPA with EMImTFSI (run 26), HMImTFSI (run 33), and BMImTFSI (run 34). The extraction solvent: acetone.

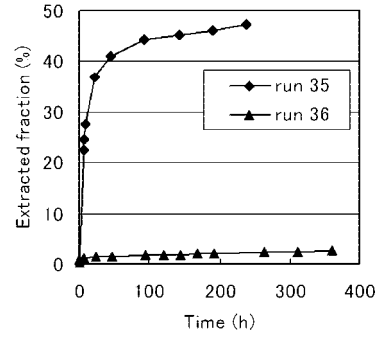

Figure 9. Time dependence of the extracted LiTFSI fraction from BADGE/Tetrad-X/TEPA film with 34 wt % LiTFSI (run 35) or 20 wt % LiTFSI (run 36). The extraction solvent: acetone.

glassy film (run 34, BADGE/Tetrad-X/(34 wt %)TEPA/BMImTFSI).

Preparation of BADGE/Tetrad-X/TEPA/LiTFSI Films. To a mixture of BADGE (340 mg, 1.0 mmol), Tetrad-X (400 mg, 1.0 mmol), and LiTFSI (473 mg, 1.65 mmol for 34 wt % LiTFSI sample, or 230 mg, 0.80 mmol for 29 wt % LiTFSI sample) was added TEPA (178 mg, 0.943 mmol). After stirring, the mixture was put into a PTFE mold (55 mm × 18 mm × 0.5 mm) and kept at 70 °C for 5 h and 130 °C 10 h. Removal of the PTFE mold gave yellow transparent glassy films (run 35, BADGE/Tetrad-X/TEPA/(34 wt %)LiTFSI or run 36, BisA/Tetrad-X/TEPA/(20 wt %)LiTFSI).

Characterization and Evaluation of the Obtained Materials. IR spectra were recorded on a Perkin-Elmer SPECTRUM ONE spectrometer equipped with a universal ATR Sampling Accessory. Scanning electron microscopy (SEM) was performed with a Hitachi SEMEDX-III type N microscopy system in the low vacuum composition mode using a back scattering electron (BSE) detector.Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument Inc. DSC-6200 with an aluminum pan under a 20 mL/min N_2 flow at the heating rate of 10 °C/min. Thermogravimetry (TGA) was performed with a Seiko Instrument Inc. TG-DTA 6200 with an alumina pan under a 50 mL/min N_2 flow at a heating rate of 10 °C/min. Stress−strain data were taken on Seiko Instrument Inc. TMA 6200 measuring stress in the length control mode at room temperature. 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 100 KHz.

Solvent Extraction of Ionic Liquids from the Films. A small piece of the cured epoxy/ionic liquid film (ca. 15 mm × 7 mm) was weighed and immersed in methanol or acetone (40 mL) in a vial with a screw cap. The vial was shaken well, and the ionic conductivity of the solution at designated time was measured with Mettler Toledo Seven Easy conductivity meter S30. The amount of extracted ionic liquid was estimated, using a calibration curve drawn by measuring known concentration ionic liquid solutions.

Soxhlet Extraction of Ionic Liquid from the Films. A small piece of the cured epoxy/ionic liquid composite film (ca. 15 mm × 15 mm) was weighed and put in a flask of Soxhlet extraction equipment. Acetone (100 mL) was added to the flask, and the

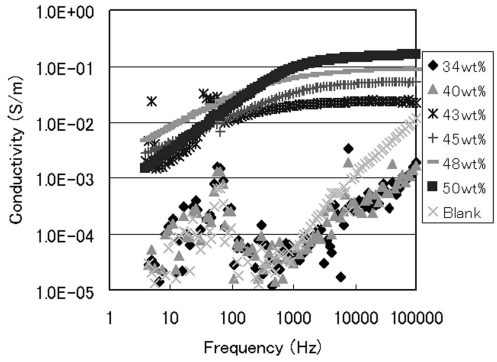

Figure 10. Ion conductivity as a function of alternative current frequency for the films of BADGE/Tetrad-X/TEPA with various EMImTFSI contents (runs 26, 28−32) and BADGE/TetradX/TEPA without EMImTFSI (blank sample).

