

# Thermal Analysis and Ionic Conductivity of Ionic Liquid Containing Composites with Different Crosslinkers

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**ABSTRACT:** Conductive polymer composites were synthesized by the polymerization of methylmethacrylate in the presence of ionic liquid solvents. These composites were characterized by attenuated total reflectance infrared spectroscopy, differential scanning calorimetry, and dynamic mechanical analysis. AC impedance measurements were performed on these composites as a function of ionic liquid type, ionic liquid concentration, crosslinker density, and molecular weight between crosslinks at various temperatures. 1-Butyl-3-methylimidazolium thiocyanate produced composites with a greater conductivity than 1-ethyl-3-methylimidazolium trifluoromethanesulfonimide, despite having a higher viscosity. The viscosity of the virgin ionic liquid could not be used to predict the order of ionic conductivity for composites made from these ionic liquids. The effect of crosslink density within the range of 0–0.6 mmol crosslinking agent per gram of monomer was studied. Composites with 25% ionic liquid (w/w) appeared to have an optimum

crosslink density for maximum ionic conductivity. In the range of crosslink densities studied, composites with greater ionic liquid concentration exhibited no significant effect of crosslink density on ionic conductivity. This could be due to the fact that the difference in crosslink density did not effectively change the  $T_g$  of these composites. The composite with the lowest theoretical molecular weight between crosslinks had the lowest ionic conductivity. This could be due to restriction of ion movement at this molecular weight between crosslinks. The composite with the highest molecular weight between crosslinks had comparable ionic conductivity to an uncrosslinked composite. This study showed that these materials have ionic conductivities practical for advanced energy applications over a wide range of morphologies with dimensional stability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2963–2970, 2009

**Key words:** composites; conducting polymers; crosslinking

## INTRODUCTION

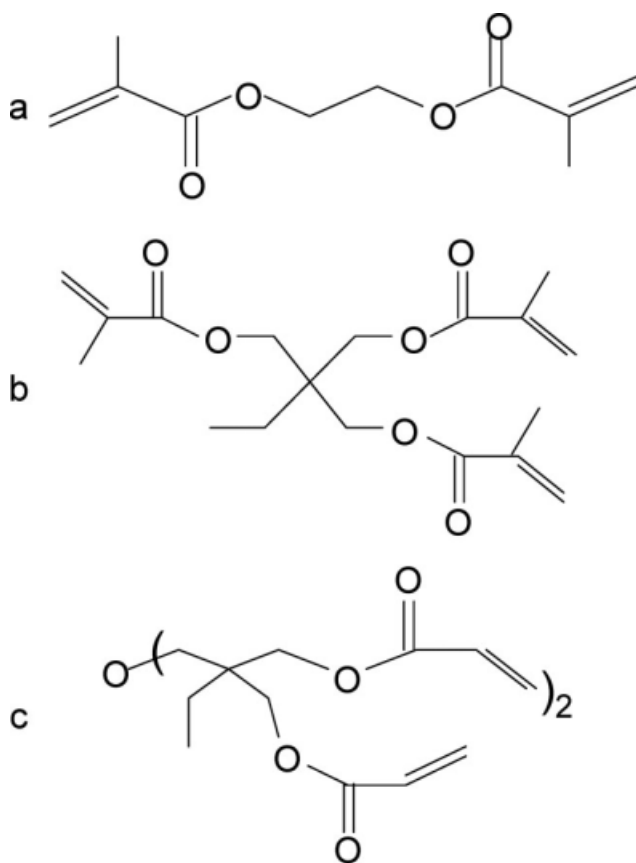
Research in conductive polymers and conductive polymer composites has important applications in advanced energy conversion. One approach has recently incorporated ionic liquids into a polymer network to generate a conductive material.<sup>1,2</sup> Ionic liquids are salts that are liquid (mainly at room temperature or below) and in molten form consist completely of ions. Initial excitement over ionic liquids was generated due to their environmental advantage over traditional organic solvents. The use of ionic liquids with negligible vapor pressure as a replacement for organic solvents promises to decrease the emission of organic solvents into the environment by eliminating evaporative loss of solvent.<sup>3–11</sup> The interest in ionic liquids extends beyond the environmental impact of these solvents.<sup>12–14</sup>

Watanabe and coworkers<sup>1</sup> reported a new class of both salt in polymer and polymer in salt electrolyte. This work yielded a conductive ion gel through incorporating 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) in poly(methylmethacrylate) (PMMA). These exciting results yielded materials with conductivities as high as  $10^{-2}$  S cm<sup>-1</sup>. The use of pure ionic liquids in lithium batteries, dye sensitized solar cells, and fuel cells is being explored.<sup>15–21</sup> When commercial applications require dimensional stability, amorphous linear polymers are problematic because they have a tendency to flow at high temperatures. Although semicrystalline polymers can lend dimensional stability, they tend to decrease conductivity due to diffusional limitations of the ions. It has been demonstrated in polyether/salt, polysiloxane/salt, and polyphosphazene/salt composites with low levels of crosslinkers that mechanical properties can be improved without losing significant conductivity.<sup>22–25</sup>

