

## Ion Gels Prepared by in Situ Radical Polymerization of Vinyl Monomers in an Ionic Liquid and Their Characterization as Polymer Electrolytes

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**Abstract:** To realize polymer electrolytes with high ionic conductivity, we exploited the high ionic conductivity of an ionic liquid. In situ free radical polymerization of compatible vinyl monomers in a room temperature ionic liquid, 1-ethyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide (EMITFSI), afforded a novel series of polymer electrolytes. Polymer gels obtained by the polymerization of methyl methacrylate (MMA) in EMITFSI in the presence of a small amount of a cross-linker gave self-standing, flexible, and transparent films. The glass transition temperatures of the gels, which we named "ion gels", decreased with increasing mole fraction of EMITFSI and behaved as a completely compatible binary system of poly(methyl methacrylate) (PMMA) and EMITFSI. The temperature dependence of the ionic conductivity of the ion gels followed the Vogel–Tamman–Fulcher (VTF) equation, and the ionic conductivity at ambient temperature reached a value close to  $10^{-2} \text{ S cm}^{-1}$ . Similarly to the behavior of the ionic liquid, the cation in the ion gels diffused faster than the anion. The number of carrier ions, calculated from the Nernst–Einstein equation, was found to increase for an ion gel from the corresponding value for the ionic liquid itself. The cation transference number increased with decreasing EMITFSI concentration due to interaction between the PMMA matrix and the TFSI<sup>-</sup> anion, which prohibited the formation of ion clusters or associates, as was the case for the ionic liquid itself.

### Introduction

The development of novel highly ion-conducting polymer electrolytes for potential application in a wide variety of solid-state electrochemical devices has received an upsurge of interest, driven by the intrinsic properties of the polymer electrolytes, such as thin-film forming ability, flexibility, and transparency as well as the relatively high ionic conductivity and wide electrochemical window.<sup>1</sup> Conventional electrolytes of this variety, typically polyether-based polymer electrolytes, are solid solutions of electrolyte salts in polymers. The ionic motion in these polymer electrolytes is coupled with the local segmental motion, where the relaxation time for the segmental motion is coupled with the conduction relaxation time, and a decrease in the ionic mobility caused by the rapid increase in the glass transition temperature ( $T_g$ ) offsets the effect of the increasing carrier-ion density with increasing ion concentration. These facts are mirrored in the appearance of a maximum conductivity in polyethers at a relatively low salt concentration with increasing salt concentration. Innovation of systems, where the polymer electrolytes have a glass transition low enough to remain rubbery at room temperature while preserving high conductivity and

good electrochemical stability, has therefore been an intriguing domain of recent research.

The notion that a small amount of a high-molecular weight polymer would suffice to give rubbery compliance with high ionic conductivity is evident for certain salt–polymer systems, which show high ionic conductivity with significantly low  $T_g$  in the range of high salt concentrations.<sup>2</sup> In these salt–polymer systems, known as polymer-in-salt electrolytes, the number of carrier ions and their mobility increase with increasing the electrolyte concentration. Consequently, high ionic conductivity that is not coupled with the segmental motion of the polymers is likely to be achieved. However, the electrolyte salts for such a polymer-in-electrolyte system need to possess some essential characteristics, such as low  $T_g$  and melting point,  $T_m$ , and capability of forming (supercooled) liquids at ambient temperature while retaining high ionic conductivity and compatibility with the host polymers.<sup>2</sup>

Ionic liquids, also known as room-temperature molten salts, due to, inter alia, their immeasurably low vapor pressure, high ionic conductivity, and greater thermal and electrochemical

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stability<sup>3–5</sup> are considered to be suitable electrolyte salts for polymer-in-salt systems. Ionic liquids meet all of the requirements of plasticizing salts and offer the potential for improved thermal and mechanical properties and may expand the temperature range where flexible polymers can be used. We have preliminarily reported polymer-in-salt electrolytes, prepared by dissolving compatible polymers in chloroaluminate<sup>2a,c,6a</sup> and non-chloroaluminate molten salts,<sup>6b</sup> which exhibit high ionic conductivity as well as a rubbery electrolyte property. Scott et al. have reported ionic liquids based on imidazolium salts as excellent plasticizers for poly(methyl methacrylate) with improved thermal stability and ability to significantly reduce the glass transition temperatures.<sup>7</sup> Carlin and co-workers also reported highly ion-conducting rubbery gel electrolytes from non-chloroaluminate ionic liquids and poly(vinylidene fluoride-co-hexafluoropropylene).<sup>8</sup>

While most of the studies are concerned with the doping of polymers with electrolyte salts, the solubility of a large number of vinyl monomers in ionic liquids has prompted us to carry out polymerization of the vinyl monomers in ionic liquids to afford polymer electrolytes.<sup>9a</sup> **In situ free radical polymerization of the compatible vinyl monomers in ionic liquids yields transparent, mechanically strong, and highly conductive polymer electrolyte films.** Like conventional polymer gels, the obtained polymer electrolytes are comprised of polymer networks and liquids,<sup>9</sup> ionic liquid in our case. If the incorporation of ionic liquid into polymer networks affords a completely compatible combination, we name the obtained polymer gels “ion gels”,<sup>10</sup> which are distinctly **discriminated** from conventional polymer gels in terms of nonvolatility and high thermal stability of the liquids incorporated in the network polymers. Since task-oriented properties, such as proton conduction, lithium-ion conduction, and electronic charge transport, can be molecularly designed into the ionic liquids, the scope and the utility of the ion gels as new polymer electrolytes will immediately expand to fuel cells,<sup>11</sup> lithium batteries,<sup>12</sup> and solar cells.<sup>13</sup>