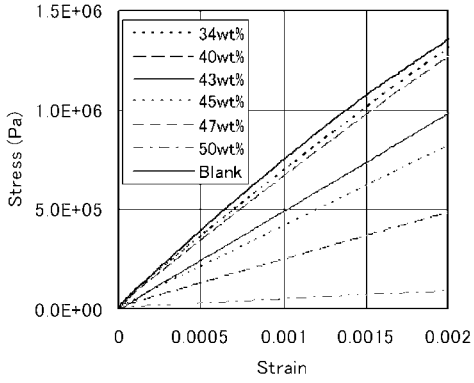

Figure 11. Stress−strain curves for the films of BADGE/Tetrad-X/TEPA with various EMImTFSI contents (runs 26, 28−32) and BADGE/Tetrad-X/TEPA without EMImTFSI (blank sample).

Table 5. Young's Moduli of BADGE/TetradX/TEPA and EMImTFSI Films

sample	EMImTFSI content (%)	Young's modulus (MPa)
BADGE/Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 26)	34	690
BADGE/Tetrad-X/TEPA/(40 wt %)EMImTFSI (run 28)	40	650
BADGE/Tetrad-X/TEPA/(43 wt %)EMImTFSI (run 29)	43	480
BADGE/Tetrad-X/TEPA/45 wt %EMImTFSI (run 30)	45	390
BADGE/Tetrad-X/TEPA/(47 wt %)EMImTFSI (run 31)	47	240
BADGE/Tetrad-X/TEPA/(50 wt %)EMImTFSI (run 32)	50	45
BADGE/Tetrad-X/TEPA	0	800

mixture was heated for 180 h under reflux. The obtained extraction solution was concentrated, and the residue was dried by heating under vacuum (70 °C /0.5 Torr) for 3 h. The extracted fraction of the ionic liquid was calculated by the weight ratio of the obtained residue to the initial amount of the ionic liquid contained in the sample.

Results and Discussion

Synthesis of BADGE/TEPA/EMImTFSI Films. Among many ionic liquids known so far, EMImTFSI was chosen at the beginning of this study, since it is a widely investigated hydrophobic ionic liquid compatible with various organic compounds. In fact, EMImTFSI is compatible with many epoxy resins and amine curing agents. EMImTFSI-containing BADGE networked polymers were easily prepared by heating a homogeneous mixture of BADGE, TEPA, and EMImTFSI at 70 °C for 5 h and 130 °C for 10 h. Samples with 34 wt % EMImTFSI were prepared (runs 1−12 in Table 1). By heating at 70 °C, the mixtures gradually became turbid, and finally glassy white translucent films with 34 wt % EMImTFSI were obtained. Figure 2shows a typical FTIR spectrum of the film (run 5). The absorption at 914 cm^{-1} attributed to the epoxy groups in BADGE almost disappeared, indicating that the curing was completed under this condition. The glass transition temperature (T_g) of the film (run 5) was estimated at 119 °C by DSC measurement, which is slightly lower than that (134 °C) of the BADGE/TEPA blank film obtained without EMImTFSI (Table 4).

The effect of TEPA on the epoxy curing was examined by varying the mole equivalence of the added [TEPA] from 0.88 to 1.70 toward BADGE, where the stoichiometry of TEPA to BADGE ([TEPA]/[BADGE]) should be 2/7 in an ideal case, and several films were prepared. The curing degrees were compared by the extracted fractions of ionic liquid from the films. Figure 3 shows the results of the methanol extraction (at room temperature for 91 h) of the materials prepared with various equivalence of TEPA to BADGE. Samples with equivalence from 1.00 to 1.12 showed a minimum extracted fraction, which indicated that the epoxy resin was the most effectively cured in this feed ratio range.

Then, the ionic liquid confinement in the BADGE/TEPA/(34 wt %)EMImTFSI film was examined by observing the time evolution of the extracted fraction of the ionic liquid from the material. The results for BADGE/TEPA/(34 wt %)EMImTFSI film (run 13) with methanol and acetone are shown in Figure 5. The extraction rate was relatively slow and the extracted fraction of ionic liquid was low at the beginning (in 100 h). However, the rate gradually increased, and the extracted fraction finally reached 18% at 500 h in methanol and 48% in acetone. The confinement was insufficient because the network density in this BADGE/TEPA curing system may not be high enough for the ionic liquid confinement.

