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# Anion exchanged polymerized ionic liquids: High free volume single ion conductors

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#### ABSTRACT

In this study, we investigate the isolated effect of anion type on the chemical, thermal, and conductive properties of imidazolium-based polymerized ionic liquids (PILs). PILs with various anions at constant average chain length were prepared by ion exchange with a water-soluble PIL precursor, (poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium bromide) (poly(MEBIm-Br)). NMR, IR, and elemental analysis confirm that anion exchange of ploy(MEBIm-Br) with bis(trifluoromethanesulfonyl) imide (TFSI), tetrafluoroborate (BF<sub>4</sub>), trifluoromethanesulfonate (Tf), and hexafluorophosphate (PF<sub>6</sub>) in water resulted in nearly fully exchanged PILs. As a function of anion type, the glass transition temperature plays a dominant role, but not the sole role in determining ion conductivity. Other factors affecting ionic conductivity include the size and symmetry of the anion and dissociation energy of the ion pair. Both the Vogel-Fulcher-Tammann (VFT) and Williams-Landel-Ferry (WLF) equations were employed to investigate the temperature dependent ionic conductivities. The  $C_2^{f}$  (9.03) and  $C_2^{f}$  (168 K) values obtained from the WLF regression of these PILs greatly deviate from the classical WLF values originally obtained from the mechanical relaxation of uncharged polymers ( $C_1^g = 17.44$ ,  $C_2^g = 51.6$  K) and the WLF values obtained from the conductive properties of other polymer electrolytes. This suggests that the fractional free volume ( $f(T_g) = B/(2.303C_1^g)$ ) and Vogel temperature ( $T_0 = T_g - C_2^g$ ) are strong functions of ion concentration, where high free volume allows for ion mobility at temperatures farther below the glass transition temperature of the polymer.

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#### 1. Introduction

Polymerized ionic liquids (PILs), or polymers synthesized by polymerizing ionic liquid monomers, have attracted recent attention and their application as polymer electrolytes, sorbents, dispersing agents, and nanomaterials has recently been reviewed [1,2]. Overall, the interests in PILs are many fold, but in general, PILs are of interest due to the unique properties of ionic liquids (ILs) (e.g., negligible vapor pressure, nonflammability, high ionic conductivity, a wide electrochemical window, and good chemical and thermal stability) and the broad range of new polymer electrolytes that can be realized with a highly tunable and facile synthesis [3–7]. Unlike ionic liquid (IL)/polymer mixtures, the IL moiety is covalently attached to the macromolecule in a PIL (see Scheme 1). Therefore, PILs differ in that the organic cation or anion is restricted in mobility compared to its more mobile counterion (i.e., single ion conductor), unlike ILs or IL/polymer mixtures where both the cation and anion are mobile. The former alleviates shortcomings of liquid electrolytes in electrochemical devices (e.g., leakage, stability), but usually results in lower ionic conductivity when compared to the latter. Although PILs are of great interest as solid-state polymer electrolytes, surprisingly, there are relatively few reports on the ionic conductivity of PILs [6–12]. It is evident based on these few investigations that a number of factors can impact ionic conductivity in PILs, such as polymer chemistry, glass transition temperature, molecular weight, and polymer morphology. However, there is still a limited fundamental understanding of ion transport in PILs.

One method for increasing the ionic conductivity in a PIL is to replace the mobile ion with another via ion exchange. Chen et al. [6] observed enhancements in ionic conductivity in a PIL when the tetrafluoroborate ( $BF_4$ ) anion was replaced with the bis(tri-fluoromethanesulfonyl) imide (TFSI) anion. This was the result of a significant reduction in the glass transition temperature of the polymer, which facilitated higher segmental motion of the polymer and therefore higher anion mobility. This is unique to PILs, where these anion differences typically do not have the same effect in ILs. Therefore, with a wide variety of anions available, understanding ion conduction as a function of anion type in PILs is of great interest.





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Scheme 1. Synthesis of anion exchanged PILs (poly(MEBIm-X)). (1) 2-bromoethanol, triethylamine, dichloromethane, room temperature, 18 h. (2) 1-butylimidazole, 40 °C, 24 h. (3) AIBN, DMF, 60 °C, 6 h. (4) salt, DI water, room temperature, 48 h.

However, there are only a few investigations that have focused on the effects of anion type on ionic conductivity in PILs.

In several previous studies [9,13–15], PILs with different anions were prepared by anion exchange of the IL monomer followed by polymerization under different reaction conditions. This resulted in PILs with a variety of molecular weights or different average chain lengths, which also can affect the glass transition temperature and ionic conductivity. Therefore, anion type and molecular weight were convoluted parameters in these studies. These two parameters can be deconvoluted if the PILs undergo anion exchange at the polymer stage. Only a few investigations have produced PILs with this method [16]. However, these investigations did not explore the effect of anion type on ion conduction.

The purpose of this study was to synthesize PILs with different anions at constant average polymer chain length and investigate the effect of anion type on ion conductivity as well as other properties related with these anion exchanged single ion conductors. The effectiveness of exchanging anions at the polymer stage in PILs is largely dependant on the anion type, PIL, and the experimental procedure. In order to achieve a high purity exchange, solubility of the PIL before and after exchange in the solvents used can be a critical issue. In general, imidazolium-based ILs and PILs neutralized with halide anions are water soluble, while these same ILs and PILs neutralized with fluorine-containing anions are water insoluble [17]. We utilize this difference in solubilities to achieve high purity anion exchanged PILs.