**More recent studies provide insight into the kinetics and the types of polymers formed by the free radical polymerization reactions of vinyl monomers in ionic liquids as a solvent.**<sup>14</sup> Ionic liquids have also been proved to be suitable for controlled atom transfer radical polymerization (ATRP),<sup>15</sup> reverse ATRP,<sup>16</sup> and radical addition fragmentation transfer (RAFT) polymerization<sup>17</sup> of acrylates and styrene in ionic liquids. In a recent study, **Snedden et al.**<sup>18</sup> have investigated the **polymer–ionic liquid interactions to the design of composite materials and discussed the solubility of a range of polymers in the selected ionic liquids, polymerization and copolymerization in the ionic liquids, the characterization of targeted polymer–ionic liquid composites, and the role of cross-linking and gelation.**

Through numerous attempts so far made, the prospect of ionic liquids, as electrolyte salts for polymer electrolytes, has been well understood; however, the art of realizing highly conducting polymer electrolytes and characterizing their ion transport behavior remains in a rudimentary stage. To bring perspective in this burgeoning field of polymer electrolytes, we aim at understanding the ion-transport property of the highly conductive polymer electrolytes based on ionic liquids. This paper deals with in situ polymerization of vinyl monomers in 1-ethyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide (EMITFSI) to present a new methodology affording highly conductive polymer electrolytes. **The compatibility of the ionic liquid with the polymer matrix has been analyzed to develop the criteria for such a binary system to belong to this novel category of polymer electrolytes.** Finally, the characterization and ion transport behavior of ion gels have been targeted to achieve the goal of molecular design of highly conductive polymer electrolytes.

## Experimental Section

**Preparation and Characterization of EMITFSI.** EMITFSI was prepared following the procedure reported earlier with a slight modification.<sup>19</sup> 1-Ethyl-3-methyl imidazolium bromide (EMIBr) was first prepared by **the quaternization reaction of 1-methyl imidazole with ethyl bromide** at 80 °C for 24 h in **cyclohexane** under refluxing condition. The crude product was purified by repeated recrystallization using a mixture of **ethyl acetate** and **isopropyl alcohol** (volume ratio, 1:1) as the solvent. This yielded white crystalline hygroscopic EMIBr ( $T_m = 78$  °C). The structure of the prepared EMIBr was confirmed by <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>, chemical shift,  $\delta$ /ppm relative to TMS): 9.34 (s, 1H), 7.88 (t, 1H, and  $J = 1.65$  Hz) 7.79 (t, 1H, and  $J = 1.65$

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**Table 1.** Compatibility of EMITFSI with Monomers<sup>a</sup> and Their Polymers<sup>b</sup>

	monomer	polymer
methyl methacrylate	compatible	compatible
acrylonitrile	compatible	phase-separated
vinyl acetate	compatible	no polymerization
styrene	compatible	phase-separated
2-hydroxyethyl methacrylate	compatible	phase-separated
methyl acrylate	compatible	compatible
acrylamide	compatible	phase-separated

<sup>a</sup> Ionic liquids and monomers are mixed at 1:1 molar ratio. <sup>b</sup> Polymerization was carried out in the presence of 2 mol% BPO for monomers at 80 °C for 12 h.

Hz), 4.24 (q, 2H, and  $J = 7.26$  Hz) 3.89 (s and 3H), 1.42 (t, 3H, and  $J = 7.26$  Hz). It was further characterized by fast atom bombardment mass spectroscopic (FAB-MS, glycerol matrix) results. Positive FAB: molecular weight of EMI cation = 111.17 and the mass-to-charge ratio,  $m/z$ , for the molecular ion peak = 111. The quasi-molecular ion peaks with an  $m/z$  of 301 and 303 in the positive FAB corresponded to the species with two EMI cations attached to a bromide ( $\text{Br}^-$ ) with the indication of the formation of ion clusters in the EMIBr system.<sup>20</sup>

Finally, the anion exchange reaction from  $\text{Br}^-$  to bis(trifluoromethane sulfonyl)imide (TFSI<sup>-</sup>) was carried out by heating an equimolar mixture of EMIBr and LiTFSI (kindly supplied by Dai-ichi Kogyo Seiyaku Co.) in water at 70 °C for 24 h to be phase-separated into hydrophobic ionic liquid and aqueous phases. The obtained EMITFSI was repeatedly washed with pure water and then dehydrated under vacuum at 120 °C for 72 h. This yielded a clear, colorless liquid ( $T_m = -16$  °C, vide infra). The structure of EMITFSI was identified by <sup>1</sup>H NMR spectra (DMSO-*d*<sub>6</sub>,  $\delta$ /ppm relative to TMS): 9.10 (s and 1H), 7.77 (t, 1H, and  $J = 1.65$  Hz), 7.68 (t, 1H, and  $J = 1.65$  Hz), 4.19 (q, 2H, and  $J = 7.26$  Hz), 3.85 (s and 3H), 1.42 (t, 3H, and  $J = 7.26$  Hz). The FAB-MS (glycerol matrix) results (Positive FAB: molecular weight of EMI cation = 111.17 and  $m/z$  the molecular ion peak = 111. Negative FAB: molecular weight of TFSI anion = 280.17 and  $m/z$  of the molecular ion peak = 280) further characterized EMITFSI. Similarly to EMIBr, the quasi-molecular ion peak with an  $m/z$  of 502 in the positive FAB corresponded to the species with two EMI cations attached to a TFSI anion and suggested ion cluster formation in the ionic liquid system.<sup>20</sup> The samples were stored in an argon atmosphere glovebox (VAC, [O<sub>2</sub>] < 1 ppm, [H<sub>2</sub>O] < 1 ppm).

**Radical Polymerization of Vinyl Monomers in Ionic Liquid and Preparation of Ion Gels.** Using EMITFSI as a polymerization solvent, we tried to polymerize seven common vinyl monomers. Prior to polymerization, methyl methacrylate (MMA), acrylonitrile, vinyl acetate, styrene, 2-hydroxyethyl methacrylate, methyl acrylate, and acrylamide were purified by distillation or recrystallization and bubbled with nitrogen gas to ensure an oxygen-free atmosphere in the case of liquid monomers. The equimolar mixtures of EMITFSI and the monomers were compatible, and therefore, radical polymerization was carried out by heating the solutions at 80 °C for 12 h in the presence of 2 mol % of benzoyl peroxide (BPO) as an initiator. The obtained polymers, poly(methyl methacrylate) (PMMA), and poly(methyl acrylate) showed good compatibility with EMITFSI in the resulting vinyl polymers, while polyacrylonitrile, polystyrene, poly(2-hydroxyethyl methacrylate), and polyacrylamide were incompatible with the ionic liquid. Under the experimental conditions, free radical polymerization reaction did not occur for vinyl acetate, possibly due to the inhibition caused by a trace amount of dissolved oxygen in the system. The compatibility of the vinyl monomers and polymers with EMITFSI is summarized in Table 1.

