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Radically crosslinked branched poly(*N*-allylethylenimine) with lithium triflate as a solid state polymer electrolyte

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Abstract

Branched poly(*N*-allylethylenimine) (BPAEI), a solid state polymer electrolyte host, was synthesized by allylation of branched poly(ethylenimine) (BPEI). Allylation was essentially complete with the 2 and 1° nitrogen atoms of BPEI being mono-allylated and di-allylated, respectively, and with little or no quaternization. BPAEI can be radically cross-linked with and without lithium trifluoromethanesulfonate (LiTf) present to form free-standing, homogeneous, minimally hygroscopic films. BPAEI has a glass transition temperature (T_g) of -65 °C, as measured by differential scanning calorimetry (DSC), which increases with the concentration of initiator upon cross-linking using V-50 (2,2-azobis(2-amidino-propane) dihydrochloride) to -15 °C at a 10:1 nitrogen to initiator molar ratio (N:initiator). BPAEI with 20:1 N:Li^+ (molar ratio) LiTf has a T_g of -48 °C, which increases with the concentration of radical initiator upon cross-linking using V-50 to 3 °C at 10:1 N:initiator. At compositions near 60:1 N:initiator, an unusual decrease in the rate at which T_g changes with cross-linking was observed, both with and without LiTf present, indicating that some undefined morphological changes occur. The effect of this morphological change resulted in the highest Ac conductivities at 60:1 N:initiator for all LiTf concentrations studied. At 20:1 N:Li^+ LiTf and 60:1 N:initiator, the room temperature Ac conductivity was 1×10^{-8} S/cm which increased to 1×10^{-5} S/cm at 80 °C, the highest conductivity observed in the concentration ranges studied. Infrared spectroscopy (IR) showed that the concentrations of the individual ionic species present were largely independent of either LiTf concentration or cross-linking density, suggesting that changes in ion mobility, likely resulting from morphological changes, substantially control the ionic conductivity.

Keywords: Branched poly(ethylenimine); Conductivity; Glass transition temperature

1. Introduction

Research on solid state polymer electrolytes (SPE) that can be used to construct highly flexible and leak-free electrochemical devices as convenient portable electricity sources has been ongoing for more than 20 years [1,2]. Poly(ethylene oxide) (PEO) and its heteroatom analog poly(ethylenimine) (PEI) have been studied as polymer electrolyte hosts for solid state polymer electrolytes. [3–5]. However, neither PEO or PEI SPEs have sufficient ionic conductivity or mechanical properties needed for practical applications. Therefore, they need to be modified for better performance. Commercially available, inexpensive branched poly(ethylenimine) (BPEI), is a convenient starting material for PEI modifications. Unlike linear PEI that has only secondary nitrogens, BPEI has primary, secondary, and tertiary nitrogen atoms [6]. Although BPEI has a low glass transition temperature, its T_g markedly increases with the addition of salt from ~ -50 (neat) to ~ 50 °C (N:$Li^+ = 4:1$) [7], along with concomitant significant decreases in ionic conductivity. A maximum conductivity of 10^{-6} S/cm at 20 °C has been reported for BPEI:LiTf at a 20:1 (N:Li^+) composition [7,8]. Chemically modified BPEI-type dendrimers, poly(propyleneimine) tetrahexacontaamine (DAB-AM-64) and poly(amidoamine) (PAMAM), have been reported by Dillon et al. [9]. The optimum conductivity of complexes formed by these dendrimers and $Li[(CF_3SO_2)_2N]$ ranges from 6.3×10^{-7} S/cm at room temperature to 1.0×10^{-4} S/cm at 100 °C [9]. Attempts have been made to improve the physical properties of PEI by chemical modification of the backbone nitrogen atoms [10,11]. Cross-linking by substitution reactions using bifunctional crosslinkers with leaving groups on both ends is one method to improve polymer physical properties [12]; however, with PEIs this method creates charged ammonium moieties that affect ion transport and speciation, that is, the complex equilibrium between various ionic species that may exist in the polymer

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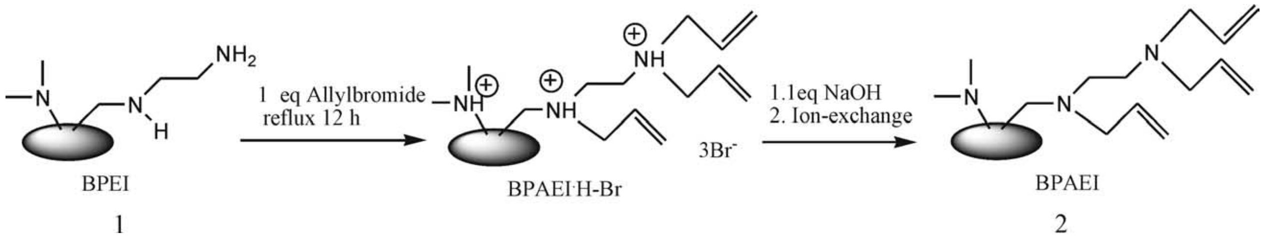

Fig. 1. Synthesis of BPAEI (with an empirical formula (–CH_2CH_2NH–), BPEI is shown schematically as its exact structure is variable).

electrolyte. Therefore, it is desirable to develop a neutral, crosslinked SPE host based on commercially available BPEI.

