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Influence of DGEBA crosslinking on Li^+ ion conduction in poly(ethyleneimine) gels

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Abstract

We characterize the DC conductivity (σ_0) of solution electrolytes prepared by adding $LiCF_3SO_3$ (LiTf) salt to a (50/50 w/w) solution of branched poly(ethyleneimine) (PEI) in *N*,*N*-dimethylformamide (DMF). The value of σ_0 increases with decreasing LiTf concentration over the range of compositions studied due to the formation of contact ion pairs at higher LiTf concentrations, with the highest value of σ_0 exceeding 10^{-3} S cm^{-1} at 20 °C. Rubber-like gel electrolytes are prepared by epoxide–amine crosslinking of selected solutions by addition of diglycidyl ether of bisphenol A (DGEBA). Holding the [N]:[Li] mole ratio fixed, increasing the crosslink density dramatically decreases σ_0 at all temperatures studied. The decrease in σ_0 cannot be attributed to an increase in the glass transition temperature, as little variation in T_g is noted amongst the samples due to their high solvent content. Rather, we propose that the decrease in conductivity is due to loss of fast segmental motions associated with chain ends, which become tethered to the network upon crosslinking.

Keywords: DGEBA; Gel electrolyte; Poly(ethyleneimine)

1. Introduction

Compared to conventional nickel–cadmium (Ni–Cad) batteries, rechargeable lithium ion batteries offer higher energy density, longer lifetimes, and lighter weight [1]. Because of these technological advantages, materials research efforts of the past 25 years have been directed toward developing and improving safe, commercially feasible lithium ion batteries for use in portable electronics. Recent efforts have focused on developing safe electrolyte materials that exhibit minimal flammability and toxicity while preserving high DC ionic conductivity (typically $10^{-3}\ \mathrm{S\,cm^{-1}} < \sigma_0 < 10^{-2}\ \mathrm{S\,cm^{-1}}$) and lithium transference number over the widest possible temperature range. Commercial liquid electrolyte formulations generally contain a mixture of a lithium salt with solvents, polymers, and fillers, but liquid formulations pose the risk of leakage from a punctured or ruptured cell. Plasticized polymer electrolytes, including solid polymers and lightly crosslinked gels, offer ionic conductivity approaching that of polymer solution electrolytes, while solid or rubber-like mechanical properties reduce the likelihood of leakage from a ruptured cell. Widespread efforts have therefore been devoted to development of readily processable plasticized polymer electrolytes that offer safe performance, thermal and electrochemical stability, high ionic conductivity, and good mechanical strength over a broad temperature range [2].

Previous studies of plasticized polymer electrolytes have considered numerous systems based upon polymers including poly(ethylene oxide) (PEO) [3–9], poly(acrylonitrile) (PAN) [10–21], poly(methyl methacrylate) (PMMA) [22–32], poly(vinylidene fluoride) (PVdF) [33–41], and others [2,8]. Among the numerous "gel" formulations studied, one must distinguish between (1) plasticized semicrystalline polymers, where crystal lamellae serve as physical crosslinks; (2) two-phase electrolytes where the solvent fills a network of pores in a solid, insoluble polymer scaffold; and (3) solvent-swollen,

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chemically crosslinked polymer networks. Covalently crosslinked gel electrolytes are attractive because the solvent or plasticizer increases the mobility of the Li^+ cations, while crosslink junctions maintain rubber-like mechanical behavior. In crosslinked gels, the conductivity is not hampered by the presence of crystalline microdomains as in plasticized semicrystalline solid polymers, and no continuous pathways exist for possible lithium dendrite growth as in porous "gel" electrolytes [8,42,43]. However, excessive dilution of crosslinked gel electrolytes also generally degrades mechanical properties, so there exists a trade-off between maximizing conductivity (increasing solvent content) and maintaining desirable mechanical behavior [8].

Among numerous studies of gel electrolytes, those based upon poly(ethyleneimine) or PEI [44,45], a polyamine having ($-CH_2CH_2NH-$) backbone repeat units, are promising due to their low glass transition temperatures, high ionic conductivities, and ease of random crosslinking via primary and secondary amine groups. The amines in the backbone and end groups of PEI coordinate with the Li^+ cation, reducing the binding energy between Li^+ and the counter-anion (e.g. SbF_6^-, $CF_3SO_3^-$) [46,47], and increasing the concentration of loosely bound Li^+ cations available for conduction. Several studies of PEI-based electrolytes have appeared recently. Glatzhofer et al. studied electrolytes of poly(*N*-(2-(2-methoxyethoxy)-ethyl)ethylenimine), a PEO–PEI copolymer, which exhibited σ_0 as high as 7×10^{-5} S cm^{-1} at 60 °C [48]. Frech et al. characterized PEI gel electrolytes crosslinked by tetraethylene glycol diacrylate with diglyme as solvent, which had σ_0 as high as 2×10^{-4} S cm^{-1} at 20 °C [44]. Armand et al. have examined solid PEI–PEO–PEI triblock copolymer electrolytes, which serve as a dual matrix for Li^+ and Cu^{2+} ions [49,50].