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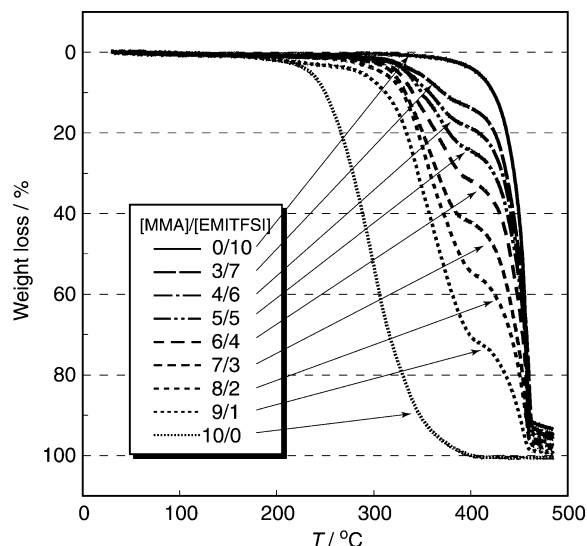
Because of the favorable compatibility of PMMA with EMITFSI, a network polymer of PMMA was chosen as a matrix of the EMITFSI. Deoxygenated MMA, ethylene glycol dimethacrylate (EGDMA, 2 mol % based on MMA), and BPO (2 mol % based on MMA) as an initiator were dissolved in EMITFSI. The mixtures were injected with a syringe between two glass plates separated by a poly(tetrafluoroethylene) (Teflon) spacer (0.5 mm in thickness), and in situ radical polymerization was conducted at 80 °C for 24 h. As for the samples for conductivity and NMR measurements, a further heat treatment at 140 °C for 30 min was carried out in order to complete the polymerization (vide infra). The composition of [MMA]/[EMITFSI] was varied from 9/1 to 3/7, and in all cases the obtained films of ion gels were flexible, transparent, and self-standing. In addition, PMMA (bulk) films, which did not contain any EMITFSI, were also prepared as a reference material following the polymerization technique identical to that of an ion gel.

**Thermal Properties.** Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments DSC 220C under a nitrogen atmosphere. The samples were tightly sealed in Al pans in the glovebox. The measurements were conducted with the samples heated to 200 °C followed by cooling to -150 °C, and then heating again up to 200 °C at a cooling and heating rate of 10 °C min<sup>-1</sup>. The glass transition temperature (the midpoint temperature of the heat capacity change,  $T_g$ ) and melting point (onset temperature of the endothermic peak,  $T_m$ ) were determined from the DSC thermograms during the programmed reheating steps. Thermogravimetric (TG) measurements of the samples were conducted using open Al pans on a Seiko Instruments thermogravimetry/differential thermal analyzer (TG-DTA 6200) from room temperature to 550 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

**Dynamic mechanical analysis** (DMA) was performed under a nitrogen atmosphere by using a Seiko Instruments DMS 210. The samples of the films of the ion gels were cut into strips (5 mm × 30 mm) in the argon atmosphere glovebox and were rapidly cooled from ambient temperature to -150 °C, and the measurements were performed at the frequency of 1 Hz with the heating rate of 2 °C min<sup>-1</sup> up to 150 °C.

**Ionic Conductivity Measurements.** The ionic conductivity ( $\sigma$ ) was determined in a hermetic cell by means of the complex impedance measurements with stainless steel blocking electrodes, using a computer-controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 Hz to 13 MHz at an AC amplitude of 10 mV. An ionic liquid sample was filled between two mirror-finished stainless steel electrodes using a Teflon ring spacer in a constant volume cylindrical cell (13 mm outer diameter, 7 mm inner diameter, 2 mm thickness) and was sealed in a Teflon container in the glovebox. For the polymer electrolytes, a film (12 mm diameter, 1.13 cm<sup>2</sup> area, ca. 0.5 mm thickness) was sandwiched between mirror-finished stainless steel electrodes, sealed in a Teflon container, and subjected to the impedance measurements. The measurements were conducted at controlled temperatures while cooling from 100 to -20 °C in a Tabai Espec SU-220 temperature chamber. The samples were thermally equilibrated at each temperature for at least 1 h prior to the measurements. The accuracy of all of the results was checked by replicate measurements under identical experimental conditions.

**Self-Diffusion Coefficient Measurements.** The self-diffusion coefficients of the ions and the polymer matrix in the ion gels were determined by pulsed-gradient spin-echo NMR (PGSE-NMR) measurements, which were made by using a JEOL GSH-200 spectrometer with a 4.7 T wide bore superconducting magnet controlled by a TecMAG Galaxy and a Mac NMR systems equipped with JEOL pulse field gradient probes and a current amplifier. The <sup>19</sup>F and <sup>1</sup>H spectra were measured with a <sup>19</sup>F/<sup>1</sup>H probe. The measurements were carried out with cooling from 100 to 30 °C, and the samples were thermally equilibrated at each temperature for 30 min before the measurements. After the measurements of 90° pulses, the longitudinal relaxation time ( $T_1$ ), and the transversal relaxation time ( $T_2$ ), the self-diffusion coef-



**Figure 1.** TG curves for MMA network polymers with different mole fractions of dissolved EMITFSI and EMITFSI bulk at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .

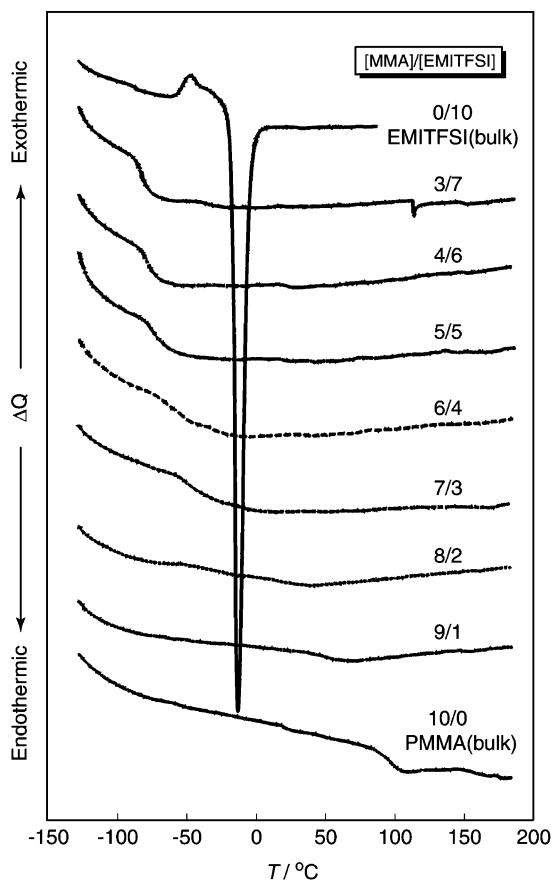
ficients were measured using the simple Hahn spin-echo (i.e.,  $90^{\circ} - \tau - 180^{\circ} - \tau - \text{Acquisition}$ ) sequence incorporating a gradient pulse in each  $\tau$  period, unless otherwise noted. The echo signal attenuation,  $E$ , is related to the experimental parameters by<sup>21</sup>

$$E = \exp(-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)) \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio,  $g$  is the amplitude of the gradient pulses of the duration  $\delta$ , and  $\Delta$  is the interval between the leading edges of the gradient pulses. In the present experiments, the  $g$  value used was constant (3.34 T/m), the  $\delta$  was in the range of 0 to 3 ms, and the value of  $\Delta$  was 50 ms. The self-diffusion coefficient of the  $\text{EMI}^+$  cation in the ion gel was obtained from the signal attenuation of the  $^1\text{H}$  on the 3-methyl group, and that of the  $\text{TFSI}^-$  anion was determined from the signal attenuation of the  $^{19}\text{F}$  nucleus. The accuracy of the experimental results was checked by replicate measurements under identical experimental conditions. The PGSE measurement involved the collection of spin-echo amplitudes as the gradient pulse strengths were varied, and the value of  $D$  could, therefore, be determined from the slope of a plot of  $\ln E$  versus  $-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)$  ( $R^2 > 0.996$  for  $\text{EMI}^+$  and  $\text{TFSI}^-$ ). The self-diffusion coefficient values of the ions in EMITFSI (bulk) were used from our previous report.<sup>4</sup>

## Results and Discussion

**Characterization of EMITFSI and Ion Gels.** Figure 1 shows the TG curves for PMMA network polymers with a different mole fraction of dissolved EMITFSI. The TG curve for EMITFSI (bulk) shows a one-step weight loss process with the detection of noticeable change only at above  $400\text{ }^{\circ}\text{C}$  (temperature corresponding to 10% weight loss,  $T_d = 444\text{ }^{\circ}\text{C}$ ) indicating high thermal stability as an ionic liquid over a wide range of temperature. The TG curves for the network polymers with dissolved EMITFSI, on the other hand, show two-step weight loss processes: the initial losses corresponding to the network polymer and the final step corresponding to the weight loss corresponding to EMITFSI in the system. The reference polymer, PMMA, undergoes a one-step weight loss process with a  $T_d$  of  $257\text{ }^{\circ}\text{C}$ . It should be noted that the onset of the weight



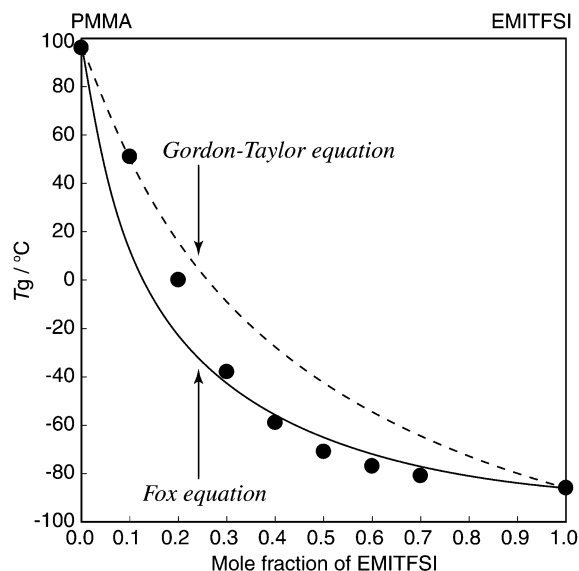
**Figure 2.** DSC thermograms for MMA network polymers with different mole fractions of dissolved EMITFSI and EMITFSI bulk at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .

loss process for PMMA in the ion gels is higher than that of the bulk PMMA, which is indicative of the higher thermal stability of the ion gels compared with that of PMMA itself, despite a decrease in the  $T_g$  with the incorporation of EMITFSI. Similar behavior has been observed in other polymer/ionic liquid systems.<sup>18</sup>

Figure 2 shows the DSC thermograms during the heating scans from  $-150$  to  $200\text{ }^{\circ}\text{C}$  (reheating step) for the ion gels along with those for bulk EMITFSI and PMMA. EMITFSI shows a sharp endothermic peak in the DSC thermogram corresponding to  $T_m$  ( $-16\text{ }^{\circ}\text{C}$ ), together with a heat capacity change corresponding to  $T_g$  ( $-86\text{ }^{\circ}\text{C}$ ). The coexistence of the  $T_m$  and  $T_g$  indicates relatively slow crystallization kinetics of EMITFSI, which has been widely observed in ionic liquids.<sup>4</sup> On the other hand, the PMMA bulk exhibits  $T_g$  at  $96\text{ }^{\circ}\text{C}$ . It is readily seen that the ion gels have only the heat capacity changes, corresponding to glass transition, in the DSC thermograms, which vary with composition.