Radical initiated carbon–carbon bond formation may serve as the best means for the synthesis of a neutrally crosslinked BPEI. Allylation of the amine groups in BPEI with allyl bromide, followed by neutralization, gave branched poly(*N*-allylethylenimine) (BPAEI) (Fig. 1). Effective radical initiated crosslink conditions were determined for this material. Subjective empirical observations of physical properties and dissolution tests were used to evaluate crosslinking of the resulting films. Infrared spectroscopy (IR) and differential scanning calorimetry (DSC) spectroscopy were used to study crosslinking. IR and conductivity studies of crosslinked BPAEI–LiTf electrolytes prepared using the effective conditions were performed.

2. Experimental

2.1. Materials

The synthesis of BPAEI is shown in Fig. 1. BPEI **1** (10.0 g, 0.233 equiv. avg. MW ca. 10,000, Aldrich) was added to 100 mL HPLC grade methanol, and the reaction vessel was cooled using an ice bath. Allyl bromide (28.2 g, 0.233 mol) was added dropwise while stirring. After warming to room temperature slowly, the solution was heated to reflux solvent for 12 h. Solvent and any excess allyl bromide were removed under reduced pressure. The residue was redissolved in 100 mL methanol. Sodium hydroxide (9.32 g, 0.233 mol) was added as pellets while stirring and the solvent was heated to reflux for 1 h. After methanol was removed, benzene (100, 50 and 50 mL) was used to extract the polymer from inorganic sodium bromide. The benzene was removed under reduced pressure and the polymer was dissolved in 50 mL H_2O. The resulting solution was passed through an OH^- ion-exchange column (DOWEX-2 400). Removal of water under reduced pressure gave neutral BPAEI **2** (18.4 g, 0.221 mol). This procedure gave a 95% yield. The resulting polymer is a light brown viscous liquid. ^1H NMR ($CDCl_3$) δ (ppm) 2.4–2.8 (br, 4H, backbone CH_2), 3.1 (d, 2H, sidechain CH_2), 5.3 (t, 2H, $=CH_2$), 6.0 (m, 1H, –CH=). IR (3072 cm^{-1}($=CH_2$), 1642 cm^{-1} (C=C), no N–H absorption from 3300 to 3500 cm^{-1}).

In order to prepare the polymer electrolyte (crosslinked BPAEI–LiTf), BPAEI **2** was dissolved in a minimum amount of methanol with a desired amount of initiator (most of the initiators were obtained from Wako Chemicals, USA) and LiTf (Aldrich) and stirred for 1 h. LiTf was dried under vacuum at 120 °C over night prior to use. The resulting homogenous solution was cast onto a glass slide and the methanol was allowed to evaporate in air for 2 h. The cast films were positioned in an oven at 80 °C for 12 h. The films were then removed from the glass slides using a razor blade and dried in a vacuum oven at 70 °C for 48 h. All the films were stored in vacuo prior to measurements. The compositions of the BPAEI–LiTf samples are described as nitrogen to cation molar ratios ($N:M^+$).

2.2. Measurements

BPAEI IR samples were directly cast onto NaCl windows from methanol solution and dried in an argon-atmosphere glovebox. All the polymer electrolyte IR samples were directly cast onto NaCl windows from the homogenous BPAEI–LiTf–initiator solutions described in the materials section and were dried under ambient conditions. The materials on these windows were crosslinked and dried using the same procedure described for crosslinking thicker films. Infrared spectra were recorded at a 1 cm^{-1} spectral resolution using a Bruker IFS66V FT-IR spectrometer with the samples under vacuum (10 mbar). Analysis of the spectral data was performed using a commercially available program (Thermo Galactic, Grams/32, version 7.0).

BPAEI samples were directly transferred into aluminum DSC pans and dried in a vacuum oven at room temperature for 24 h before being sealed. Pre-dried crosslinked BPAEI and crosslinked BPAEI–LiTf films were cut into small pieces before being sealed in aluminum pans. DSC data were collected with a Mettler DSC 820 calorimeter and were analyzed using a commercial program (STAR© version 6.10) that furnished T_gs as midpoints of the secondary transitions.

In a glove box, pre-dried polymer electrolyte films were sandwiched between two 12.5 mm stainless steel electrodes in an airtight conductivity cell which was placed in a metal container wrapped with heating tape. The metal container was placed in a desiccator and the container was heated using the heating tape. A K-type thermocouple was used to monitor the cell temperature. Complex impedance data were recorded over a frequency range of 5–10,000 Hz using an HP 4192A LF impedance analyzer with LABVIEW™ 5.1 software. Conductivity data were collected from 20 to 80 °C in 10 °C increments under a dry nitrogen purge. All the measurements were conducted throughout three heating/cooling cycles. Impedance plots were fitted using LEVM version 7.1.