Specifically, in this study, an imidazolium-based IL monomer, 1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium bromide (MEBIm-Br), was synthesized and subsequently polymerized using conventional free radical polymerization. This PIL precursor, poly (MEBIm-Br), was subsequently exchanged with other fluoridecontaining anions, TFSI, BF<sub>4</sub>, trifluoromethanesulfonate (Tf), and hexafluorophosphate  $(PF_6)$ , in water, where the resulting PIL precipitated out of solution. For comparison, the same procedure was also performed on the IL monomer. The chemistry, molecular weight, glass transition temperature, thermal decomposition temperature, and ion conductivity were characterized in all of these PILs, where anion type was the sole variable. The effect of temperature on ion conductivity was explored with the use of regressions to both the VFT and WLF models. Interestingly, the WLF parameters ( $C_1$ and  $C_2$ ) for PILs are uniquely different than neutral polymers and other salt doped polymer electrolytes (e.g., Li salt-poly(ethylene oxide) (PEO)), which suggest that fractional free volume at the glass transition temperature and Vogel temperature are significantly different in single ion conductor PILs.

#### 2. Experimental

#### 2.1. Materials

2-Bromoethanol (95%), methacryloyl chloride (97%, stabilized with 200 ppm monomethyl ether hydroquinone (MEHQ)), triethylamine ( $\geq$ 99.5%), dichloromethane (ACS reagent,  $\geq$ 99.5%, contains 50 ppm amylene stabilizer), magnesium sulfate (anhydrous, ReagentPlus®, 99%), 1-butylimidazole (98%), 2,6-di-tert-butyl-4methylphenol (99%), diethyl ether (anhydrous,  $\geq$ 99.7%, contains 1 ppm BHT inhibitor), azobisisobutyronitrile (AIBN, 97%), acetone (HPLC grade,  $\geq$  99.9%), sodium tetrafluoroborate (NaBF<sub>4</sub>, 98%), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, 97%), lithium trifluoromethanesulfonate (LiTf, 96%), lithium hexafluorophosphate (LiPF<sub>6</sub>, 98%), lithium bromide (LiBr, 99.995% metals basis), acetonitrile (anhydrous, 99.8%), N,N-dimethylformamide (DMF, ACS reagent,  $\geq$  99.8% and HPLC grade,  $\geq$  99.9%), and methyl sulfoxide- $d_6$  (DMSO- $d_6$ , 99.9%, contains 0.03% v/v TMS) were purchased from Aldrich. Ultrapure deionized (DI) water (resistivity ~ 16 M $\Omega$  cm) was used as appropriate.

#### 2.2. Synthesis of ionic liquid (IL) monomer

The synthesis method for the imidazolium-containing monomer, 1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium bromide (MEBIm—Br), is shown in Scheme 1. A typical reaction included adding a mixture of 39.37 g (0.315 mol) of 2-bromoethanol and 50 mL of dichloromethane to a three-neck 500 mL flask in an ice bath. Under nitrogen, a mixture of 33.39 g (0.33 mol) of triethylamine and 50 mL of dichloromethane was slowly added to the flask, followed by a slow addition of a mixture of 31.36 g (0.3 mol) of methacryloyl chloride and 50 mL of dichloromethane using an addition funnel. The reaction mixture was stirred at room temperature for 18 h and then filtered. The liquid filtrate was washed with 300 mL DI water four times. The water layer was removed using a separation funnel and the residual water in the organic layer was further removed with anhydrous magnesium sulfate. The organic solvent was then removed by vacuum, which yielded a clear liquid of 2-bromoethyl methacrylate (70% yield).

A typical quaternization reaction consisted of adding 40.46 g (0.21 mol) of 2-bromoethyl methacrylate, 26.03 g (0.21 mol, equimolar) of 1-butylimidazole, and a small amount of 2,6-di-tertbutyl-4-methylphenol (inhibitor) to a 250 mL flask. The mixture was stirred in an oil bath at 40 °C for 24 h and vielded a viscous liquid. The resulting MEBIm–Br monomer was dissolved in 30 mL dichloromethane and then re-precipitated three times in 200 mL diethyl ether in an ice bath. The purified MEBIm-Br monomer was a clear viscous liquid (82% yield). <sup>1</sup>H NMR (UNITYINOVA 500 MHz, DMSO- $d_6$ , ppm) and elemental analysis: 9.37 (s, 1H, N–CH=N), 7.86-7.88 (d, 2H, N-CH=CH-N), 6.03 (s, 1H, HCH=C(CH<sub>3</sub>)), 5.76 (s, 1H, HCH=C(CH<sub>3</sub>)), 4.53 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-O), 4.48 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-O), 4.21 (t, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.84 (s, 3H, CH<sub>2</sub>=C(CH<sub>3</sub>)), 1.76 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.22 (m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.89 (t, 3H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>). Anal. Found (Anal. Calcd.): C, 46.35 (49.21); H, 7.11 (6.69); O, 14.98 (10.09); N, 8.21 (8.83); Br 23.62 (25.18).

#### 2.3. Synthesis of polymerized ionic liquid (PIL)

The imidazolium-containing polymer, poly(MEBIm-Br), was synthesized by the conventional free radical polymerization as shown in Scheme 1. A typical polymerization included adding a mixture of 30.04 g ( $9.27 \times 10^{-2}$  mol) MEBIm–Br monomer and 63.0 g DMF to a 250 mL flask. The reaction mixture was then purged with nitrogen for 30 min followed by an addition of 31.4 mg  $(1.91 \times 10^{-4} \text{ mol})$  AIBN initiator to initiate polymerization, which was carried out at 60 °C for 6 h. The reaction mixture was then diluted with DMF and precipitated into acetone followed by washing with fresh acetone several times. The precipitate was then dried under vacuum at 60 °C for 72 h yielding 16.80 g of poly(MEBIm-Br) (56% yield). <sup>1</sup>H NMR (UNITYINOVA 500 MHz, DMSO-*d*<sub>6</sub>, ppm) and elemental analysis: 9.97 (s, 1H, N-CH=N), 8.10-8.17 (d, 2H, N-CH= CH-N), 4.32-4.67 (m, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-O, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.84 (s, 4H, CH<sub>2</sub>-C(CH<sub>3</sub>), N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.30 (s, 5H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.91 (s, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.32-0.64 (m, 3H, CH<sub>2</sub>-C(CH<sub>3</sub>)). Anal. Found (Anal. Calcd.): C, 47.69 (49.21); H, 6.89 (6.69); O, 13.08 (10.09); N, 8.10 (8.83); Br 23.64 (25.18).