The DSC results for the heating scans from room temperature to  $200\text{ }^{\circ}\text{C}$  (first step) are also interesting (Supporting Information 1). The PMMA bulk shows an exothermic peak at  $140\text{ }^{\circ}\text{C}$ , which can be ascribed to the heat of polymerization of unreacted MMA monomers in the system. With increasing EMITFSI content in the ion gel, the intensity of the exothermic peak gradually decreases, and for  $[\text{MMA}]/[\text{EMITFSI}] = 7/3$  or higher compositions, the peak disappears, indicating the absence of unreacted MMA monomer in the ion gels. This may indicate enhancement of the free radical polymerization of MMA in the

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**Figure 3.** Glass transition temperature ( $T_g$ ) for MMA network polymers with dissolved EMITFSI as a function of EMITFSI concentration. The points are the experimental  $T_g$ 's, and the lines are the fitted profiles. Dotted line: Gordon–Taylor equation. Solid line: Fox equation.

presence of EMITFSI. This is in good agreement with the corroborative study by Harrison et al.,<sup>14a</sup> wherein by means of pulse laser polymerization technique, they have shown that the rate constant of MMA propagation increases considerably when polymerization is carried out in an ionic liquid.

#### Compatibility of EMITFSI with PMMA in Ion Gels.

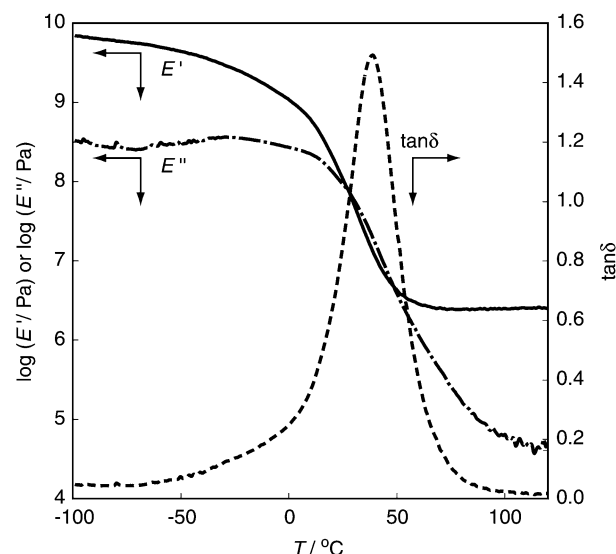
Despite two distinct components (PMMA and EMITFSI) in the binary systems, the polymer electrolytes exhibit a single  $T_g$  in the range of the compositions, and the endothermic peak corresponding to the melting point of EMITFSI vanishes (vide supra). Therefore, at all compositions of the ion gels, the system at temperatures higher than the  $T_g$  is in the rubbery state. Figure 3 shows the composition dependence of the  $T_g$  with varying [MMA]/[EMITFSI] compositions, which shows a decrease in the  $T_g$  with an increase in the mole fraction of EMITFSI and approaches the value of EMITFSI at high salt concentrations. These suggest that the network polymer of PMMA is compatible with dissolved EMITFSI. The relationship for the dependence of the  $T_g$  on composition can be understood, as was rationalized by the Gordon and Taylor equation<sup>22a</sup> for a copolymer, based on free volume considerations, and by the Fox equation<sup>22b</sup> for a plasticized polymer and a copolymer, based on additivity of the weight fraction. If the  $T_g$  of the polymer and the solvent, PMMA and EMITFSI in our case, are represented by  $T_{g, \text{PMMA}}$  and  $T_{g, \text{EMITFSI}}$ , respectively, the Gordon–Taylor equation and Fox equation are given by:<sup>23</sup>

$$T_g = v_{\text{EMITFSI}} \times T_{g, \text{EMITFSI}} + v_{\text{PMMA}} \times T_{g, \text{PMMA}} \quad (v_{\text{EMITFSI}} + v_{\text{PMMA}} = 1) \quad (2)$$

$$\frac{1}{T_g} = \frac{w_{\text{EMITFSI}}}{T_{g, \text{EMITFSI}}} + \frac{w_{\text{PMMA}}}{T_{g, \text{PMMA}}} \quad (w_{\text{EMITFSI}} + w_{\text{PMMA}} = 1) \quad (3)$$

where  $v_{\text{PMMA}}$  and  $v_{\text{EMITFSI}}$  are the volume fractions of PMMA

(22) (a) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493. (b) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123. (c) Nielsen, I. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1975; Chapter 1.



**Figure 4.** Storage modulus ( $E'$ ), loss of modulus ( $E''$ ), and loss of tangent ( $\tan \delta$ ) for EMITFSI dissolved in MMA network polymers ([MMA]/[EMITFSI] = 8/2) as a function of temperature at 1 Hz.

and EMITFSI, respectively, while  $w_{\text{PMMA}}$  and  $w_{\text{EMITFSI}}$  are the weight fractions, respectively, in the systems. The experimental results fit well both of the equations (Figure 3), and **therefore, the binary system of PMMA and EMITFSI behaves as a compatible system.** This is further revealed from the DMA results, which give a single peak for the temperature dependence of loss tangent ( $\tan \delta$ ) obtained from the storage modulus ( $E'$ ) divided by the loss of modulus ( $E''$ ) for EMITFSI dissolved in the network polymer (Figure 4).

**Ionic Conductivity and Self-Diffusion Behavior in Ion Gels.** The temperature dependence of ionic conductivity ( $\sigma$ ) for the network polymer electrolytes based on PMMA and EMITFSI along with that for bulk EMITFSI is depicted in Figure 5. The  $\sigma$  has been found to increase with an increase in the content of EMITFSI in the ion gels. At high EMITFSI concentrations, the  $\sigma$  reaches the value of ca.  $10^{-2} \text{ S cm}^{-1}$  at 30 °C, which is much higher than the values ever reported for conventional polymer electrolytes at ambient temperature. **The high ionic conductivity of the ion gels<sup>9</sup> is due to the high self-dissociating and ion-transporting abilities of the constituent ionic liquid and the decoupling of the ion transport from polymer segmental motion** (vide infra).