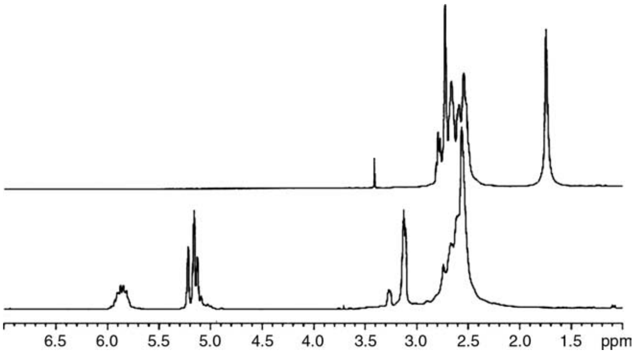

Fig. 2. Three hundred megahertz ^{1}H NMR of BPEI (upper) and BPAEI (lower) in $CDCl_3$.

3. Results and discussion

BPEI is a complicated system with primary, secondary and tertiary nitrogen atoms in a ratio of ca. 1:2:1, respectively. [6,13,14] Although its empirical formula is (–CH_2CH_2NH–), BPEI is shown in Fig. 1 schematically as its exact structure is variable. Fig. 1 does not show the exact structure of BPEI but simply illustrates that there are three types of nitrogen atoms in BPEI. One equivalent of allyl bromide was used to allylate BPEI. The disappearance of the N–H signals in the BPAEI NMR and IR spectra shows that substitution is essentially complete. The ^{1}H NMR chemical shift of an allyl methylene group α to a tri-substituted nitrogen such as *N*,*N*-diethylallylamine and *N*,*N*-dimethylallylamine is around 3.0 ppm, while that of the allyl methylene group α to a tetra-substituted, cationic nitrogen as in allyltriethylammonium iodide is around 4.1 ppm [15]. The NMR of the BPAEI does not have any signal around 4.1 ppm (Fig. 2), which is consistent with tetra-substitution of the nitrogen being negligible. As shown in Fig. 3, the more structurally accessible primary nitrogen likely reacts with allyl bromide first. Eventually the original secondary nitrogens are allylated as well. One of the hydrogen atoms on the mono-allylated primary nitrogen could be transferred to the more stericdly hindered nitrogens, forming ammonium cations. The resulting secondary nitrogen could react with allyl bromide again and form di-allylated amine. The species in this process are in equilibrium. All the nitrogen atoms are tri-alkylated and protonated at the end of the process. Once neutralized, there are only tertiary nitrogens in BPAEI.

BPAEI is an extremely viscous liquid with a light brown color and is soluble in many solvents such as water, benzene, methanol, and chloroform. The lack of absorption in the IR spectrum (3200–3600 cm^{-1}) of a sample stored under ambient conditions over a period of a week showed that BPAEI does not appear to be hydroscopic. Therefore, it is possible to manipulate and store BPAEI in the atmosphere without concerns for water absorption. When BPAEI is radically crosslinked, it becomes a light brown, shiny, transparent solid film. Crosslinked BPAEI forms flexible free-standing polymer films with moderate physical strength. The average thickness of the crosslinked BPAEI films was 0.15 mm. Crosslinked BPAEI is not soluble in common solvents. The lack of absorption in the IR spectrum (3200–3600 cm^{-1}) of a sample stored under ambient conditions over a period of a week established that the crosslinked BPAEI also does not take up water from the atmosphere. Crosslinked BPAEI–LiTf films slowly absorb water that could be removed by heating under reduced pressure. Generally, this method of making the BPEI-based neutral crosslinked polymer electrolyte does not require stringent conditions and, in our experience, can be easily scaled up with virtually 100% yield.

To optimize the crosslinking of BPAEI, the following initiators were investigated at a 30:1 (N:initiator molar ratio) initiator composition, a temperature of 80 °C, and times ranging from 12 to 60 h: VA-061 (dimethyl 2,2-azobisisobutyrate), V-50 (2,2-azobis(2-amidinopropane) dihydrochloride), VA-044 (2,2-azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride), VA-086 (2,2′-azobis [2-methyl-*N*-(2-hydroxyethyl) propionamide]), AIBN (α,α'-azobis(isobutyronitrile)), benzoyl peroxide, and V501 (4,4′-azobis(4-cyanopentanoic acid)). Crosslinking attempts in the condensed phase showed that V-50, VA-044, V-501, and AIBN gave positive results based on dissolution tests, while VA-086 gave very poor results and VA-061 did not work at all. Crosslinking studies in the presence of salt were conducted. The conditions described in the experimental section were used, and the salt (LiTf) concentration was maintained at 10% by weight. The V-50, VA-044, V-501, and AIBN initiators that were successful