Synthesis of Cured BADGE/MY721 or BADGE/Tetrad-X with EMImTFSI. To prepare samples with a higher network density, we added tetrafunctional epoxy compounds to the BADGE/TEPA system. White translucent glassy films were obtained by curing a mixture of BADGE/MY721 or BADGE/Tetrad-X with TEPA in the presence of EMImTFSI. Figure 4 shows the FTIR spectra for the films of [BADGE]/[MY721]/TEPA/(34 wt %)EMImTFSI (run 18) and [BADGE]/Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 26). The absorption at 914 cm^{-1} assigned to the epoxy groups disappeared, indicating that the curing was almost completed in these mixed systems. T_g and T_{d5} (5% weight loss temperature) of these samples determined by DSC and TGA measurements are summarized in Table 4. The material's T_g increased while the thermal decomposition temperature slightly decreased by adding MY721 or Tetrad-X.

Figure 5 shows the results of solvent extraction of ionic liquid from BADGE/MY721/TEPA/EMImTFSI(34 wt %) (runs 14−18) varying the amount of tetrafunctional epoxy resins as compared to the results of non-tetrafunctional epoxy sample BADGE/TEPA/(34 wt %)EMImTFSI (run 13). The extracted fraction decreased with the increase of tetrafunctional epoxides. Particularly, products obtained under the condition of [BADGE]/[MY721] = 1.00 showed a quite low content of extracted fraction of the ionic liquid in both methanol and acetone even at 500 h, indicating that the ionic liquid was effectively confined in the networked materials. The same results were obtained for BADGE/Tetrad-X/(34 wt %)EMImTFSI (runs 22−26). On the other hand, extracted fractions of ionic liquid from samples prepared without BADGE, MY721/TEPA/(34 wt %)EMImTFSI

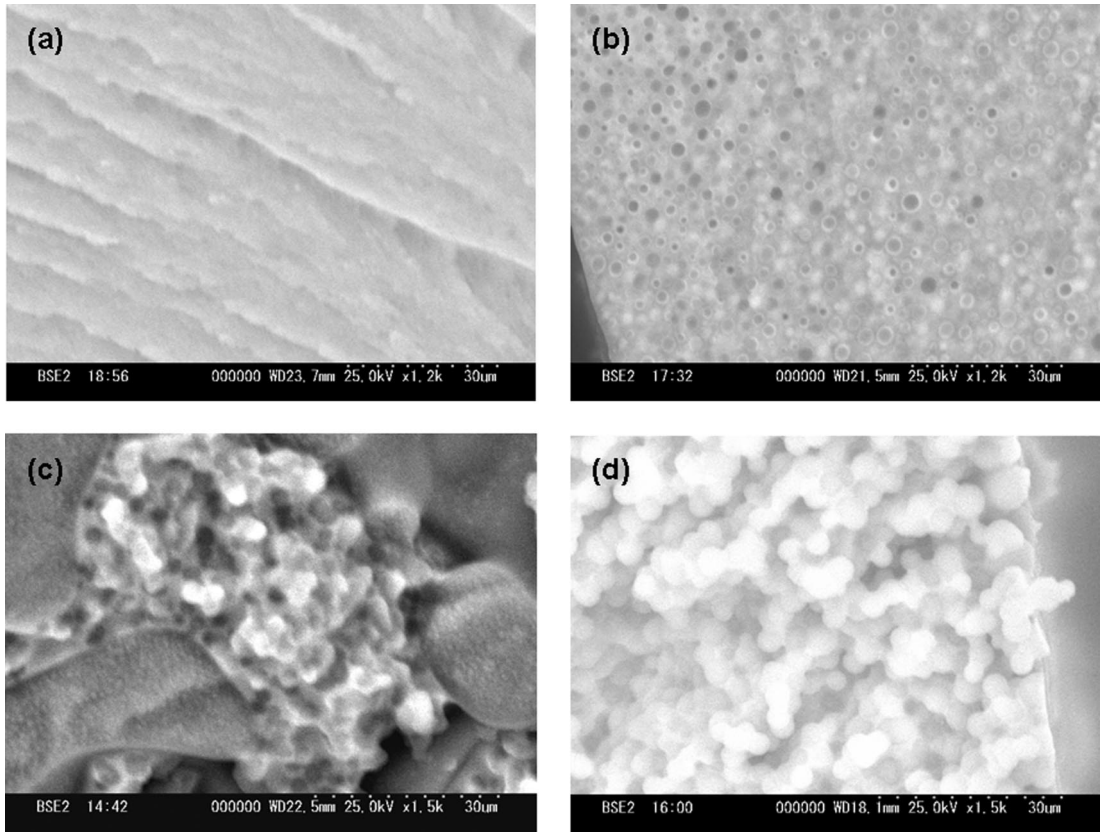

Figure 12. SEM images for the samples of BADGE/Tetrad-X/TEPA with an EMImTFSI content of (a) 34 wt % (run 26), (b) 40 wt % (run 28), (c) 45 wt % (run 30), and (d) 50 wt % (run 32).