#### 2.4. Anion exchange reactions

The anion exchange reactions for PILs (Scheme 1) and IL monomers (see Supplementary data Scheme S1) were performed in water. A general procedure for the preparation of PILs by anion exchange with poly(MEBIm–Br) is given as follows: 3.16 g (2.87  $\times$  10<sup>-2</sup> mol) NaBF<sub>4</sub> was dissolved in 10 mL of DI water and this solution was then added dropwise into 1.01 g poly(MEBIm-Br) aqueous solution with an anion mole ratio of  $BF_4/Br = 9/1$  mol/mol. The resulting waterinsoluble polymer, poly(MEBIm-BF<sub>4</sub>), precipitated out of the water phase immediately. The reaction mixture was stirred for 48 h, followed by re-precipitating and washing in fresh DI water for 72 h. Silver nitrate testing showed that the Br anion was present in the aqueous phase immediately after the exchange reaction, but no AgBr precipitated after the washing step. The resulting anion exchanged PIL was dried in vacuum oven for at least 24 h. A similar procedure was carried out with other salts, LiTFSI, LiTf, and LiPF<sub>6</sub>, to poly(MEBIm–TFSI), poly(MEBIm–Tf), produce and poly (MEBIm–PF<sub>6</sub>), respectively. <sup>1</sup>H NMR and elemental analysis results for all four PIL samples are shown below, where a residual amount of Br was present in each sample (<4 mol%). <sup>1</sup>H NMR (UNITYINOVA 500 MHz, DMSO- $d_6$ , ppm) and elemental analysis: poly (MEBIm-BF<sub>4</sub>): 9.11 (s, 1H, N-CH=N), 7.70-7.78 (d, 2H, N-CH= CH-N), 4.20-4.48 (m, 6H, N-CH2-CH2-O, N-CH2-CH2-CH2), 1.79 (s, 4H, CH2-C(CH3), N-CH2-CH2-CH2-CH3), 1.28 (s, 5H, N-CH2-CH2-CH2-CH3, CH2-C(CH3)), 0.90 (s, 6H, N-CH2-CH2-CH2-CH3, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.40-0.66 (m, 3H, CH<sub>2</sub>-C(CH<sub>3</sub>)). Anal. Found (Anal. Calcd.): F, 21.15 (20.76); Br, 0.51 (0). poly(MEBIm-TFSI): 9.18 (s, 1H, N-CH=N), 7.66-7.78 (d, 2H, N-CH=CH-N), 4.19-4.47 (m, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-O, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.78 (s, 4H, CH<sub>2</sub>-C(CH<sub>3</sub>), N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.27 (s, 5H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.90 (s, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.44-0.71 (m, 3H, CH<sub>2</sub>-C(CH<sub>3</sub>)). Anal. Found (Anal. Calcd.): F, 21.09 (22.02); Br, < 0.25 (0). poly(MEBIm-Tf): 9.19 (s, 1H, N-CH=N), 7.74-7.81 (d, 2H, N-CH=CH-N), 4.20-4.50 (m, 6H, N-CH<sub>2</sub>-CH2-O, N-CH2-CH2-CH2), 1.79 (s, 4H, CH2-C(CH3), N-CH2-CH2-CH<sub>2</sub>-CH<sub>3</sub>), 1.28 (s, 5H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.89 (s, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, CH<sub>2</sub>-C(CH<sub>3</sub>)), 0.42-0.69 (m, 3H, CH<sub>2</sub>-C(CH<sub>3</sub>)). Anal. Found (Anal. Calcd.): F, 14.47 (14.75); Br, 0.81 (0).

poly(MEBIm–PF<sub>6</sub>): 9.11 (s, 1H, N–CH=N), 7.64–7.75 (d, 2H, N–CH=CH–N), 4.18–4.43 (m, 6H, N–CH<sub>2</sub>–CH<sub>2</sub>–O, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 1.78 (s, 4H,  $CH_2$ –C(CH<sub>3</sub>), N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>), 1.28 (s, 5H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>, CH<sub>2</sub>–C(CH<sub>3</sub>)), 0.90 (s, 6H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>, CH<sub>2</sub>–C(CH<sub>3</sub>)), 0.90 (s, 6H, N–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>, CH<sub>2</sub>–C(CH<sub>3</sub>)), 0.43–0.66 (m, 3H, CH<sub>2</sub>–C (CH<sub>3</sub>)). Anal. Found (Anal. Calcd.): F, 28.47 (29.81); Br, 0.57 (0).