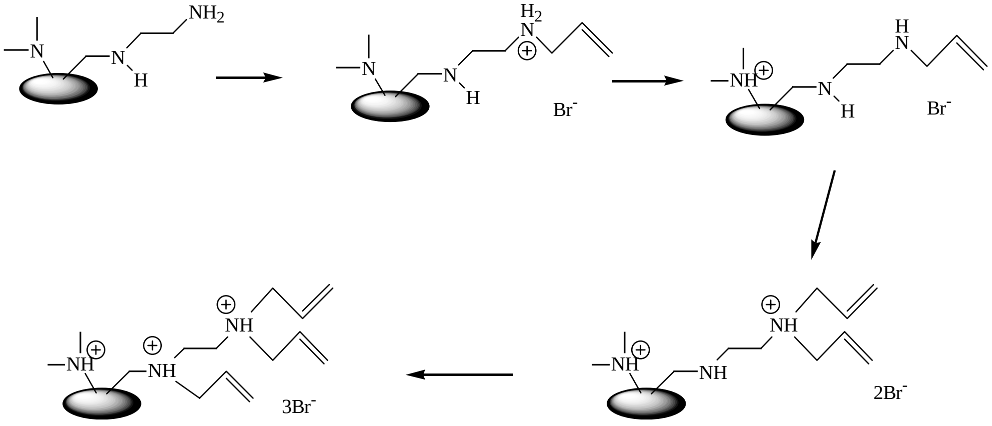

Fig. 3. Generalized reaction pathway for allylation of BPEI.

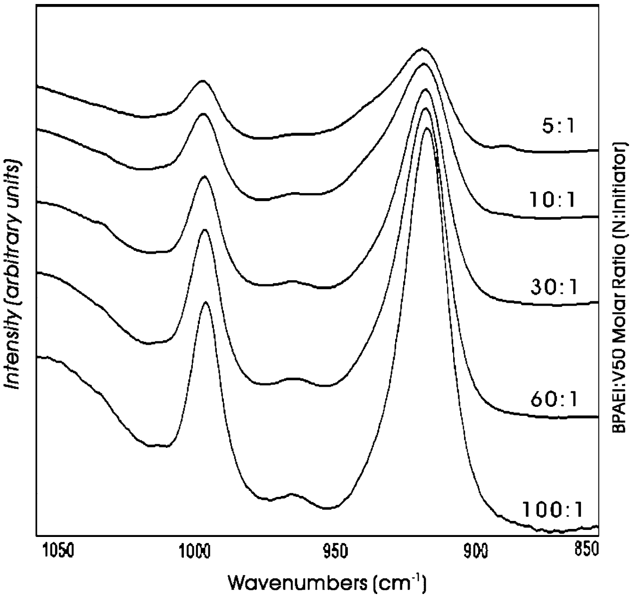

Fig. 4. IR spectra of crosslinked BPAEI films (850–1050 cm^{-1}) as a function of V-50 crosslinker composition. All spectra are scaled by normalizing the intensity of the C–H bands from 2900 to 3100 cm^{-1}.

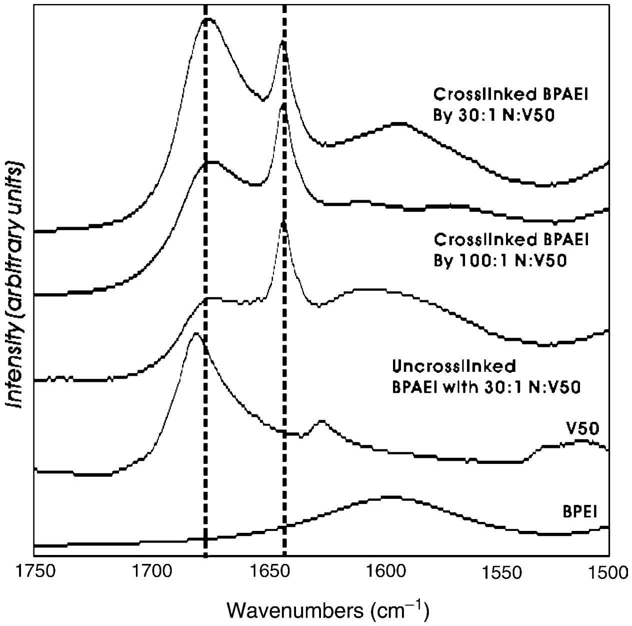

Fig. 5. IR Comparison of BPEI, neat V-50, BPAEI, and BPAEI films crosslinked using various amounts of V-50. All spectra are scaled by normalizing the intensity of the C–H bands from 2900 to 3100 cm^{-1}.

in crosslinking without salt were used. AIBN needed more than 72 h to form a crosslinked film, while V-501 and VA-044 took 48 h to form crosslinked films. However, V-50 needed only 12 h to form a well-crosslinked film with good physical properties and which could be easily peeled from the glass. None of the other three films could be easily peeled off without being broken into pieces. Therefore, V-50 was used as the initiator for further studies.