Random crosslinking of PEI in solution is an attractive and economical processing strategy to produce rubber-like electrolytes, an idea first pursued by Glatzhofer et al., who crosslinked PEI by a Michael addition reaction between acrylates and the amines of PEI [45]. However, no previous study has systematically examined how crosslink density influences ionic conductivity of PEI gel electrolytes, a key concept that is broadly applicable to optimization of any crosslinked polymer gel electrolyte system. Our study characterizes both PEI solutions and gels prepared in 50 mass% *N*,*N*-dimethylformamide (DMF) by random crosslinking with the diglycidyl ether of bisphenol A (DGEBA), a standard epoxide–amine reaction. After characterizing the influence of $LiCF_3SO_3$ (LiTf) concentration on DC conductivity in solutions, we examine how DC conductivity is affected by crosslink density (DGEBA concentration), and propose a physical interpretation of the observed trend.

2. Experimental section

2.1. Solution and gel electrolyte synthesis

Randomly branched PEI (nominal molar mass = 10,000 g mol^{-1}, 99%) was obtained from Alfa Aesar (Stock # 40331, Lot # J16R012). PEI was dried under vacuum for 18 h or more at 70 °C prior to use to remove traces of water. Diglycidyl ether of bisphenol A (DGEBA), *N*,*N*-dimethylformamide (DMF), and anhydrous, electronics-grade lithium triflate (LiTf) (99.995%) were obtained from Sigma-Aldrich and used as received. Synthesis of the PEI solutions and gels was conducted in a glovebox under anhydrous nitrogen atmosphere.

2.1.1. System I: solution electrolytes containing LiTf

LiTf was added to a stock solution of 50 mass% PEI and 50 mass% DMF. The mixture was stirred for 5 min, then allowed to stand for an additional 24 h before characterization of dielectric properties. Several solutions were prepared, each containing a different concentration of LiTf. The LiTf concentrations are reported in terms of the [N]:[Li] ratio, defined as the ratio of the moles of ($-CH_2CH_2NH-$) units to the moles of LiTf salt. The number of moles of ($-CH_2CH_2NH-$) units was calculated by dividing the mass of PEI by 43.0 g mol^{-1}. The compositions of all System I solution samples are quoted in Table 1.

2.1.2. System II: crosslinked gel electrolytes without LiTf

Neat DGEBA was added to a homogenized solution of PEI in DMF, followed by stirring for 5 min at 20 °C. The homogenized mixture was cured in a sealed container at 100 °C for 4 h. The overall DMF concentration was held fixed at 50 mass% for all gels, with the remaining 50% consisting of polymer. Samples were cured between glass plates to produce flat sheets of 1.25 mm thickness for mechanical characterization, or in sealed glass vials with minimal air space to produce cylindrical samples for swelling measurements. Samples were labeled A through I in order of increasing DGEBA content. The compositions of all System II gel samples are quoted in Table 2.

2.1.3. System III: crosslinked gel electrolytes containing LiTf

LiTf was added to a homogenized solution of PEI in DMF, and the mixture was stirred for 5 min to dissolve the salt. The amount of LiTf added was held fixed at 0.121 g LiTf per 1.0 g PEI, giving [N]:[Li] = 30:1. Neat DGEBA was added to this solution, and the mixture was stirred for an additional 5 min at 20 °C. Samples were labeled A′ through I′ in order of increasing DGEBA concentration, and the compositions of all samples are quoted in Table 3. The reaction mixture was cured

Table 1
Compositions of non-crosslinked solution electrolytes (System I)

Sample	Mass % PEI	Mass % DMF	Mass % LiTf
[N]:[Li] = 4:1	34.4	34.4	31.2
[N]:[Li] = 5:1	36.7	36.7	26.6
[N]:[Li] = 10:1	42.3	42.3	15.4
[N]:[Li] = 20:1	45.8	45.8	8.4
[N]:[Li] = 30:1	47.2	47.2	5.6

Table 2
Compositions of gels (without LiTf salt) prepared for swelling and modulus measurements (System II)

Sample	Mass % PEI	Mass % DGEBA	Mass % DMF	Mole ratio CH_2CH_2NH:DGEBA
A	48.0	2.0	50.0	190
B	46.9	3.1	50.0	119
C	46.2	3.8	50.0	95
D	44.4	5.6	50.0	63
E	43.5	6.5	50.0	53
F	42.9	7.1	50.0	47
G	42.3	7.7	50.0	43
H	41.4	8.6	50.0	38
I	40.0	10.0	50.0	32

at 100 °C for 4 h. For mechanical measurements, samples were cured between glass plates to produce flat sheets of 1.25 mm thickness. For dielectric measurements, the reaction mixture was cured between aluminum electrodes separated by 535 μm polytetrafluoroethylene (PTFE) spacers.