#### 2.5. Characterization

<sup>1</sup>H NMR spectra were collected using a UNITYINOVA 500 MHz spectrometer at room temperature with DMSO- $d_6$  as the solvent. Elemental analysis was conducted at Atlantic Microlab, Inc. in Norcross. GA. The infrared spectra were collected at room temperature using a Fourier transform infrared spectroscopy (FTIR) spectrometer (Nicolet 6700 Series; Thermo Electron) equipped with a singlereflection ATR attachment (Specac, Inc., Silver Gate™, zinc selenide crystal). The molecular weights of PILs were determined by gel permeation chromatography (GPC) at 40 °C using a Waters GPC system (breeze 2) equipped with two Styragel columns (Styragel@HR 3 and Styragel@HR 4) and a 2414 reflective index (RI) detector. PILs were dissolved in a mixture of DMF and 0.05 M LiBr. GPC measurements were performed at a flowrate of 1.0 mL/min at 40 °C using polyethylene glycol/polyethylene oxide (PEG/PEO) as standards. Thermal degradation temperatures  $(T_d)$  were measured by thermal gravimetric analysis (TGA, TA Instruments, Q50) at a heating rate of 10 °C/min under nitrogen environment. Glass transition temperatures  $(T_g)$  were measured with a differential scanning calorimeter (DSC) (TA Instruments, Q2000) under nitrogen environment (50 mL/min) using the method of heat/cool/heat at the same rate of 10 °C/min over a temperature range of -40 to 180 °C. The  $T_g$  was determined using the mid-point method on the second heating cycle thermogram. Ionic conductivity of PIL films and IL monomers was measured with an AC impedance system (Solartron, 1260 impedance analyzer, 1287 electrochemical interface, Zplot software) between 10<sup>2</sup> Hz and 10<sup>6</sup> Hz. PIL films with thickness ranging between 100 and 400 µm were prepared by solution casting from acetonitrile on Teflon Petri dishes at ambient conditions. The films were dried in a fume hood at room temperature and films were cut to  $\sim$  30 mm  $\times$  5 mm before they were completely dried. The polymer films were further dried under vacuum at 120 °C for at least 24 h, and then stored in a desiccator until use. The conductivity of IL monomers and PILs was measured in a cell with four-parallel electrodes (four-point method) in an environmental chamber (Tenney, BTRS model) with controlled temperature at the fixed relative humidity of 10%. An alternating current was applied to the outer electrodes and the real impedance or resistance, R, was measured between the two inner reference electrodes. Resistance was determined from the x-intercept of the imaginary versus real impedance data over a high frequency range. The conductivity

values were calculated from the equation  $\sigma = L/AR$ , where  $\sigma$  is conductivity (S/cm) and L and A are the distance between two inner electrodes and cross section area of the polymer film (A = Wl, W is the film strip width and l is the film thickness), respectively. For conductivity experiments, samples were equilibrated for 2 h at each temperature followed by 12 measurements over 3 h taken over 15 min increments. The values reported are an average of these steady-state measurements. Measurements for PIL films and IL monomers were carried out in a Teflon-coated stainless steel cell and a solid Teflon well-like cell, respectively. More details on these two cells and experimental procedures can be found elsewhere [18]. A small amount of di-*tert*-butyl-4-methylphenol (inhibitor) was added into the cell with the IL monomers to prevent polymerization during conductivity experiments.

#### 3. Results and discussion

## 3.1. Synthesis and chemical characterization of anion exchanged PILs

The synthesis of the IL monomer, MEBIm-Br, is shown in Scheme 1. The resulting IL monomer was a water-soluble clear viscous liquid. The homopolymer, poly(MEBIm-Br), was synthesized by conventional free radical polymerization (also shown in Scheme 1). This resulting polymer was soluble in water or methanol, but not soluble in acetone or diethyl ether. Thus, in this work, poly(MEBIm-Br) was chosen as the PIL precursor to exchange with other anions in water. A general anion exchange reaction scheme is also shown in Scheme 1. The chemical structures of the anion exchanged PILs were confirmed by chemical shifts in the <sup>1</sup>H NMR spectra as listed in Table 1, e.g., from 9.97 ppm (N-CH=N of poly (MEBIm-Br) to 9.11 ppm  $(N-CH=N \text{ of poly}(MEBIm-BF_4))$ . The <sup>1</sup>H NMR spectra shown in Fig. 1 also indicate that the C(2)-proton peak (9.97 ppm) associated with Br anion is not present in exchanged PILs, suggesting that Br has been replaced with a new anion and the amount of Br was reduced to a low level that was not detectable by <sup>1</sup>H NMR. Further, elemental analysis shows that the halide residue was negligibly small in the resulting anion exchanged PILs (<4 mol %). This data provides evidence that anion exchange reactions in water resulted in nearly fully exchanged PILs.

Fig. 2 shows the IR spectra for the exchanged PILs at ambient conditions. The characteristic infrared bands found in this study (BF<sub>4</sub>, 1046, 1011 cm<sup>-1</sup>; TFSI, 1346, 1130 cm<sup>-1</sup>; Tf, 1025, 755 cm<sup>-1</sup>; PF<sub>6</sub>, 810 cm<sup>-1</sup>) are consistent with literature (BF<sub>4</sub>, 1045, 1015 cm<sup>-1</sup> [19]; TFSI, 1348, 1136 cm<sup>-1</sup> [20]; Tf, 1032, 755 cm<sup>-1</sup> [21,22]; PF<sub>6</sub>, 808 cm<sup>-1</sup> [20]). Note that at the ambient conditions, there is significant amount of water (O–H stretching band at 3407 cm<sup>-1</sup>) in the precursor, poly(MEBIm–Br), while there is a negligible amount of water in the exchanged PILs.

Molecular weight and distribution of polyelectrolytes is often measured by GPC with a small amount of salt added to screen electrostatic repulsions and therefore minimize polymer chain aggregation [23]. In this work, results from dynamic light scattering (DLS) indicate that the addition of LiBr salt reduced the aggregation

Chemical	shifts in	<sup>1</sup> H NMR	spectra	for	PILS

Table 1

PIL	N–CH=N (ppm)	N–CH=CH–N (ppm)
Poly(MEBIm-Br)	9.97	8.10, 8.17
Poly(MEBIm-BF <sub>4</sub> )	9.11	7.70, 7.78
Poly(MEBIm-TFSI)	9.18	7.66, 7.78
Poly(MEBIm–Tf)	9.19	7.74, 7.81
Poly(MEBIm-PF <sub>6</sub> )	9.11	7.64, 7.75