(run 19) and Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 27), were 99% and 44% at 9 h in acetone, respectively. In these cases, the network density may not be as high as expected, because highly rigid polymer chains formed only by the tetrafunctional epoxy compounds with TEPA prevented enough cross-linking in the materials. These results indicated that curing a mixture of difunctional and tetrafunctional epoxy resins is crucial for the effective confinement of the ionic liquid. The ionic liquid confinement in these epoxy networked polymers was further examined by Soxhlet extraction with acetone as shown in Figure 6. Although most ionic liquid (74%) was extracted from BADGE/TEPA/(34 wt %)EMImTFSI (run 13) after 190 h Soxhlet extraction with acetone, no ionic liquid was extracted from both BADGE/MY721/TEPA/(34 wt %)EMImTFSI (run 18) and BADGE/Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 26) systems under the same extraction conditions.

The materials were further examined with BADGE/TetradX/TEPA/EMImTFSI (runs 26, 28−32) having different ionic liquid contents (34−50 wt %). Figure 7 shows the results of acetone extraction of EMImTFSI from those samples. Ionic liquid was completely confined in EMImTFSI 34 wt % and 40 wt % samples (runs 26 and 28), while a part of ionic liquid was rapidly extracted from samples with 43 wt %, 45 wt %, and 47 wt % EMImTFSI (runs 29−32). In addition, almost all of the ionic liquid was rapidly extracted (within 1 h) from the sample with 50 wt % EMImTFSI (run 32).

Synthesis of Films of Cured BADGE/Tetrad-X with Other Ionic Compounds. BADGE/TEPA epoxy network systems with other ionic compounds were examined. Films of cured BADGE with/without Tetrad-X and other ionic liquids such as HMImTFSI (run 33), BMImTFSI (run 34) or ionic solid like LiTFSI (runs 35, 36) were prepared, and the ion confinement was analogously investigated.

Figure 8 shows the results of acetone extraction of various ionic liquids from those samples. The ionic liquid confinement was in the order EMImTFSI > HMImTFSI > BMImTFSI, which is the opposite order of the steric hindrance of the cations. The reason for this remains unknown, but we assume that the hexyl or benzyl group in the cationic part may increase the compatibility of the ionic liquid with the epoxy network, and that the segmental motion of the networked polymer may be enhanced so that the ionic liquid can escape from the networked polymer. In fact, EMImTFSI-containing and HMImTFSI-containing films are translucent, and the BMImTFSI-containing film is transparent, indicating that a kind of phase separation between ionic liquid and networked polymer may occur in the cases of EMImTFSI and HMImTFSI, while no such clear phase separation occurs in the BMImTFSI-containing film. Figure 9 shows the results of acetone extraction of LiTFSI from samples in runs 35 and 36. Although LiTFSI was rapidly extracted with acetone from the sample in run 35 (34 wt % LiTFSI content), most ion was effectively confined in the sample in run 36 (20 wt % LiTFSI content) by reducing the ion content. The results in Figures 8 and 10 imply that the confinement of the second component in the networked polymer system is not limited to EMImTFSI but is also applicable to other ionic liquids or ionic solids.