The crosslinked films were studied using IR, DSC and conductivity measurements. There was no obvious difference between BPAEI and crosslinked BPAEI in the IR spectrum except in the region from 850 to 1050 cm^{-1} and the region from 1600 to 1720 cm^{-1}. As shown in Fig. 4, the alkene C–H bending vibration bands [16] centered at 995 and 916 cm^{-1} gradually decrease with the increase in V-50 concentration, although the changes are not as significant as those in the region from 1600 to 1720 cm^{-1}, which is shown in Fig. 5. In this region, the band at 1642 cm^{-1} (dashed line) is assigned to the C=C stretching vibration of unconjugated linear alkenes [15,16] while the band at 1673 cm^{-1} (dashed line) is unidentified. The band at 1673 cm^{-1} exists intrinsically in the uncrosslinked BPAEI without V-50 present and grows significantly after crosslinking while the initiator concentration is kept constant. The intensity increase in the band at 1673 cm^{-1} must be related to crosslinking. However, the initiator (V-50) has an IR absorption centered at 1680 cm^{-1}. Due to the small concentration of initiator used in crosslinking, the V-50 band at 1680 cm^{-1} is unlikely to be observed in the crosslinked BPAEI IR spectrum. Further, the frequency and the intensity of this band do not change when neat V-50 was subjected to the same reaction conditions used to crosslink BPAEI. Therefore, the intensity increase in the band at 1673 cm^{-1} is not due to the initiator and must come from some structural changes in the polymer during the crosslinking process. However, at this time it is not possible to assign this band. Therefore, this band may qualitatively indicate presence of crosslinking but cannot quantitatively indicate the crosslink density. The crosslink densities are unknown since there are unreacted C=C bonds after crosslinking as indicated by the presence of alkene vibration bands in Figs. 4 and 5. However, the strength of these films increases with initiator concentration while the swelling decreases, as expected.

Although, the exact mechanism for crosslinking BPAEI is unknown, some possible crosslinking pathways are discussed below. At first, free radicals are generated by initiator, and most either add to the double bond [17] or abstract an allyl hydrogen, generating an allylic radical. The radical can be rearranged along the sidechain and transferred among the sidechains. Thus, many different radicals could be formed in BPAEI. Fig. 6 shows some possible intermediates in the crosslinking process. Finally, intramolecular or intermolecular couplings of these radicals terminate the crosslink reaction. The whole crosslinking process is complex, and unreacted C=C bonds are still present after crosslinking. In the presence of LiTf, the situation becomes more complicated because LiTf may affect the crosslinking in many different ways. For example, the Li$^+$ could coordinate to nitrogen atoms in the polymer backbone and form some relatively stable local structures prior to crosslinking. These structures could possibly position the C=C bonds on these nitrogen atoms further away from each other or closer to each other (Fig. 7), thus helping or hindering the crosslinking process. However, the IR spectrum showed that the band at 1673 cm^{-1} gradually decreased with increasing LiTf concentration when the initiator concentration was kept constant (Fig. 8). Therefore, it is likely that LiTf somewhat suppresses the BPAEI radical crosslinking process.

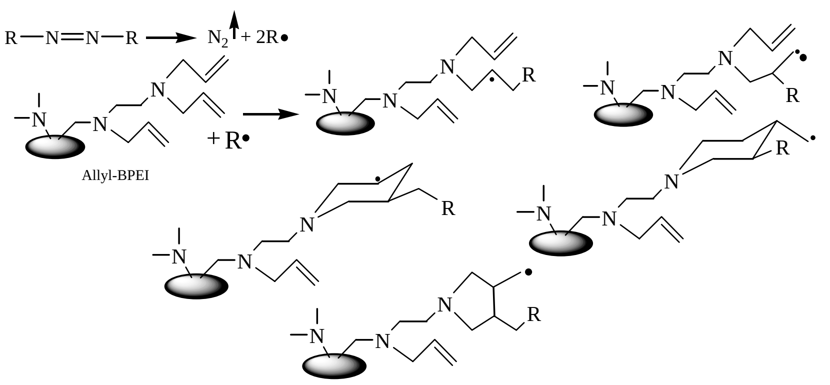

Fig. 6. Possible radical intermediates in the crosslinking mechanism (R–N=N–R represents V-50).