of the PILs in DMF, where there was a monomodal distribution of hydrodynamic size at 0.05 M LiBr salt concentration (see Supplementary data Fig. S2a). A bimodal distribution in hydrodynamic size was observed without the addition of salt (see Supplementary data Fig. S2b). Fig. 3 shows the GPC chromatograms for PILs measured in this study, where monomodal peaks were observed indicating good separation with 0.05 M LiBr salt concentration. In literature, both PS [24] and PEG/PEO [25] have been used as standards for molecular weight measurements on polyelectrolytes. Table 2 lists the molecular weight average and distribution of PILs against both PS and PEG/PEO standards, respectively. Interestingly, the molecular weight average and distribution against PS standards are much higher and narrower than those against PEG/PEO standards. The polydispersities against PS standards ranged from 1.21 to 1.31 and are much smaller than what is typically observed for polymers synthesized by free radical polymerization. The reason for this is that there is a significant interaction between PS and the Styragel packing materials (crosslinked poly(styrene-divinylbenzene) particles) in the DMF solvent [26,27]. As a result, the elution time for polystyrene becomes longer (see Supplementary data Fig. S3). Thus, the molecular weight averages and polydispersities against PS standards are often significantly larger than their true values. In contrast, polydispersity values against the PEG/PEO standards give more reasonable values, ranging from 2.45 to 2.77. This indicates that molecular weights of PILs measured against PEG/PEO standards are closer to their true molecular weights when compared to PS standards, which interact with column packing materials.

#### 3.2. Thermal properties of PILs

Fig. 4 shows the thermal stability of PILs characterized by TGA under nitrogen environment. The thermal decomposition temperatures  $(T_d)$  of PILs were measured at 5% loss and are listed in Table 3. The precursor PIL with Br anion has the lowest decomposition temperature of all PILs ( $T_d = 534$  K), while the TFSI-exchanged PIL has the highest decomposition temperature ( $T_d = 636$  K). The overall thermal stability of these PILs scales with anion type as:  $Br < PF_6 < BF_4 < Tf < TFSI$ . The order of relative stability follows a similar trend reported in literature for ILs [28-30] suggesting that the decomposition temperature of the PIL is strongly dependant on the anion type. With respect to the decomposition mechanism, it is generally accepted that the nucleophilicity of an anion affects the thermal stability and a low decomposition temperature associated with a halide anion is attributed to the attack of highly nucleophilic halide on the primary alkyl group via an  $S_N 2$  reaction with an alkyl halide as a byproduct [31]. As compared with Br anion, it is well known that other anions are more thermally stable than halides. However, the detailed decomposition mechanism for these are still not well understood. For example, the TFSI anion is a weak or nonnucleophilic anion and one possible pathway for the decomposition of the TFSI anion is that it undergoes degradation via sulfur dioxide release instead of dealkylation or proton transfer [32], which makes it more difficult to thermally decompose. Also, from Fig. 4, it is clear that PILs paired with PF<sub>6</sub>, BF<sub>4</sub>, Tf, and TFSI anions undergo a one-step thermal decomposition, while the precursor PIL paired Br appears to undergo a two-step thermal decomposition. The two-step decomposition agrees with the work of Vygodskii et al. [33] For the poly(MEBIm–Br), the first thermal decomposition step ( $T_d = 261 \, ^{\circ}$ C) can be attributed to the degradation of the Br anion, while the second decomposition step at  $\sim$  340 °C is in good agreement with the thermal decomposition temperature of poly (vinylimidazole) ( $T_d \sim 335 \ ^{\circ}$ C) [34].

The glass transition temperatures ( $T_g$ ) of the PILs as a function of anion type are listed in Table 3. For the same polymer chain length, the  $T_g$  values follow the following order: Br > PF<sub>6</sub> > BF<sub>4</sub> > Tf > TFSI.



Fig. 1. <sup>1</sup>H NMR spectra of the PIL precursor and anion exchanged PILs. X on figure represents the corresponding anion.



Fig. 2. Infrared spectra of PILs at ambient conditions. Spectra offset for clarity.

Overall, there is a 95 K depression in  $T_g$  from poly(MEBIm–Br) ( $T_g = 375$  K) to poly(MEBIm–TFSI) ( $T_g = 280$  K). Therefore by removing the effect of polymer chain length (each PIL has the same degree of polymerization), the value of  $T_g$  here is largely dependent on the plasticizing effect of the anion. In particular, the TFSI anion has a more significant impact on  $T_g$  depression compared to other anions, such as Tf and BF<sub>4</sub>. This can be attributed to not only the difference in size, but also lower symmetry, extensive charge delocalization [35], and the flexibility of the TFSI anion [36]. Also, in the temperature range from 233 K to 573 K, no melting behavior



**Fig. 3.** GPC chromatograms for PILs using DMF columns: poly(MEBIm-Br) (black), poly (MEBIm-BF<sub>4</sub>) (blue),  $poly(MEBIm-PF_6)$  (green), poly(MEBIm-Tf) (magenta), poly (MEBIm-TFSI) (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

lable Z	
Molecular weights and polydispersities of PILs.	

PIL	PEG/PEO standard		PS standard	
	$M_w$	PDI	$M_w$	PDI
Poly(MEBIm-Br)	58,700	2.56	367,000	1.30
Poly(MEBIm-BF <sub>4</sub> )	61,100	2.77	427,000	1.27
Poly(MEBIm–TFSI)	43,080	2.54	312,000	1.21
Poly(MEBIm–Tf)	56,680	2.45	356,000	1.32
Poly(MEBIm-PF <sub>6</sub> )	54,970	2.53	340,000	1.32

was observed for all of these PILs, which suggests that these PILs are amorphous in nature.

#### 3.3. Ionic conductivity

Fig. 5a shows the measured ionic conductivities of PILs as a function of temperature. Note that the precursor polymer, (poly (MEBIm—Br)), is water soluble and thus only the hydrophobic PILs are compared here under dry conditions (10% RH). The conductivities of the PILs follow the order: TFSI > Tf > BF<sub>4</sub> > PF<sub>6</sub>, which is the reverse order of  $T_g$  shown in Table 3. These results suggest that polymer chain relaxation plays a dominant role in ion transport. Specifically, the PIL with TFSI is significantly higher in ionic conductivity compared to the other PILs and this coincides with the significantly lower  $T_g$  (Table 3). Also, with increasing temperature, the difference in ionic conductivity between PILs with different anions decreases, suggesting that at a high temperature the importance of  $T_g$  becomes less pronounced.