Ionic Conductivity. Figure 10 shows the alternating current frequency dependence of ionic conductivity for the films of cured BADGE/TetradX/TEPA-EMImTFSI (runs 26, 28−32) and blank film of cured BADGE/TetradX-1.00/TEPA without EMImTFSI. Samples in runs 26 and 28 (34 wt % and 40 wt % EMImTFSI) showed very low and similar frequency dependence to the blank sample, indicating that these samples are insulating. On the other hand, samples in runs 29−32 with more than 43 wt % EMImTFSI showed much higher conductivity, indicating

that they are ion conductive. In these samples, the ionic conductivity increased with the increase of EMImTFSI content. The ionic conductivity of the BADGE/TetradX/TEPA/(50 wt %)EMImTFSI is 0.1−0.12 S/m in the frequency range from 1 to 100 KHz, which is quite high and corresponds to about 1/8 of the reported bulk EMImTFSI conductivity (0.84 S/m). These data indicate that the samples confining the ionic liquid in the materials are insulating and that the samples not confining the ionic liquid are ion conductive. This seems reasonable because there are no freely mobile ions in the samples containing 34 wt % and 40 wt % EMImTFSI, in which ions are locally confined by rigid and glassy polymer networks. The T_g of the BADGE/Tetrad-X/TEPA/(34 wt %)EMImTFSI (run 26) determined by DSC was 129 °C (Table 3), which is much higher than room temperature.

Mechanical Property of BADGE/Tetrad-X/TEPA and EMImTFSI Films. A similar EMImTFSI content dependence of mechanical property was also observed for the materials. Figure 11 shows the stress−strain curves for BADGE/Tetrad-X/TEPA/EMImTFSI films with various EMImTFSI contents (runs 26, 28−32) and a blank sample of BADGE/Tetrad-X/TEPA. Curves for samples in runs 26 and 28 (34 wt % and 40 wt % EMImTFSI) are very similar to the blank sample (without EMImTFSI). On the other hand, with an EMImTFSI content over 40 wt %, the slope of the stress−strain curve gradually decreases, implying that the materials became softer. The Young's moduli calculated from the initial slopes of the plots are summarized in Table 5, showing an abrupt decrease of the Young's modulus beyond 40 wt % EMImTFSI.

Morphologies of the BADGE/TetradX/TEPA and EMImTFSI Films. The morphologies of the BADGE/TetradX/TEPA and EMImTFSI samples were investigated by SEM. Figure 12 shows typical SEM images of the fractured surface of the films with different EMImTFSI contents (runs 26, 28, 30, and 32). In the composites with 34 wt % EMImTFSI (run 26), SEM reveals a homogeneous surface. It is true that the composites had a certain microphase separated structure because the film was translucent, but the scale of the phase separation in the sample was so small that it could not be detected by SEM. In the sample with 40 wt % EMImTFSI (run 28), on the other hand, many discrete and spherical domains with 3 μm diameters were observed, which may be due to the aggregated EMImTFSI domains in the networked epoxy resin matrix. Furthermore, in the sample with 50 wt % EMImTFSI (run 32), larger regular structure was formed and the fractured surface became very rough. This may be due to the formation of continuous phase by EMImTFSI. In the sample with 45 wt % EMImTFSI (run 30), both phase structures were observed, a structure with the discrete spherical EMImTFSI domains in a networked epoxy resin matrix, and that formed by the continuous EMImTFSI phase. These SEM observations clearly indicate that a structure transition occurs in the range of 40 wt % and 50 wt % EMImTFSI.

We consider that the drastic change of the characteristic properties in the materials between 40 wt % and 50 wt % EMImTFSI as described in the former section may be due to this transition of morphology. The material having a discrete EMImTFSI phase with a continuous epoxy network phase confines the ionic liquid in the materials. As a result, the material is insulating and maintains mechanical stiffness of the epoxy network. On the other hand, the material having a continuous EMImTFSI phase does not confine the ionic liquid any more, becomes ion conductive, and loses mechanical stiffness.

Conclusions

Ionic-liquid-containing epoxy-based networked polymers were synthesized by curing epoxy resins with an amine in the presence of an ionic liquid. The materials obtained from a mixture of BADGE and a tetrafunctional epoxy resin exhibited a high ability to confine the ionic liquid, in which a negligible amount of ionic liquid was extracted by either methanol or acetone. The confinement drastically decreased when the ionic liquid content was over 40 wt %. The ionic liquid confinement was closely related to the material's ionic conductivity and mechanical strength. Materials confining ionic liquid were insulating with a high Young's modulus, while those not confining ionic liquid were ion conducting with a low Young's modulus. SEM observation revealed that the drastic change of the fundamental properties in the materials may be due to the morphology transition of the materials, in which the ionic liquid transforms discrete phases to continuous phases in the epoxy-based networks. These results suggest that the addition of ionic liquids can be a new and facile method to control the morphology of networked polymers.

References and Notes

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