Additional work is needed to explore the physical properties of polymer composites with ionic liquids to incorporate these types of materials into advanced energy sources. In this work, we report the effect of crosslinker density, molecular weight between crosslinks, ionic liquid type, and ionic liquid concentration

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**Figure 1** Structure of the three crosslinking agents used in this study. a. ethylene glycol dimethacrylate b. trimethylolpropane trimethacrylate c. di(trimethylolpropane) tetraacrylate.

on the ionic conductivity of these composites. Once above the molecular weight of entanglements, the properties of the polymer–salt interactions do not vary much. However, side chain segmental motions can effect these types of interactions below a certain molecular weight.<sup>26</sup> Understanding the effect of the crosslinker in these systems is important because it has been demonstrated that segmental motion of the polymer chains has an influence on ionic conductivity.<sup>27,28</sup> Crosslinking can have a large effect on the mechanical properties of the composite and may improve the thermal and chemical resistance of these materials.

The effect of crosslinking on polymer properties is difficult to predict due to the fact that other properties can change in the process. For example, when the effect of crosslink density on the gas permeability of rubber was studied by changing the sulfur content, the differences in gas permeability results could have also been explained by the differences in glass transition temperature due to the introduction of more polar sulfur groups.<sup>29</sup> The crosslinkers in this study as seen in Figure 1 have therefore been

chosen to minimize the effect of the difference in chemical composition that could arise from introducing crosslinkers to the composite. This study provides the first insight on the role of crosslinking on the ionic conductivity and thermal properties in this class of materials.

The type of ionic liquid is important for many applications of the conductive composite material. For example, a polymer electrolyte layer for use in lithium batteries must support lithium ion solubility. We have found that the lithium salts (lithium perchlorate and lithium trifluoromethanesulfonimide) commonly found in batteries are several orders of magnitude more soluble in 1-butyl-3-methylimidazolium thiocyanate than in EMITFSI.<sup>30</sup> Therefore, we found it of practical importance to report on the ionic conductivity of these composites containing the 1-butyl-3-methylimidazolium filler.

## EXPERIMENTAL

### Reagents and composite synthesis

Methyl methacrylate (MMA), ethylene glycol dimethacrylate [Fig. 1(a), EGDMA], trimethylolpropane trimethacrylate [Fig. 1(b), TMPTMA], di(trimethylolpropane) tetraacrylate [Fig. 1(c), DTMPTA], 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF<sub>6</sub>), 1-butyl-3-methylimidazolium acetate (bmimACET) and 1-butyl-3-methylimidazolium thiocyanate (bmimSCN) were used as received from Sigma-Aldrich. Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. EMITFSI was synthesized in as described in the literature.<sup>1,31</sup> Composites were synthesized by the free-radical polymerization of methyl methacrylate using 2% AIBN dissolved in the monomer as initiator. AIBN was first weighed out, followed by the addition of the monomer and ionic liquid by syringe. Crosslinker was added by 100  $\mu$ L micropipette. The samples were sonicated to eliminate bubbles and argon gas was then bubbled through the reaction mixture for 20 minutes to displace dissolved oxygen. The solution was then added to the appropriate mold depending on the analytical technique it was intended for and was kept at 80°C for 24 hours in a Tenney Jr. environmental chamber to ensure completion of the polymerization reaction.

### Fourier transform infrared spectroscopy

Attenuated total reflectance infrared spectroscopy (FTIR-ATR) was used to determine the conversion of acrylate groups. The measurements were performed on a Thermo Electron Corporation Nicolet Avater 370 DTGS with a Pike Technologies Miracle ATR accessory equipped with a TempPRO Isothermal

Temperature Control Accessory. The disappearance of the olefin peak at  $810\text{ cm}^{-1}$  was monitored.<sup>32</sup>

### Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC Q20 under a nitrogen atmosphere. The samples were tightly sealed in Al pans. The measurements were conducted with the samples heated to  $150^\circ\text{C}$  followed by cooling to  $-140^\circ\text{C}$ , and then heating again up to  $150^\circ\text{C}$  at a cooling and heating rate of  $10^\circ\text{C min}^{-1}$ . The glass transition temperature determined as the midpoint temperature of the heat capacity change were determined from the DSC thermograms during the second heat of the measurement.