2.2. Swelling experiments

Swelling experiments were performed on System II gels (without LiTf) to examine the crosslinking reaction without the complicating effects of added salt. Each gel contained equal mass fractions of DMF and polymers, so DMF concentration during crosslinking was held constant. Swelling of gels in DMF was accomplished by completely submerging cylindrical gels of initial diameter $D_0 = 0.94$ cm and initial length L_0, in DMF for one week, during which time the DMF was replaced with fresh solvent daily. The equilibrium degree of swelling was defined as

$$\mathrm{DS} = (L_e/L_0)(D_e/D_0)^2 \tag{1}$$

where L_e and D_e are the length and diameter of the swollen cylinder at equilibrium. DS is a volume swelling ratio referenced to the original gels, which contained 50 mass% DMF, and is not referenced to the "dry" state. DS = 1.0 corresponds to a gel that underwent no additional swelling upon immersion in DMF.

Table 3
Compositions of gels (with LiTf salt) prepared for mechanical measurements and dielectric spectroscopy (System III), and the estimated glass transition temperature for each (DMA, 1 Hz)

Sample	Mass % LiTf	Estimated T_g (°C)
A′	5.48	-30 ± 3
B′	5.36	-30 ± 3
C′	5.28	-33 ± 3
D′	5.09	-31 ± 3
E′	4.99	-25 ± 3
F′	4.92	-26 ± 3
G′	4.85	-30 ± 3
H′	4.76	-28 ± 3
I′	4.61	-32 ± 3

2.3. Dynamic mechanical analysis (DMA)

Modulus measurements were performed on a TA Instruments Q800 DMA in oscillatory shear at 30 °C at 1 Hz and strain amplitude of 0.5%. At $\omega = 1$ Hz, $G''(\omega) << G'(\omega)$ for all samples studied, so the shear modulus was taken as $G \approx G'(\omega)$. Data were acquired and analyzed by the TA Instruments Universal Analysis software. Glass transition temperatures of System III gels (with added salt) were measured by performing a constant-frequency temperature ramp over the range ($-90\,°C < T < 30\,°C$). The peak value of the mechanical loss tangent at a frequency of 1 Hz, $\tan\delta \equiv G''(\omega)/G'(\omega)$, was taken as an approximation to T_g.

2.4. FT-IR spectroscopy

Polymer films were cast between 2 mm thick ZnSe windows and characterized in transmission using a Digilab FTS 800 (Scimitar Series) FT-IR spectrometer from 500 cm^{-1} to 4000 cm^{-1} at intervals of 1.0 cm^{-1}. A nitrogen purge was maintained to eliminate as much moisture and carbon dioxide as possible; 25 transients were collected and combined, and all spectra were corrected for background by subtracting a reference spectrum obtained with clean ZnSe windows in the beam.

2.5. Broadband dielectric spectroscopy

Dielectric (impedance) spectra were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency range 10^{-2}–10^{6} Hz with an applied voltage of 1.5 V. Non-crosslinked solution electrolytes (System I) were characterized in a liquid cell, which consisted of a bottom "cup" electrode and a top plate separated by a PTFE spacer. Crosslinked gel electrolytes (System III) were confined between polished aluminum electrodes kept at constant separation by a PTFE spacer of 535 μm thickness and 20 mm diameter. Temperature was held constant for each measurement while a frequency sweep was performed. Temperatures were controlled to within 0.2 °C over the range −20 °C to 60 °C. Conductivities were measured at 20 °C before and after the dielectric measurement procedure to ensure that no thermal or electrochemical processes altered the sample properties during measurement. Data was collected on the WinDETA program and fitted by the Novocontrol WinFit program. Values of DC conductivity σ_0 were obtained by fitting the dielectric loss in the conductive regime by

$$\varepsilon''(\omega) = \left(\frac{\sigma_0}{\omega\varepsilon_{\mathrm{vac}}}\right)^n \tag{2}$$

where ω is the radial frequency and $\varepsilon_{\mathrm{vac}}$ is the vacuum permittivity.