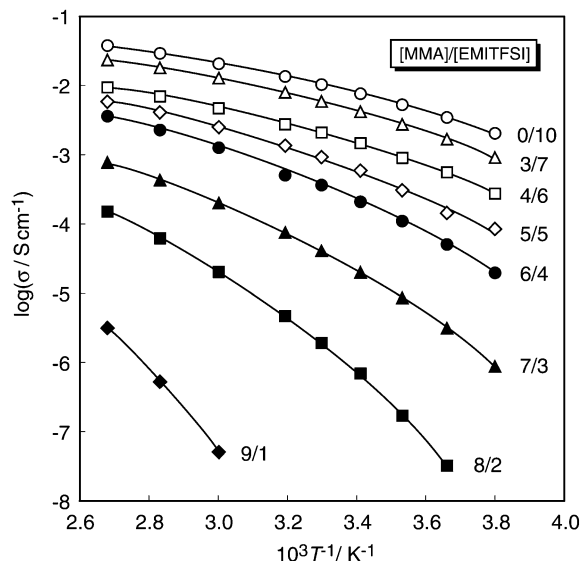
The Arrhenius plots of the temperature dependency of the  $\sigma$  exhibits convex upward curved profiles; therefore, experimental data have been fitted with the Vogel–Tamman–Fulcher (VTF) equation<sup>24</sup> for conductivity for such electrolytic materials (Figure 5). The VTF equation is

$$\sigma = \sigma_0 \exp[-B/(T - T_0)] \quad (4)$$

where the constants,  $\sigma_0$  ( $\text{S cm}^{-1}$ ),  $B$  (K), and  $T_0$  (K) are adjustable parameters. The best-fit parameters are shown in

(23) Usually, the Fox equation is used to predict the glass transition temperatures for random copolymers. However, the equation is expected to be applicable to polymer–diluent systems, which are compatible and not too strongly polar. Data on copolymers and on polymer–diluent systems illustrated this to be substantially true.<sup>9b,22b,c</sup> Free volume considerations, as in the Gordon–Taylor equation, can also predict new  $T_g$ 's when polymers are plasticized by molecular solvents (diluent) and are compatible with them at the molecular level.<sup>22a,c</sup>

(24) (a) Vogel, H. *Phys. Z.* **1921**, *22*, 645. (b) Fulcher, G. S. *J. Am. Ceram. Soc.* **1923**, *8*, 339.



**Figure 5.** Temperature dependence of ionic conductivity for MMA network polymers with different mole fractions of dissolved EMITFSI and EMITFSI bulk.

**Table 2.** VTF Equation Parameters for Ionic Conductivity Data and Glass Transition Temperatures for MMA Network Polymer with Dissolved EMITFSI and EMITFSI Bulk

$\sigma = \sigma_0 \exp[-B/(T - T_0)]$					
[MMA]/[EMITFSI]	$\sigma_0/S\text{ cm}^{-1}$	$B/K$	$T_0/K$	$R^2$	$T_g/^\circ K$
0/10	$5.51 \times 10^{-1}$	$5.34 \times 10^2$	167	0.999	187
3/7	$3.08 \times 10^{-1}$	$4.79 \times 10^2$	178	0.999	192
4/6	$2.72 \times 10^{-1}$	$5.67 \times 10^2$	176	0.999	196
5/5	$2.78 \times 10^{-1}$	$6.66 \times 10^2$	175	0.999	202
6/4	$2.89 \times 10^{-1}$	$8.21 \times 10^2$	177	0.999	214
7/3	$2.51 \times 10^{-1}$	$1.06 \times 10^3$	177	0.999	235
8/2	$1.58 \times 10^{-1}$	$1.30 \times 10^3$	194	0.999	273
9/1	$4.13 \times 10^{-3}$	$2.21 \times 10^3$	272	0.999	324

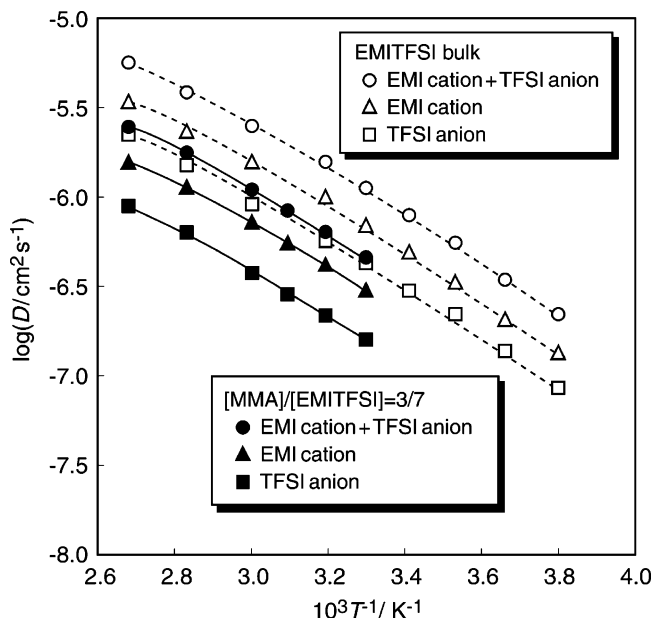
<sup>a</sup> The midpoint temperature of the heat capacity change ( $T_g$ ) during heating scans from  $-150^\circ\text{C}$  by using differential scanning calorimetry.