### Dynamic mechanical analysis

For dynamic mechanical analysis (DMA) tests, cylindrical specimens were prepared by filling a stainless steel mold ( $2\text{ mm} \times 5\text{ mm}$ ) with unpolymerized material, taking care to minimize entrapped air. The lower surface of the mold was overlaid with a glass slide covered with a Mylar sheet to avoid adhesion with the unpolymerized material. The completed assembly was placed in a Tenney Junior environmental chamber preheated at  $80^\circ\text{C}$ . Specimen were allowed to react for 24 hours to ensure completion of the reaction. Then, the mold was dismantled and the composite was carefully removed by unscrewing the stainless steel mold. The specimen were stored for 7 days at room temperature before testing. Three specimen were prepared for each composite. DMA tests were performed on a Diamond dynamic mechanical analyzer (Perkin Elmer) using compression plates. Measurements were made at a frequency of 1 Hz.

Due to the fact that these composites are highly filled with ionic liquids, the solvent swelling approach for crosslink density was not used. Instead, it was estimated from mechanical properties. The elastic modulus was determined by DMA and was inserted in the following equation:  $\nu_e = E' / 3RT$  where  $E'$  is the elastic modulus in the rubbery plateau,  $R$  is the gas constant and  $T$  is the temperature where  $E'$  was reported ( $25^\circ\text{C}$ ) in this experiment.<sup>33</sup> This model takes both crosslinking and chain entanglements into account, thereby usually resulting in a value that is higher than the one obtained by swelling measurements.<sup>34</sup>

### AC impedance measurements

The ionic conductivity ( $\sigma$ ) was measured by AC impedance spectroscopy in the temperature range of  $25\text{--}75^\circ\text{C}$ . Two platinum wires with a 1 mm diameter

were each sealed in glass and polished to a mirror finish. The platinum disk electrodes were placed in  $2.5\text{ cm} \times 2.5\text{ cm} \times 1.2\text{ cm}$  Teflon blocks held together with screws. The sample was cut from the bulk material and placed between the Teflon blocks in a silicone spacer made from 0.156 cm thick silicone sheet. A third platinum wire was introduced from the side of the apparatus before the screws were tightened to serve as the reference electrode. The sample cell constant was standardized by taking impedance measurements of 1.00, 0.100, and 0.0100 M KCl (aq) solutions of known conductivity and found to be  $3.80\text{ cm}^{-1}$ . The measurements were taken on a CH Instruments 601B Electrochemical Analyzer over the frequency range of 1 Hz–1 MHz with an AC excitation of 5 mV. Conductivity measurements were performed in a Tenney Junior environmental chamber. Samples were heated to  $75^\circ\text{C}$  and allowed to thermally equilibrate for 20 minutes. An impedance spectrum was taken at that temperature, then the temperature was lowered by  $10^\circ\text{C}$ , and the sample was allowed to thermally equilibrate for 20 minutes before the next scan was taken. Measurements were made at 75, 65, 55, 45, 35, and  $25^\circ\text{C}$ .  $R_{\text{bulk}}$  was determined from the Nyquist plot and was divided into the cell constant to calculate ionic conductivity.

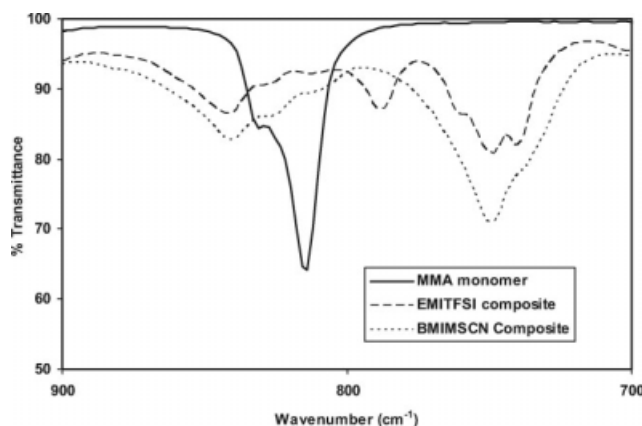
### Viscosity measurements

A Ubbelohde 10 mL glass viscometer was standardized with distilled water. All liquids were at  $20^\circ\text{C}$  and atmospheric pressure. Each liquid (10 mL) was drawn into the tube and timed with a stopwatch. Each liquid was tested three times, and the average run time was used to calculate the viscosity.