BPAEI has a glass transition temperature (T_g) of −65 °C, which is somewhat lower than the T_g of BPEI (−50 °C), likely as a result of decreased H-bonding. When BPAEI was crosslinked in the presence of 20:1 N:LiTf, the T_g gradually increased with crosslinking initiator concentration (Fig. 9). As shown in Fig. 10, the crosslinked BPAEI films with different V-50 concentration exhibited higher T_gs than the films without LiTf. There are two factors likely contributing to the loss of polymer flexibility during the crosslinking process: structural changes and/or crosslinking of the polymer chains, which restricts polymer backbone motion, and the coordination between Li^+ and nitrogen atoms in the polymer. In Fig. 10, the lower line represents the T_g of crosslinked BPAEI at different initiator concentration and the top line represents the T_g of crosslinked BPAEI–LiTf (20:1 N:Li^+) at different initiator concentrations. In the uncrosslinked BPAEI–LiTf 20:1 (N:Li^+) sample, there is only a contribution from the N–Li^+ coordination, which causes a T_g increase of 17 °C. In the presence of LiTf, the crosslinking of polymer chains and N–Li^+ coordination combine synergistically, instead of additively, to contribute to the increase in T_g. At the compositions near 60:1 (N:initiator), unusual changes in the rates of T_gs increasing were observed both with and without LiTf. These samples were remade fresh and same phenomenon was observed reproducibly. This suggests some undefined morphological changes occur in the crosslinked polymer electrolyte around these initiator concentrations.

The triflate ion SO_3 symmetric stretching ($\nu_S(SO_3)$) vibrational mode has been extensively studied in PEO and PEI complexes with LiTf. In PEO electrolytes containing LiTf, the bands in the $\nu_S(SO_3)$ region have been assigned as free ions (1032 cm^{-1}), contact ion pairs (1041 cm^{-1}), and aggregate species (1050 cm^{-1}) [18–20]. As shown in Fig. 11, the $\nu_S(SO_3)$ band was observed at 1030 cm^{-1} at all LiTf concentrations in the crosslinked BPAEI–LiTf films, suggesting that most of the triflate ions in crosslinked BPAEI were 'free' ions. At higher salt concentrations, a shoulder at 1040 cm^{-1} grew, suggesting the existence of small amounts of contact ion pairs. Therefore, the relative concentrations of various triflate ion species present were fairly independent of salt concentration. IR spectra of BPAEI–LiTf before and after crosslinking showed that the $\nu_S(SO_3)$ band for the BPAEI–LiTf complexes appeared at 1030 cm^{-1} and the relative concentrations of the triflate species were unchanged before and after crosslinking. IR spectra of BPAEI–LiTf crosslinked using various initiator concentrations showed that the relative concentrations of the triflate species appeared to be independent of crosslink density.

A preliminary ionic conductivity study at compositions from 40:1 to 10:1 (N:Li^+) with the polymer repeat unit to

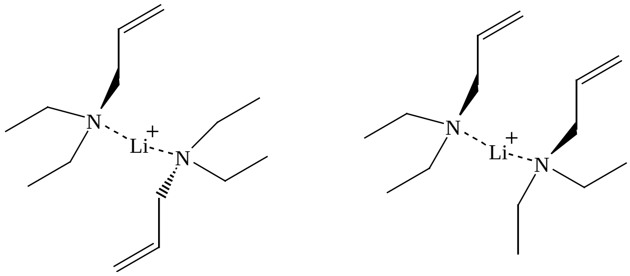

Fig. 7. Possible local conformational structures in BPAEI–LiTf prior to crosslinking, anions are omitted for clarity.

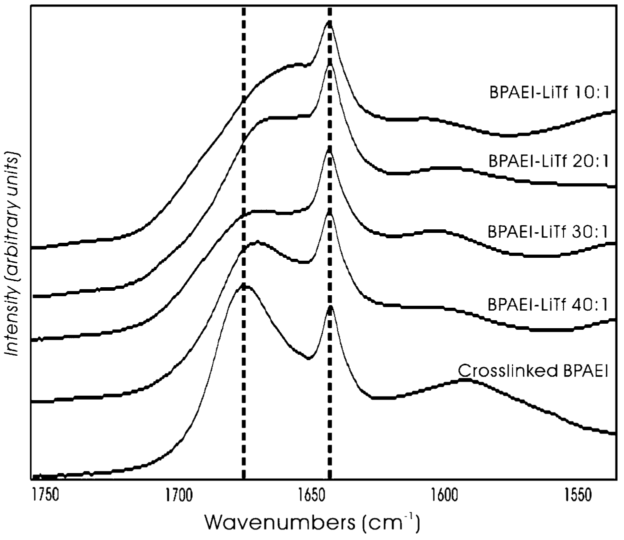

Fig. 8. Infrared spectra of crosslinked BPAEI–LiTf films with 30:1 N:V-50 at various salt compositions (1550–1750 cm^{-1}). All spectra are scaled by normalizing the intensity of the C–H bands from 2900 to 3100 cm^{-1}.