**Table 3.** VTF Equation Parameters for Self-Diffusion Coefficient Data for EMITFSI Bulk and MMA Network Polymer with Dissolved EMITFSI

$D = D_0 \exp[-B/(T - T_0)]$				
	$D_0/\text{cm}^2\text{ s}^{-1}$	$B/K$	$T_0/K$	$R^2$
Ionic Liquid (EMITFSI Bulk)				
cation	$1.56 \times 10^{-4}$	$9.14 \times 10^2$	134	0.999
anion	$2.55 \times 10^{-4}$	$1.30 \times 10^3$	100	0.999
cation + anion	$3.45 \times 10^{-4}$	$1.03 \times 10^3$	123	0.999
Ion Gel ([MMA]/[EMITFSI] = 3/7)				
cation	$4.27 \times 10^{-5}$	$6.87 \times 10^2$	165	0.999
anion	$1.30 \times 10^{-4}$	$1.33 \times 10^3$	105	0.999
cation + anion	$1.10 \times 10^{-4}$	$8.58 \times 10^2$	147	0.999

Table 2. A close value of the  $T_g$  to  $T_0$  for EMITFSI (bulk) is normal and well rationalized. However, with a decrease in the EMITFSI content in the PMMA/EMITFSI electrolytes, the difference between the  $T_0$  and  $T_g$  has been found to increase, and the ion conduction, therefore, showed a tendency to be decoupled from the structure glass transition. We shall discuss the phenomenological detail of the physical processes in the ion gel system elsewhere.

The diffusion behavior, studied by PGSE-NMR measurements, in association with the ionic conductivity provides valuable information on the ion transport behavior in the ion



**Figure 6.** Temperature dependence of self-diffusion coefficient for MMA network polymers with dissolved EMITFSI ([MMA]/[EMITFSI] = 3/7) and EMITFSI bulk.

gels. Figure 6 shows the temperature dependency of the self-diffusion coefficients of different diffusive species in the ion gel with [PMMA]/[EMITFSI] = 3/7 along with those in EMITFSI (bulk). The experimental data have been fitted with the VTF equation<sup>24</sup> for diffusivity:

$$D = D_0 \exp[-B/(T - T_0)] \quad (5)$$

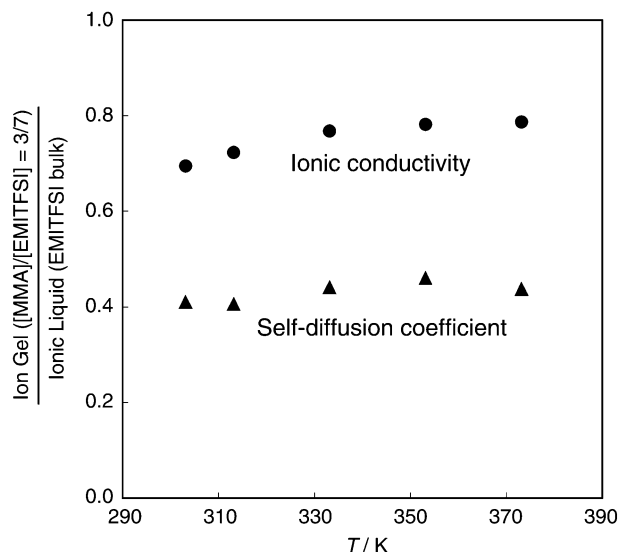
where  $D_0$  ( $\text{cm}^2\text{ s}^{-1}$ ),  $B$  (K), and  $T_0$  (K) are constants. The best-fit parameters of the self-diffusion coefficients are summarized in Table 3. The EMI cation diffuses faster than the TFSI anion in the ion gel, similar to that in the ionic liquids. Interestingly, the decrease in the ionic diffusivity in the ion gel is rather small, compared with that of bulk EMITFSI, although the ion gel behaves as a soft solid.

**Ion Transport Mechanism in Ion Gels.** A comparison of the temperature dependency of the  $\sigma$  and self-diffusion coefficient ( $D_{\text{EMI}} + D_{\text{TFSI}}$ ) for EMITFSI (bulk) and an ion gel ([PMMA]/[EMITFSI] = 3/7) shows that the gelation results in a decrease in both the ionic conductivity and self-diffusion coefficient, as is the case for conventional polymer-in-salt electrolytes. However, the ratio of the ionic conductivity ( $\sigma_{\text{ion gel}}/\sigma_{\text{ionic liquid}}$ ) for the ion gel ([PMMA]/[EMITFSI] = 3/7) and ionic liquid (EMITFSI bulk) at a particular temperature is significantly higher than that of the self-diffusion coefficient ( $D_{\text{ion gel}}/D_{\text{ionic liquid}}$ ) for a range of temperatures (Figure 7).

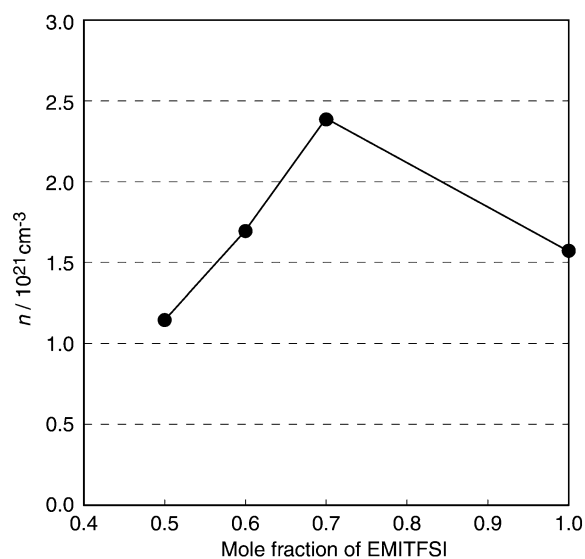
The Nernst–Einstein equation, which correlates ionic conductivity with diffusivity, is given by

$$\sigma = nq^2(D_{\text{cation}} + D_{\text{anion}})/kT \quad (6)$$

where  $n$  is the number of ion carriers,  $q$  is the electric charge on each ionic carrier,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. The larger value of the  $\sigma_{\text{ion gel}}/\sigma_{\text{ionic liquid}}$  compared to the  $D_{\text{ion gel}}/D_{\text{ionic liquid}}$  at a particular temperature in the ion gel, therefore, indicates an increase in the number of ion carriers when EMITFSI has been incorporated into network polymers by radical polymerization. The carrier number ( $n$ ),