Compared to the PILs, the IL monomers provide an upper limit of ionic conductivity since the restriction of polymer chain relaxation is eliminated and a large number of ions and their counter ions are available for ion transport. Fig. S4 (see Supplementary data) shows that the ionic conductivity of the IL monomers is approximately two to three orders of magnitude higher than their corresponding PILs. The conductivities of the IL monomers follow the order: TFSI > BF<sub>4</sub>>Tf > PF<sub>6</sub>, where the difference in conductivity for TFSI compared to the other anions is not as significant compared to the



**Fig. 4.** Thermal stability of PILs: poly(MEBIm–Br) (black), poly(MEBIm–BF<sub>4</sub>) (blue), poly(MEBIm–PF<sub>6</sub>) (green), poly(MEBIm–Tf) (magenta), poly(MEBIm–TFSI) (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 3

Thermal degradation temperatures  $(T_d)$  and glass transition temperatures  $(T_g)$  of PILs.

PIL	<i>T</i> <sub>d</sub> (K)	$T_{g}\left(\mathrm{K} ight)$
Poly(MEBIm-Br)	534	375
Poly(MEBIm-BF <sub>4</sub> )	586	358
Poly(MEBIm–TFSI)	636	280
Poly(MEBIm–Tf)	608	337
Poly(MEBIm–PF <sub>6</sub> )	579	367

PILs. Also, the order in conductivity differs from the PILs, where the differences in  $T_g$  (see Supplementary data Table S4) are minor compared to the PILs; maximum difference of 11 K for the IL monomers compared to 95 K for the PILs. Unlike the glass transition-dependant PIL system, the IL monomer conductivity differences are dictated by other factors; most probably liquid viscosity, which has been shown by many other investigators for common ILs [37,38].

The glass transition dependence for the PIL system can be seen more clearly in Fig. 5b, where conductivity is plotted versus a normalized temperature,  $T_g/T$ . However, the data does not collapse onto one single curve. This suggests that other factors in addition to  $T_g$  can impact ion transport. After normalizing for  $T_g$ , poly(MEBIm—TFSI) has the lowest conductivity, where it shows the highest conductivity in Fig. 5a (before normalization). The differences in conductivity may be attributed to the symmetry and size of the anions and the dissociation energy of the ion pairs, where the PILs with BF<sub>4</sub> and PF<sub>6</sub> have the highest conductivities when the effects of  $T_g$  are removed [39].

#### 3.3.1. VFT regression

For a solid polymer electrolyte system, the temperature dependent ionic conductivity is often regressed to the Vogel-Fulcher-Tammann (VFT) equation [40–42]:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{b}{T - T_0}\right) \tag{1}$$

where  $\sigma_0$  (S cm<sup>-1</sup>) is the infinite temperature conductivity, *b* (K) is a constant that can be related to the Arrhenius activation energy, and  $T_0$  (K) is the Vogel temperature.  $T_0$  has been interpreted as the temperature at which the configurational entropy vanishes, [43] the polymer relaxation time becomes infinite, [44] or the mobility of ions goes to zero [45] and is typically ~ 50 K below the measured  $T_g$ of the polymer [46]. The physical meaning of the VFT equation is not straightforward, but has been explained in terms of the free volume model [47] and the configurational entropy model [43]. Fig. 6a shows the temperature dependant ionic conductivity for the PILs regressed to the VFT equation (solid lines), which requires three fitting parameters (regressed values listed in Table 4).

Alternatively, Eq. (1) can be recast into the following form:

$$\sigma(T) = \sigma(T_r) \exp\left(-b\left(\frac{1}{T-T_0} - \frac{1}{T_r - T_0}\right)\right)$$
(2)

where  $\sigma$  ( $T_r$ ) is the conductivity at a reference temperature,  $T_r$ . In this study, we choose an experimentally measured value for the reference temperature,  $T_r = T_g + 50$  K. The introduction of  $T_r$  in Eq. (2) reduces the number of fitting parameters in the VFT equation from three to two, *b* and  $T_0$ . Fig. 6b shows the PIL conductivity data regressed to Eq. (2), where the resulting fitting constants are also listed in Table 4. Interestingly, the three-parameter regression results in  $T_g - T_0$  values close to the expected 50 K, whereas the two-parameter regression results in  $T_g - T_0$  values that are much larger (ranging from 116 to 146 K).



**Fig. 5.** lonic conductivity versus (a) 1000/T (K<sup>-1</sup>) and (b)  $T_g/T$  of PILs: poly(MEBIm–BF<sub>4</sub>) (blue diamonds), poly(MEBIm–PF<sub>6</sub>) (green squares), poly(MEBIm–Tf) (magenta triangles), poly(MEBIm–TFSI) (red circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