## RESULTS AND DISCUSSION

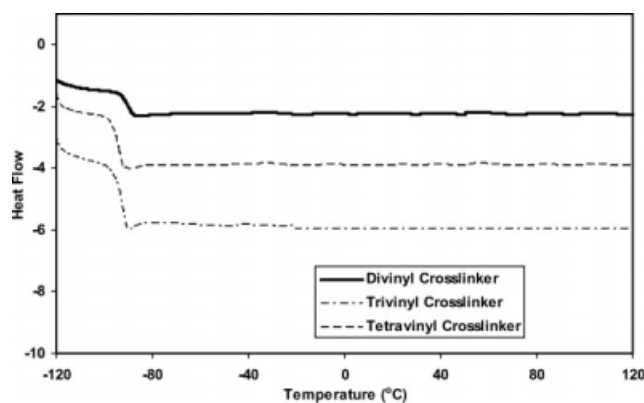
FTIR-ATR was used to determine the conversion of the acrylate monomer alkene functional groups. The carbon-carbon double bond of the acrylate monomer was monitored at approximately  $810\text{ cm}^{-1}$  for all of the composites. Figure 2 shows the spectra obtained for typical composites that contained either EMITFSI or BMIMSCN ionic liquids. As evidenced by the disappearance of the peak at  $810\text{ cm}^{-1}$  the infrared spectra indicate that the conversion of alkene functional group was nearly 100%. We found this to be the case in all of the samples that were prepared, but included only two spectra for clarity in the figure.

Figure 3 shows the DSC thermograms of a representative series of composites that were synthesized with different molecular weight between crosslinks. This was accomplished by varying the identity of the crosslink agent.<sup>35</sup> Divinyl, trivinyl, and tetravinyl



**Figure 2** FTIR-ATR spectrum of the methyl methacrylate monomer. The conversion of the monomer was followed by observing the disappearance of the alkene peak at  $810\text{ cm}^{-1}$ . All of the composites containing either EMITFSI or BMIMSCN were measured. The disappearance of this peak was observed in all of the composites. Representative spectra of each type of composite are shown here.

crosslinking agents were used while keeping the same total number of crosslinking sites the same. For example, when the divinyl crosslinking agent in the polymerization has a concentration of  $1.00\text{ M}$ , the trivinyl crosslinking agent would be used with a concentration of  $0.667\text{ M}$  and the tetravinyl crosslinking agent would be used at a concentration of  $0.50\text{ M}$ . All three polymerizations would contain crosslinkable double bonds at a concentration of  $2.00\text{ M}$ . This specific series of composites represent the data from the samples prepared with 25 wt % MMA and 75 wt % BMIMSCN with 0.2 mmol of the divinyl crosslinking agent/g MMA [Fig. 1(a)], 0.13 mmol of the trivinyl crosslinking agent/g MMA [Fig. 1(b)] and 0.1 mmol of the tetravinyl crosslinking agent/g MMA [Fig. 1(c)]. The glass transition temperatures were measured and reported in Table I. The  $T_g$  values measured for each series of crosslink density and crosslinker type was narrowly distributed, suggesting that the crosslink concentration and the crosslinker identity did not have a significant impact on the  $T_g$  of the prepared composites.

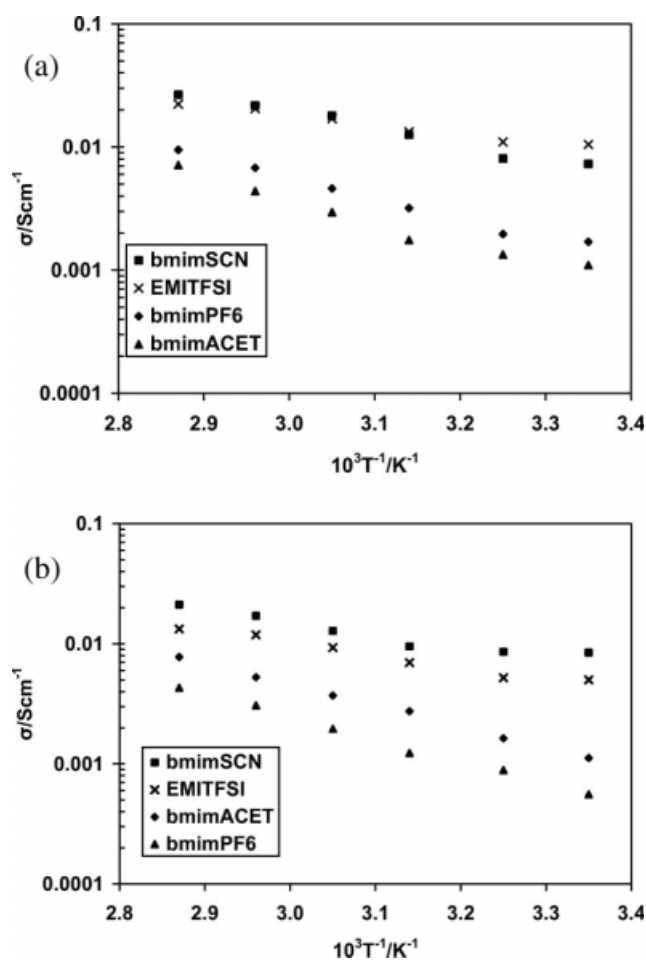


**Figure 3** Differential scanning calorimetry thermograms of a representative series of composites that were synthesized with different molecular weight between crosslinks. This specific series of composites represent the data from the samples prepared with 25 wt % MMA and 75 wt % BMIMSCN with 0.2 mmol of the divinyl crosslinking agent/g MMA [Fig. 1(a)], 0.13 mmol of the trivinyl crosslinking agent/g MMA [Fig. 1(b)] and 0.1 mmol of the tetravinyl crosslinking agent/g MMA [Fig. 1(c)].