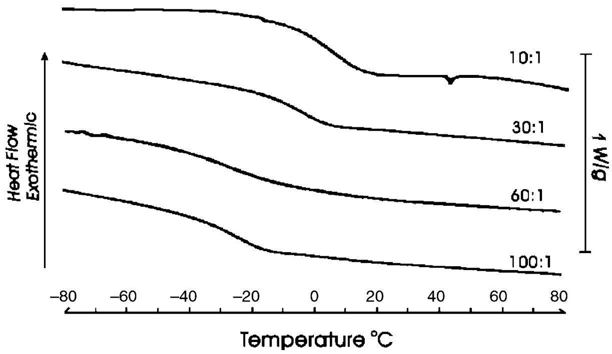

Fig. 9. DSC curves of crosslinked BPAEI films with 20:1 N:LiTf as a function of V-50 crosslinker composition (100:1, 60:1, 30:1, and 10:1).

initiator ratio kept at 30:1 showed that the 20:1 (N:Li$^+$) sample had the best conductivity. Ionic conductivities were measured as a function of initiator composition to determine the most effective initiator concentration (Fig. 12). In this series of measurements, the LiTf composition was 20:1 (N:Li$^+$). For each initiator composition, conductivity samples were individually prepared twice. For each sample, three temperature dependent cycles of measurements were undertaken. After the measurements were performed, IR spectroscopy was used to verify the dryness of the samples. As shown in Fig. 12, the 60:1 (N:initiator) sample was observed to reproducibly perform the best. The fact that the ionic speciation did not change significantly with crosslink density implies that the number of charge carriers was reasonably constant. Therefore, the decrease in polymer segmental motion due to the formation of crosslinks (as related to the T_g of the films) is expected to decrease the ionic mobility, in turn decreasing the ionic conductivity [21]. This trend was observed in every sample except the 60:1 (N:initiator) sample. It should be noted that this sample reproducibly exhibited unusual T_g behavior in the DSC analysis. It is possible that in this sample there is a change in the structure/morphology of the polymer electrolyte which causes an unusual increase in ion mobility even when the general trend of T_g is still increasing.

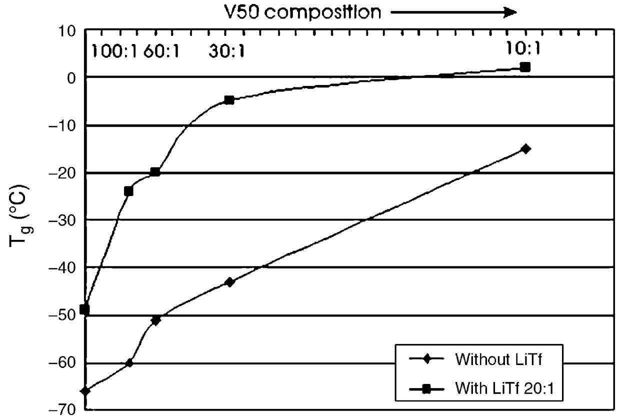

Fig. 10. Glass transition temperatures of BPAEI and crosslinked BPAEI films as a function of V-50 crosslinker concentration, with and without 20:1 N:LiTf present.

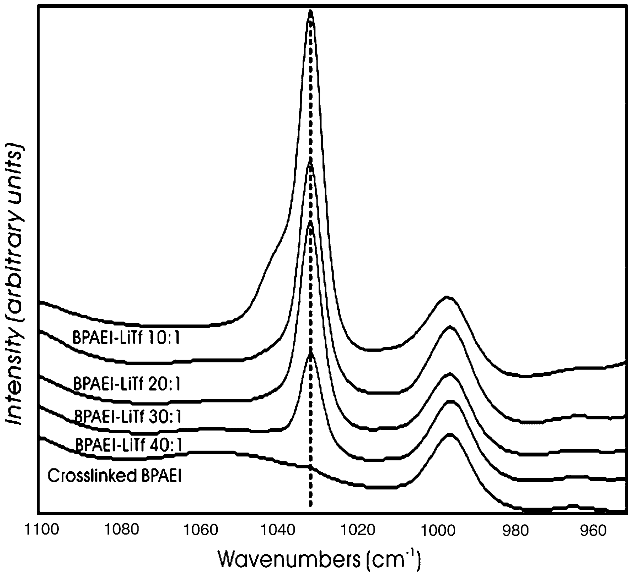

Fig. 11. LiTf composition dependent IR spectra of BPAEI and BPAEI–LiTf films crosslinked using 60:1 N:V-50. All spectra are scaled by normalizing the intensity of the C–H bands from 2900 to 3100 cm^{-1}.

Conductivity measurements at temperatures between 20 and 80 °C of a series of samples in which the LiTf composition was varied while maintaining the optimum initiator composition (60:1) demonstrated that 20:1 was still the optimum salt composition (Fig. 13). The number density of ‘free’ ions, the primary charge carriers, might be expected to increase with increasing salt concentration, and conductivity should increase accordingly. Indeed this is observed at low salt concentration. However, as the salt concentration increases, the increasing number of N–Li coordination interactions decreases the segmental motion of the polymer chains between covalent crosslink sites. This decreases the ionic conductivity. At some composition between 30:1 and 20:1 these two factors balanced each other and an optimum conductivity was achieved.