#### 3.3.2. WLF regression

The temperature dependence of ionic conductivity for solid polymer electrolytes (e.g., Li salt-poly(ethylene oxide) (PEO) mixtures) can also be regressed to the Williams-Landel-Ferry (WLF) equation:

$$\log\left(\frac{\sigma(T)}{\sigma(T_g)}\right) = \frac{C_1^g(T - T_g)}{C_2^g + (T - T_g)}$$
(3)

where  $\sigma$  (*T*) and  $\sigma$  (*T<sub>g</sub>*) are the conductivities at a given temperature, *T*, and the glass transition temperature, *T<sub>g</sub>*, and *C<sup>g</sup>*<sub>1</sub> and *C<sup>g</sup>*<sub>2</sub> (K) are fitting parameters. Similarly, the WLF equation can be recast in terms of an experimentally measurable reference temperature, *T<sub>r</sub>*:

$$\log\left(\frac{\sigma(T)}{\sigma(T_r)}\right) = \frac{C_1^r(T - T_r)}{C_2^r + (T - T_r)}$$
(4)

where  $C_1^g$  and  $C_2^g$  in Eq. (3) can be related to  $C_1^r$  and  $C_2^r$  with the following equations:

$$C_1^g = \frac{C_1^r C_2^r}{C_2^r + (T_g - T_r)}$$
(5)

$$C_2^g = C_2^r + T_g - T_r (6)$$

Fig. 7 shows a master regression of all the PIL conductivity data to the modified WLF equation (Eq. (4)) and Table 5 lists the regressed values,  $C_1^r$  and  $C_2^r$ , from this master regression and also each individual PIL (individual regressions not shown here). Table 5 also lists the  $C_1^g$  and  $C_2^g$  values calculated from Eqs. (5) and (6). Note that although the WLF (Eq. (3)) and VFT (Eq. (1)) equations have different origins, they are actually mathematically equivalent, where  $b = 2.303C_1^g C_2^g$  and  $T_0 = T_g - C_2^g$ . Therefore, the  $C_2^g$  and  $2.303C_1^g C_2^g$  values listed in Table 5 determined from the WLF regression are in a good agreement with the  $T_g - T_0$  and b values listed in Table 4 determined from the two-parameter VFT regression. This analysis confirms the high  $T_g - T_0$  ( $C_2^g$ ) value observed from the two-parameter VFT regression. Actually, the master WLF regression shows that  $C_1^g$  and  $C_2^g$  values are 9.03 and 168 K, respectively, which greatly deviate from the classical values originally obtained from mechanical relaxation of uncharged polymers  $(C_1^g = 17.44, C_2^g = 51.6 \text{ K}).$ 

Based on the free volume theory developed by Doolittle [48], Williams et al. [46] interpreted the physical meaning of  $C_1^g$  and  $C_2^g$ by relating them to the fractional free volume, *f*, and the thermal expansion coefficient,  $\alpha$ , at  $T_g$ .

$$f(T_g) = \frac{B}{2.303 \, C_1^g} \tag{7}$$



**Fig. 6.** VFT regression of the temperature dependent ionic conductivity of PILs: (a) three-parameter regression (Eq. (1)) and (b) two-parameter regression (Eq. (2)). PILs: poly (MEBIm–BF<sub>4</sub>) (blue diamonds), poly(MEBIm–PF<sub>6</sub>) (green squares), poly(MEBIm–Tf) (magenta trianlges), poly(MEBIm–TFSI) (red circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

 Table 4

 VFT equation regression values of temperature dependent conductivity data for PILs.

PIL	Three-parameter regression (Eq. (1))				Two-parameter regression (Eq. (2))		
	$\sigma_0$ (S cm <sup>-1</sup> )	b (K)	T <sub>0</sub> (K)	$T_g - T_0$ (K)	b (K)	Т <sub>0</sub> (К)	$T_g - T_0$ (K)
Poly(MEBIm-BF <sub>4</sub> )	0.029	302	303	55	2507	220	138
Poly(MEBIm-TFSI)	0.152	466	215	65	2187	164	116
Poly(MEBIm-Tf)	0.061	373	282	55	2323	216	121
Poly(MEBIm-PF <sub>6</sub> )	0.009	232	318	49	2550	221	146

$$\alpha(T_g) = \frac{B}{2.303 \, C_1^g C_2^g} \tag{8}$$

In Eqs. (7) and (8), we assume B = 1. Originally, Doolittle also assumed B = 1 [48]. Others have calculated B from volume-temperature data of polymers (without pressure dependence) and estimated  $B = 0.9 \pm 0.3$  or  $1.6 \pm 0.6$  depending on the estimation method [49]. Most reports, however, have adopted *B* equal to unity, including reports on charged polymers [50]. The values for  $f(T_g)$  and  $\alpha(T_g)$ , calculated from the WLF regressed  $C_1^g$  and  $C_2^g$  values, are listed in Table 5, where the fractional free volumes for the PILs are on average double that of what has been classically observed for uncharged polymers ( $f(T_g) = 0.025$ ).

One should note the universal parameters for uncharged polymers ( $C_1^g = 17.44$  and  $C_2^g = 51.6$  K,  $f(T_g) = 0.025$ ) are based on a master regression of data from many polymers. If one were to determine these parameters from regressing data for each polymer individually (data in Ref. [51]), the average and standard deviation of all of these individual regressed values are  $C_1^g = 16.79 \pm 5.43$ ;  $C_2^g = 63.7 \pm 28.1$  K;  $f(T_g) = 0.028 \pm 0.01$ . For our PILs, regressions from both individual polymers and a master regression are listed in Table 5. The average and standard deviation from our individual regressions are  $C_1^g = 7.92 \pm 0.28$ ;  $C_2^g = 131 \pm 13$  K;  $f(T_g) = 0.055 \pm 0.001$ . Therefore, despite the high deviation of the WLF regressed values for uncharged polymers, there is still a significant difference compared to the WLF values obtained in this study on PILs.



**Fig. 7.** WLF master regression (Eq. (4)) of the temperature dependent ionic conductivity of all PILs: poly(MEBIm $-BF_4$ ) (blue diamonds), poly(MEBIm $-PF_6$ ) (green squares), poly(MEBIm-Tf) (magenta triangles), poly(MEBIm-TFSI) (red circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 5

WLF equation regression values of temperature dependent conductivity data for PILs.