DMA of the composites was performed at 1 Hz. The value of the elastic modulus ( $E'$ ) is reported in Table I. The crosslink density ( $\nu_e$ ) was determined from this measurement as described in the experimental section. The measurements are reported for three of the series of composites that were fabricated. It has been established that decreasing the crosslink concentration typically decreases the crosslink density in acrylic polymer composites.<sup>36–38</sup> In one specific study, the amount of water added (20–65 vol %) with a mixture of crosslinked polyacrylates exhibited the expected, but non-ideal decrease in crosslink density. This was explained by ineffective crosslinks due to cyclization reactions during gel formation at high diluent concentrations. This type of behavior was similarly noticed in these systems where the acrylate polymer systems were polymerized in the presence of a high concentration of ionic liquid. As seen in Table I, as the concentration of the divinyl crosslinker [Fig. 1(a)] was increased from 0.2 mmol/g of MMA to 0.6 mmol/g MMA in

**TABLE I**  
Elastic Modulus ( $E'$ ), Crosslink Density ( $\nu_e$ ) and  $T_g$  for Three Series of Composites Differing in Crosslink Density or Molecular Weight Between Crosslinks

Sample	$E'$ (Pa) @ 1 Hz; 25 °C	$\nu_e \times 10^3$ (mol/cm <sup>3</sup> )	$T_g$ (°C)
25EMI/75MMA: 0.6 mmol divinyl/g MMA	$5.3 \times 10^7$	7.1	–21
25EMI/75MMA: 0.4 mmol divinyl/g MMA	$2.8 \times 10^7$	3.7	–22
25EMI/75MMA: 0.2 mmol divinyl/g MMA	$1.1 \times 10^7$	1.5	–19
25EMI/75MMA: 0.13 mmol trivinyl/g MMA	$4.2 \times 10^7$	5.6	–20
25EMI/75MMA: 0.10 mmol tetravinyl/g MMA	$4.5 \times 10^7$	6.0	–23
75BMIMSCN/25MMA: 0.2 mmol divinyl/g MMA	$2.7 \times 10^6$	0.4	–89
75BMIMSCN/25MMA: 0.13 mmol trivinyl/g MMA	$3.9 \times 10^6$	0.5	–94
75BMIMSCN/25MMA: 0.10 mmol tetravinyl/g MMA	$4.5 \times 10^6$	0.6	–92



**Figure 4** a. Arrhenius plots of ionic conductivity for pure ionic liquids. b. Arrhenius plots of ionic conductivity for composites with 75% ionic liquid and PMMA for different ionic liquids.

the composites with 25 wt % EMITFSI and 75 wt % MMA, the elastic modulus increased in the system from  $1.1 \times 10^7$  Pa to  $5.3 \times 10^7$  Pa in the rubbery regime of the composite. This resulted in a corresponding increase in calculated crosslink density from  $1.5 \text{ mol/cm}^3$  for the lowest concentration of crosslinker to  $7.1 \text{ mol/cm}^3$  for the highest concentration of crosslinker.

Two other series looked at the effect of decreasing molecular weight between crosslinks. The first series consisted of composites containing 25 wt % EMITFSI and 75 wt % of MMA with a series of divinyl [Fig. 1(a)], trivinyl [Fig. 1(b)] and tetravinyl [Fig. 1(c)] crosslinkers that should have theoretically maintained a constant crosslink concentration. Interestingly, the calculated crosslink density increased slightly with what should have been decreasing molecular weights between crosslinks due to the measured increase of elastic modulus. This trend was also observed for the series of composites prepared with 75 wt % of BMIMSCN and 25 wt % MMA with a series of divinyl [Fig. 1(a)], trivinyl [Fig. 1(b)] and tetravinyl [Fig. 1(c)]