At a fixed N:V-50 ratio of 60:1, apparent energies of activation calculated from the temperature dependent conductivity data increased monotonically from 17.8 to

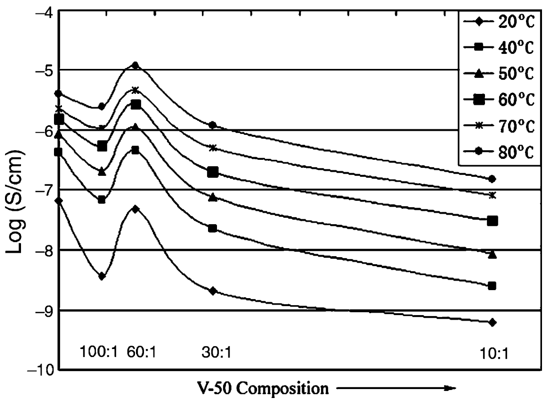

Fig. 12. Ionic conductivity of crosslinked BPAEI–LiTf films as a function of V-50 concentration and temperature with 20:1 (N:Li$^+$) LiTf.

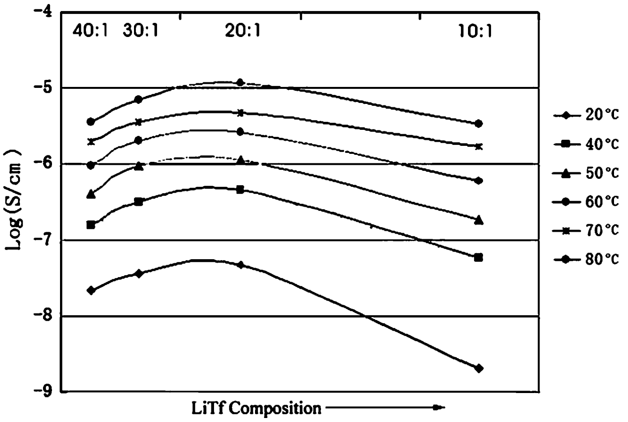

Fig. 13. Ionic conductivity of BPAEI–LiTf films crosslinked using 60:1 (N:initiator) V-50 as a function of LiTf concentration and temperature.

25.8 kcal/mole as a function of increasing LiTf concentration (40:1–10:1 N:Li, respectively). The IR data for these samples shows speciation to remain relatively constant as a function of LiTf concentration and temperature (data not shown). Therefore, the increase in the apparent energy of activation is likely due mostly to decreases in ion mobility stemming from morphological changes induced by the presence of LiTf as reflected in the increasing T_g for the samples. At a fixed N:Li ratio of 20:1, apparent energies of activation calculated from the temperature dependent conductivity data were 15.7, 22.1, 18.5, 22.0, and 19.9 kcal/mol as a function of increasing cross-linker (V-50) concentration (none, 100, 60, 30, and 10:1 N:V-50, respectively). The IR data for these samples also shows speciation to remain relatively constant as a function of LiTf concentration and temperature. Therefore, the variability in the apparent energy of activation is again likely due mostly to changes in ion mobility stemming from a combination of morphological changes on cross-linking as reflected in the variable T_g for the samples, including the unusual minimum for the 60:1 N:V-50 sample.

One issue of using V-50 as radical initiator is that V-50 is a hydrochloride salt. In the polymer electrolyte, these chloride ions may migrate under the electric field to the interfacial area between the electrolyte and lithium cathode and form thin layers of lithium chlorides, blocking the transportation of lithium ion in and out the cathode. This could potentially affect the ionic conductivity of the crosslinked BPAEI polymer electrolyte in battery applications. To address this issue, a crosslinked BPAEI polymer electrolyte (20:1 N:Li^+) was prepared using VA-061 (dimethyl 2,2-azobisisobutyrate) (30:1 N:VA-061), a radical initiator without chloride. Using similar crosslinking conditions, longer time (>72 h) was needed to form a solid film and the resulting electrolyte had less physical strength than the electrolyte prepared using V-50. Based on IR (data not shown), the ionic speciation of the polymer electrolyte was found not to change with different initiators. The conductivity of a polymer electrolyte prepared using VA-061 was of the same magnitude as that of a comparable sample using V-50 (data not shown).

4. Conclusions

BPEI may be allylated to give a polyamine that can be radically cross-linked to form mechanically coherent, free-standing films. With LiTf present during cross-linking, solid polymer electrolytes (SPEs) were formed. Ionic conductivity of these SPEs was a strong function of temperature and morphology resulting from the cross-linking and, to a lesser extent, lithium salt concentration. The conductivity measurements were consistent with spectroscopic studies which showed that ionic speciation is relatively invariant with cross-link or salt concentration. Thermal studies suggesting that T_g, and therefore, ion mobility, is very dependent on both cross-linking and LiTf concentration. These SPEs showed a maximum conductivity of ca. 10^{-5} S/cm at 80 °C, the minimum conductivity needed for fabrication of functioning lithium batteries. Cross-linking of allylated PEI-based polymers that have been modified to increase ion mobility is therefore, a viable strategy for the formation of useful SPEs.

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