PIL	$C_1^r$	$C_2^r$	$C_1^g$	$C_2^g$	2.303 $C_1^g C_2^g$	$f(T_g)$	$\alpha(T_g)$
Poly(MEBIm-BF <sub>4</sub> )	5.79	188	7.89	138	2508	0.055	$4.0 \times 10^{-4}$
Poly(MEBIm-TFSI)	5.72	166	8.18	116	2185	0.053	$4.5  imes 10^{-4}$
Poly(MEBIm–Tf)	5.75	175	8.05	125	2318	0.054	$4.3  imes 10^{-4}$
Poly(MEBIm-PF <sub>6</sub> )	5.61	196	7.53	146	2532	0.057	$4.0  imes 10^{-4}$
All PILs	6.97	218	9.03	168	3494	0.049	$2.9\times 10^{-4}$

Understanding the considerable deviation of  $C_1^g$  (9.03) and  $C_2^g$ (168 K) for the PILs studied here compared to classical values determined from uncharged polymers ( $C_1^{g} = 17.44$  and  $C_2^{g} = 51.6$  K) is of great interest. WLF constants obtained from charged polymer systems (solid polymer electrolytes) would serve as a better comparison. There are few reports of WLF regressions to PIL conductivity data. However, there are a number of studies that have examined WLF behavior of Li salt-PEO polymer electrolyte systems. The  $C_1^g$  and  $C_2^g$  values were examined as a function of salt type [52], salt concentration [53,54], as well as, polymer chain length [55]. However, there is no universal agreement on the  $C_1^g$  and  $C_2^g$  values for these systems. Although some studies showed that  $C_1^g$  values are close to 17.44 [56] or  $C_2^g$  values are close to 51.6 [57], most studies showed deviations of  $C_1^g$  or  $C_2^g$  from these classical values. Specifically, numerous studies report values for  $C_1^g$  at ~7–12 for the Li salt-PEO system (8.5–10.6 [58], 7.8–12.5 [52], 9.6–11.8 [59], 8.0 [60], 8.1–12.0 [50]). In particular, Watanabe et al. [53] studied the effect of Li salt concentration in PEO on  $C_1^g$  and  $C_2^g$  values, where  $C_1^g$ decreased from 13.5 to 10.1 and  $C_2^g$  increased from 39.4 to 97.9 with increasing salt concentration from 0.015 to 0.062 ([salt]/[EO unit]). However, a detailed explanation for the reason behind these deviations has not yet been presented.

In this work, we report  $C_1^g$  values that are far from uncharged polymers [46]. This suggests a higher fractional free volume at  $T_g$  for PILs. Also, the  $C_2^g$  value for the PILs in this study deviates significantly from both uncharged polymers and the Li salt-PEO charged polymer system, suggesting a lower Vogel temperature (the temperature at which free volume becomes zero). At temperatures below  $T_g$ , the interaction of the bulky cation and anion in imidazolium-based PILs results in increased free volume due to the impact of steric hindrance on polymer chain packing [61]. It is interesting to note that the typical Li salt-PEO systems investigated has a salt concentration on the order of 0.1 mol Li salt/mol EO repeat unit, whereas the PIL system in this study has an ionic concentration on the order of 1 mol IL salt/mol MMA repeat unit. It is also important to note that Li salt-PEO systems is PEO doped with a Li salt, where both cation (Li) and anion (e.g., TFSI) are both mobile compared to the PIL in this study, where the cation is tethered to the polymer backbone and therefore is a single anion conductor. Therefore, these results suggest that the higher ion concentration and tethered cations (single anion conductor) in PILs may be key factors that result in lower Vogel temperatures compared to salt doped polymer electrolytes.

#### 4. Conclusions

In this study, imidazolium-based PIL single ion conductors of constant average chain length were paired with different anions, BF<sub>4</sub>, TFSI, Tf, and PF<sub>6</sub>, at the polymer stage to solely explore the effect of anion type on the chemical structures, thermal properties, and ion conduction. Chemical analysis confirms that the anion exchange reactions for both PILs and IL monomers in water resulted in nearly fully exchanged PILs and IL monomers. GPC results show that the molecular weights of PILs measured against PEG/PEO

standards are closer to their true molecular weights when compared to PS standards, which interact with column packing materials. Anion type had a significant effect on the degradation and glass transition temperatures, where poly(MEBIm—TFSI) had the highest degradation temperature and the lowest glass transition temperature, indicating a much wider operating temperature window for practical applications. The ionic conductivity of PILs scales with the glass transition temperature, where poly (MEBIm—TFSI) had a significantly lower glass transition temperature and a significantly higher ionic conductivity compared with PILs exchanged with other anions. Ion transport was also influenced by other factors, including the size and symmetry of the anion and dissociation energy of the ion pair.

The temperature dependent ionic conductivity of all PILs studied follows VFT behavior. Interestingly, the results obtained from a three-parameter VFT regression were different from those obtained from a two-parameter VFT regression, where the latter was consistent with the results obtained from a mathematically equivalent WLF regression. The  $C_1^g$  (9.03) and  $C_2^g$  (168 K) values obtained from the WLF regression for these PILs deviate significantly from the classical values obtained from the mechanical relaxation of uncharged polymers ( $C_1^g = 17.44$ ,  $C_2^g = 51.6$  K). The fractional free volume for the PILs at the glass transition temperature, calculated from  $C_1^g$  value, was on average double that of what has been classically observed for uncharged polymers. While  $C_1^g$  value obtained here for PIL single ion conductors was close to some Li salt-PEO charged polymer systems, the  $C_2^g$  value was significantly higher than any other charged polymer systems reported in the literature. This suggests that the salt or ionic concentration in charged polymers can affect free volume and the Vogel temperature ( $T_0 = T_g - C_2^g$ ), where ion mobility at temperatures farther below the glass transition temperature can be achieved at higher salt or ionic concentrations in single ion conductors. Therefore, anion type and salt or ion concentration are two key parameters that can be tuned to affect the temperature dependent ionic conductivity in PILs.

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#### Appendix. Supplementary data

Supplementary data associated with this article can be found online at doi:10.1016/j.polymer.2011.01.031. http://www.elsevier.com/.

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