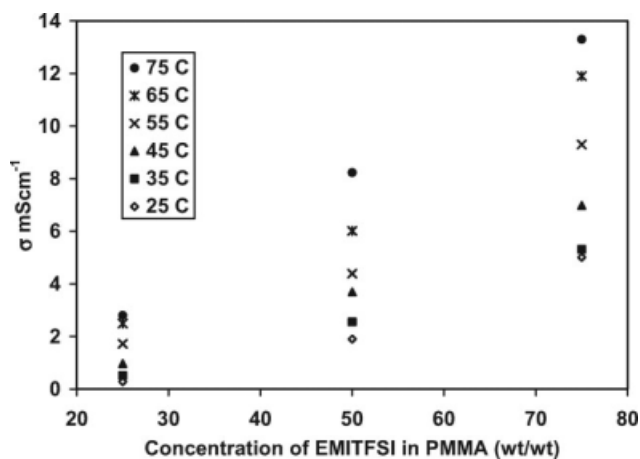
crosslinkers that should have theoretically maintained a constant crosslink concentration. These differences in measured crosslink density could be due to the fact that this calculation comes from a model that does not differentiate between different degrees of chain entanglements in each system. However, the effective crosslink density is inversely proportional to the molecular weight between crosslinks as defined by the following equation:  $v_e = \rho_p/M_c$  where  $\rho_p$  is the polymer film density and  $M_c$  is the molecular weight between crosslinks.<sup>39</sup> Therefore, since each of the composites in these two series have approximately the same density, the calculated increase in crosslink density is likely due to a decrease in the molecular weight between crosslinks as the number of crosslinking sites per crosslinker increases.

To determine what effect the crosslink density and molecular weight between crosslinks has on ionic conductivity in this type of composite system, we measured the ionic conductivity of several series of ionic liquid containing composites. As a control, the conductivity of the pure ionic liquid was measured between 25 and 75°C. Figure 4(a) shows the Arrhenius plot of the conductivity of each pure ionic liquid as a function of temperature. Although EMITFSI is widely used as an ionic liquid with relatively high conductivity, it was found that bmimSCN had approximately the same conductivity as EMITFSI from 55 to 75°C. The bmimPF6 and bmim acetate were less conductive than EMITFSI and bmimSCN by about one order of magnitude. Table II describes the room temperature viscosity differences between the various ionic liquids. Ionic conductivity of an ionic liquid typically correlates to the viscosity of the liquid. This trend was generally observed for the ionic liquids, especially at room temperature. The bmimACET, which had the highest viscosity, had the lowest ionic conductivity.

The temperature dependent conductivity of composites as a function of ionic liquid type in the composite was determined. Figure 4(b) shows the conductivity of PMMA with different ionic liquids, 75% by weight ionic liquid, as a function of temperature. Arrhenius plots are useful to show the temperature dependence of conductivity in pure ionic liquids. Arrhenius plots were used to depict the

**TABLE II**  
Viscosity and Ionic Conductivity of the Pure Ionic Liquids Used in Making the Polymer Composites

Ionic liquid	Viscosity at RT (Pa s)	Ionic conductivity at RT ( $\text{S cm}^{-1}$ )
EMITFSI	$1.95 \times 10^{-2}$	$1.1 \times 10^{-2}$
bmimSCN	$5.0 \times 10^{-2}$	$7.3 \times 10^{-3}$
bmim PF <sub>6</sub>	$1.6 \times 10^{-1}$	$1.7 \times 10^{-3}$
bmimACET	$3.7 \times 10^{-1}$	$1.1 \times 10^{-3}$



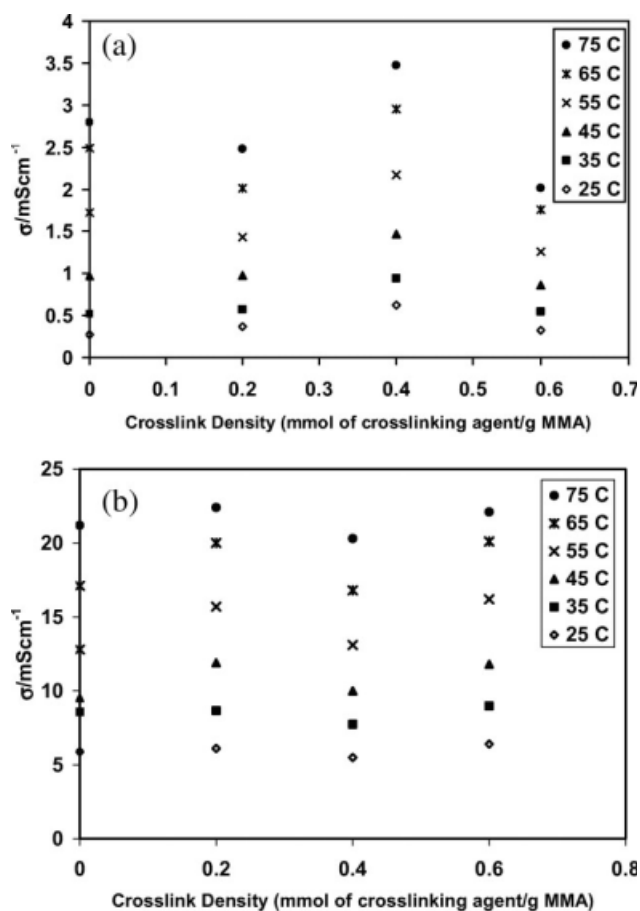
**Figure 5** Ionic conductivity as a function of ionic liquid concentration for composites with 25–75 wt % EMITFSI in PMMA from 25 to 75°C.