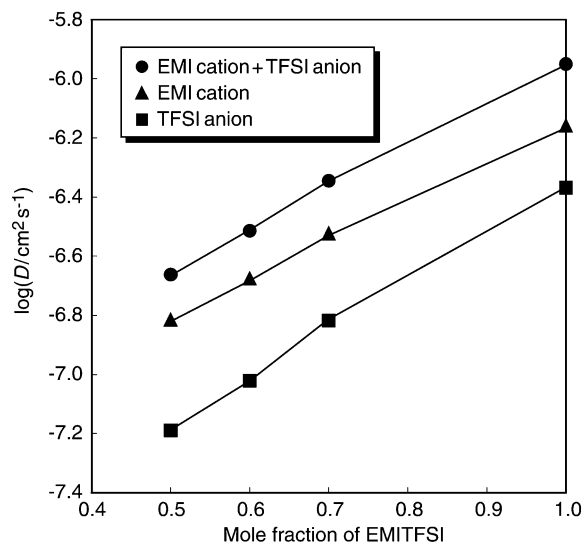
**Figure 7.** Ratio of ionic conductivity and self-diffusion coefficient for MMA network polymers with dissolved EMITFSI ([MMA]/[EMITFSI] = 3/7) to those for bulk EMITFSI at different temperatures.



**Figure 8.** Carrier numbers for EMITFSI dissolved in MMA network polymers as a function of the mole fraction of EMITFSI at 30 °C.

calculated from eq 6 for some ion gels with different compositions and bulk EMITFSI, has been plotted against the mole fraction of EMITFSI at 30 °C in Figure 8. It is worth mentioning that, due to the very small  $T_2$  values for some of the ion gels, the self-diffusion coefficients used for the calculation of  $n$  for all of the ion gels in Figure 8 were determined using a stimulated echo sequence (i.e.,  $90^\circ - \tau_1 - 90^\circ - \tau_2 - 90^\circ - \tau_1 - \text{Acquisition}$ ) to ensure precise results. Surprisingly, the  $n$  for the ion gel with [PMMA]/[HTFSI] = 3/7 is higher than that of bulk EMITFSI, though the volume fraction of EMITFSI decreases. The nonconductive species in the ionic liquids seem to interact with the polymer matrix, which might cause the generation of new carrier ions in the ion gels.

Since ionic liquids are highly concentrated electrolytes, an ion is surrounded by the oppositely charged ions and, therefore, may form ion clusters or aggregates. This is supported by FAB-MS results (vide supra), which is in agreement with the observation of Abdul-Sada et al.,<sup>20</sup> wherein they also evidenced



**Figure 9.** Self-diffusion coefficients for EMITFSI dissolved in MMA network polymers as a function of the mole fraction of EMITFSI at 30 °C.

molecular ion peaks for ion clusters for a number of imidazolium salts. Because of such ionic aggregation, not all of the diffusive species in ionic liquids contribute to the ionic conduction, since some associated species are neutral and do not carry electric charge. In fact, ion conduction in EMITFSI has been found to be contributed by 30–50% of the total ions in the bulk EMITFSI system.<sup>4</sup> If the polymer matrix can have some specific interaction with either the cation or anion, the tendency to form ion clusters or aggregates should decrease, resulting in the increase in the number of ion carriers in the ion gels. To clarify, we have plotted the self-diffusion coefficients for different [PMMA]/[EMITFSI] compositions as a function of EMITFSI concentration at 30 °C in Figure 9. It is apparent here that a decrease in the self-diffusion coefficient for the TFSI<sup>-</sup> anion is larger than that for the EMI<sup>+</sup> cation with increasing PMMA content in the ion gels. This is indicative of an interaction between the polymer matrix and the TFSI<sup>-</sup> anion in the ion gels. The cation transference number ( $D_{\text{cation}}/(D_{\text{cation}} + D_{\text{anion}})$ ) of the EMI<sup>+</sup> cation in the ion gels at 30 °C changed from 0.619 to 0.703 for the change in the mole fraction of EMITFSI from 1.0 to 0.5. The increase in the cation transference number with decreasing EMITFSI concentration corresponds to the relative increase in the cationic mobility, resulting from the interaction between the PMMA matrix and the TFSI<sup>-</sup> anion, which prohibits the formation of ion clusters or associates. This interaction leads to an increase in the  $n$  in the ion gels (Figure 8). It is a tradeoff between the generation of new ionic carriers by the specific interaction of the anion with PMMA and the decrease in total ionic species in the solid polymer matrix with increasing mole fraction of PMMA, which determines the overall carrier ion density for the ionic conduction in the ion gels.

## Conclusion

An ionic liquid has been successfully used with compatible polymers for the preparation of a novel series of polymer electrolytes. In situ radical polymerization of suitable vinyl monomers in an ionic liquid generates ion gels that exhibit high ionic conductivities at room temperature and possess sufficient mechanical strength, transparency, and flexibility, which are considered to be the basic requirements for polymer electrolytes.

The ion gels are completely compatible binary systems of a network polymer and an ionic liquid, but the liquid is nonvolatile and thermally stable, giving them distinct characteristics over conventional polymer gels. The specific interaction of the polymer matrix with the ionic component of the ionic liquid (the TFSI<sup>-</sup> anion in our case) fascinatingly aids to increase the total carrier number in the ion gel from the corresponding value in the ionic liquid. The elucidation of the mechanism of the compatibility of the polymer matrix with EMITFSI as well as other ionic liquids and investigation of the type of interaction between the polymer matrix and an ionic liquid by spectroscopic methods (e.g., IR, Raman) need to be further explored. We would, therefore, explore a systematic understanding of the physical processes involved and determination of the factors controlling ion transport behavior in these novel polymer electrolytes aiming at tuning the molecular engineering aspects of ion gels to have desirable properties.

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**Supporting Information Available:** DSC thermograms for MMA network polymers with dissolved EMITFSI in the first heating step from room temperature to 200 °C at a heating rate of 10 °C min<sup>-1</sup>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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