temperature dependence on conductivity in these samples to determine the succession of conductivity of the ionic liquid in the polymer composites. The conductivity of these composites follows a Vogel Tammann Fulcher (VTF) relationship for ionic conductivity in this type of polymer electrolyte system.<sup>1</sup> The use of an Arrhenius plot for this purpose will not change the succession of ionic conductivity for ionic liquid type in these composites. The bmimSCN composite was slightly more conductive than the EMITFSI composite over the range of all of the temperatures measured. This is different than the virgin ionic liquids where EMITFSI is more conductive at 25 and 35°C and the two ionic liquids have comparable ionic conductivities from 45 to 75°C. The more viscous composites with bmimACET and bmimPF<sub>6</sub> were the least conductive composites. For these samples, even though the pure bmimACET has a lower ionic conductivity than bmimPF<sub>6</sub>, the composite containing 75% bmim acetate ionic liquid had a higher ionic conductivity. These studies suggest that the order of ionic conductivity of virgin ionic liquids does not necessarily translate to the order of ionic conductivity for composites made from these ionic liquids. The degree of interaction of the cation and anion with the polymer backbone affects the relative mobility or transference of the ion in the composite. This in turn affects the overall ionic conductivity of the system.

The effect of ionic liquid concentration on ionic conductivity was determined. Initial impedance measurements determined the effect on conductivity of ionic liquid concentration in the composite. As expected, increasing ionic liquid content increased the conductivity of all the ionic liquid types that were added to the composite. Figure 5 shows the effect of ionic liquid concentration of EMITFSI on ionic conductivity at a range of temperatures. The

composite with a higher weight fraction of ionic liquid had a higher ionic conductivity, whereas the composite with the lowest weight fraction of ionic liquid had the lowest ionic conductivity. This trend was the same for all four ionic liquids studied.

The effect of crosslink density was explored as the concentration of crosslinker has a significant effect on the mechanical properties of the composite. The amount of crosslinker added ranged from 0 to 0.6 mmol per gram of MMA monomer with composites that were composed of 25–75 weight percent of the EMITFSI ionic liquid. The effect of crosslink density on a sample that contained 25 weight percent ionic liquid was more pronounced. Figure 6(a) shows the results of these experiments with 25 weight percent ionic liquid. Figure 6(a) shows the data plotted as a function of crosslink concentration for each sample from 25 to 75°C. The sample with 0.4 mmol of EGDMA per gram of MMA exhibited the highest conductivity compared with a sample with either no crosslinker present, 0.2 mmol of EGDMA per gram

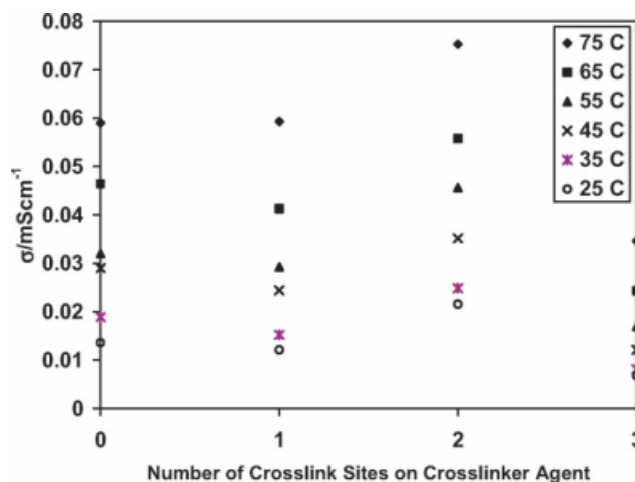


**Figure 6** a. Ionic conductivity as a function of crosslink density of a composite containing 25% EMITFSI in PMMA at different temperatures. b. Ionic conductivity as a function of crosslink density of a composite containing 75% BMIMSCN in PMMA at different temperatures.

of MMA or 0.6 mmol of EGDMA per gram of MMA. It is not surprising that the samples with no crosslinker and very low crosslinking density have comparable ionic conductivities as the crosslinker would remain quite flexible at 0.2 mmol of EGDMA per gram of MMA. The addition of the low level of crosslinking agent did not change the morphology of the material. Both samples were gel like in consistency. It was surprising to see the trend of enhanced conductivity with 0.4 mmol of EGDMA per gram of MMA. The subsequent decrease in conductivity would be expected at 0.6 mmol of EGDMA per gram of MMA. The segmental chain motion would begin to decrease as the samples become more glass-like in morphology.

It appears that there is not a significant trend of crosslink density on ionic conductivity in the range of densities tested with 50–75 wt % of the BMIM ionic liquid in the composite. These results were unexpected because as the crosslink concentration increased, the material became more glass-like in character. This property would likely decrease ion mobility. However, as seen in Figure 6(b), the sample with 0.2 mmol of EGDMA per gram of MMA or 0.6 mmol of EGDMA per gram of MMA had the highest ionic conductivity values. The samples with no crosslinking agent or 0.4 mmol of EGDMA per gram of MMA typically had a slightly lower ionic conductivity value than the other two sets of samples. Although the materials were not as gel-like in consistency at the higher range of crosslink density, the composite was still highly plasticized with the ionic liquid. As a result, the restrictions of segmental motion must be insignificant for composites with these compositions.

The final variable explored in this study monitored the effect of the molecular weight between cross-links on ionic conductivity as a function of temperature. This was accomplished by varying the identity of the crosslink agent.<sup>35</sup> Divinyl, trivinyl and tetravinyl crosslinking agents were used while keeping the same total number of crosslinking sites the same. For example, when the divinyl crosslinking agent in the polymerization has a concentration of 1.00 M, the trivinyl crosslinking agent would be used with a concentration of 0.667 M and the tetravinyl crosslinking agent would be used at a concentration of 0.50 M. All three polymerizations would contain crosslinkable double bonds at a concentration of 2.00 M. This specific series of composites represent the data from the samples prepared with 25 wt % MMA and 75 wt % BMIMSCN with 0.2 mmol of the divinyl crosslinking agent/g MMA [Fig. 1(a)], 0.13 mmol of the trivinyl crosslinking agent/g MMA [Fig. 1(b)] and 0.1 mmol of the tetravinyl crosslinking agent/g MMA [Fig. 1(c)]. Figure 7 shows the effect of molecular weight between cross-



**Figure 7** Ionic Conductivity as a function of crosslink sites per crosslink agent. Control composites with no crosslinking agent had 0 crosslink sites. Composites that were made with divinyl, trivinyl and tetravinyl crosslinking agents respectively had 1, 2, and 3 crosslinking sites. This specific series of composites represent the data from the samples prepared with 25 wt % MMA and 75 wt % BMIMSCN with 0.2 mmol of the divinyl crosslinking agent/g MMA [Fig. 1(a)], 0.13 mmol of the trivinyl crosslinking agent/g MMA [Fig. 1(b)] and 0.1 mmol of the tetravinyl crosslinking agent/g MMA [Fig. 1(c)]. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

links on ionic conductivity of the composite as a function crosslinking sites on the crosslinking agent over a range of temperatures. The number of crosslinking sites in a system with no crosslinking agent is defined as zero. The number of crosslinking sites in the divinyl, trivinyl, and tetravinyl crosslinking agents were defined respectively as 1, 2, and 3. As the number of crosslinkable bonds increased on the crosslink agent, the molecular weight between crosslinks decreases. As the molecular weight decreases between crosslink units, the segmental motion of the polymer chain should become more restricted. However, a decrease in corresponding ionic conductivity was not observed for the samples that included no crosslinking agent, a divinyl crosslinking agent and a trivinyl crosslinking agent. In fact, a slight increase in ionic conductivity was measured for the trivinyl crosslinking agent. Only when the tetravinyl crosslinking agent was used was a relatively significant decrease in the ionic conductivity observed.

## CONCLUSIONS

Conductive polymer composites were synthesized by the polymerization of methylmethacrylate in the presence of ionic liquid solvents. AC impedance measurements were performed on these composites as a function of ionic liquid type, ionic liquid concentration, crosslinker type, crosslinker density and

molecular weight between crosslinks. As expected, conductivity increased with temperature and percent ionic liquid contained in the composite. 1-butyl-3-methylimidazolium thiocyanate produced composites with a greater conductivity than 1-ethyl-3-methylimidazolium trifluoromethanesulfonimide. The viscosity of the virgin ionic liquid could not be used to predict the order of ionic conductivity for composites made from these ionic liquids. Crosslinker density and the molecular weight between crosslinks had a limited effect on conductivity, thereby producing conductive materials with a wide range of mechanical properties. For a series of composites with increasing crosslinker concentration, there was an increase in the elastic modulus of the material. However, the ionic conductivities for all the composites within the series ranged within one order of magnitude. This is likely due to the fact that the glass transition temperatures of the materials were not effectively different. It appeared that there may be an optimum crosslink density for maximum ionic conductivity for composites with 25 wt % of ionic liquid. However, it was not clear why this trend was observed based on the thermomechanical characterization of these composites. The composite with the lowest theoretical molecular weight between crosslinks had the lowest ionic conductivity. This could be due to restriction of ion movement at this molecular weight between crosslinks. The composite with the highest molecular weight between crosslinks had comparable ionic conductivity to an uncrosslinked composite. Materials with a wide range of mechanical properties were produced with ionic conductivities suitable for use in advanced energy conversion applications.

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