2.6. Nuclear magnetic resonance (NMR) spectroscopy

The branched PEI received from the supplier was characterized by ^{15}N NMR in D_2O solution. Data were obtained on a Bruker AMX-2-500 operating in the quadrature mode at 25 °C. The ^1H and ^{15}N resonance frequencies for this instrument are 500.13 MHz and 50.68 MHz, respectively. Ammonium chloride (98 atom% ^{15}N, Sigma-Aldrich) was used as an external chemical shift reference, taken to have $\delta = 24$ ppm with respect to $^{15}NH_3$ [51]. Shifts reported here are referenced to $^{15}NH_3$. ^{15}N data without decoupling were obtained with a spectral width of 20,883 Hz, a pulse width of 5 μs ($\pi/2 \sim 10$ μs) and a relaxation delay of 1.8 s; 43,890 transients were acquired. ^{15}N data with ^1H decoupling were obtained with the same spectral width and a pulse width of 7 μs using inverse gated decoupling. In this experiment the WALTZ-16 ^1H decoupling is only turned on during data acquisition. A long (10 s) relaxation delay without ^1H decoupling was used to suppress negative NOE effects observed with shorter relaxation delays (2 s).

3. Results and discussion

3.1. PEI precursor characterization: ^{15}N NMR spectroscopy

PEI is available in both branched and linear architectures, which differ in their relative content of primary (1°), secondary (2°), and tertiary (3°) amine functional groups. The PEI in this study is a randomly branched, amorphous polymer of nominal molar mass $M_n = 10\ \mathrm{kg\,mol^{-1}}$ (quoted by the supplier). The PEI was characterized by ^{15}N NMR spectroscopy in D_2O solution (Fig. 1). ^1H-decoupled spectra were obtained as described in Section 2, but no significant effect of decoupling was observed, indicating that each resonance in Fig. 1 corresponds to nitrogen in a different chemical bonding environment. In other words, the closely spaced peaks are not doublets arising from $^{15}N{-}^1H$ coupling. In addition, the lack of $^{15}N{-}^1H$ coupling indicates that rapid exchange of hydrogen/deuterium occurs between the amines and water.

By comparison to chemical shift ranges quoted in earlier ^{15}N NMR studies of branched PEI [52,53], some conclusions can be drawn regarding the relative proportions of 1°, 2°, and 3° amines in the PEI. Resonances A1 (40.9 ppm) and A2 (40.4 ppm) fall in the range expected for either protonated 2° ($R_2{-}NH_2^+$) or protonated 3° ($R_3{-}NH^+$) amines. Resonances B1 (36.3 ppm) and B2 (35.8 ppm) fall in the range expected for either non-protonated 2° ($R_2{-}NH$) or non-protonated 3° ($R_3{-}N$) amines. Singlet C (22.7 ppm) is attributed to non-protonated 1° terminal amines ($-RNH_2$). Comparison of integrated resonances suggests that the sample contained approximately 22 mol% 1° amines and 78 mol% combined 2° and 3° amines. Thus, the unmodified PEI is quite highly branched, with about one of every five N atoms belonging to a terminal $-CH_2CH_2NH_2$ group. We note the possibility that the 1°, 2° and 3° amines in PEI may have different T_1 relaxation times due to differences in segmental mobility [54], but the integrals obtained from spectra without $^1H{-}^{15}N$ decoupling (1.8 s relaxation delay) were similar to those obtained with inverse gated decoupling (10 s relaxation delay), suggesting that our results are nearly quantitative.

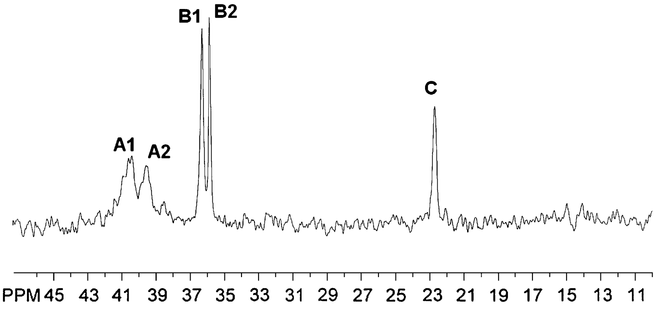

Fig. 1. ^{15}N NMR spectrum of branched PEI as received from the supplier (D_2O solvent).

3.2. Characterization of solution electrolytes (System I)

Solution electrolytes having [N]:[Li] mole ratios of 30:1, 20:1, 10:1, 5:1, and 4:1 were prepared, where [N] is defined as the calculated molar concentration of PEI repeat units, and excludes the nitrogen from DMF. FT-IR spectra for these non-crosslinked solutions are presented in Fig. 2 over the region (1010–1060 cm^{-1}). Curves are plotted as continuous lines rather than discrete data points for clarity. The band centered near 1033 cm^{-1} is attributed to the SO_3 symmetric stretch of the Tf counterion, and the shoulder peak near 1042 cm^{-1} is attributed to formation of LiTf contact ion pairs [47,55–67]. Formation of ion pairs and/or triple ions is also observed in DMF/LiTf solutions (without polymer), and contact ion pairs are favored over free ions as LiTf concentration increases [55]. Formation of contact ion pairs at high LiTf concentrations was also observed by Frech et al. in solvent-

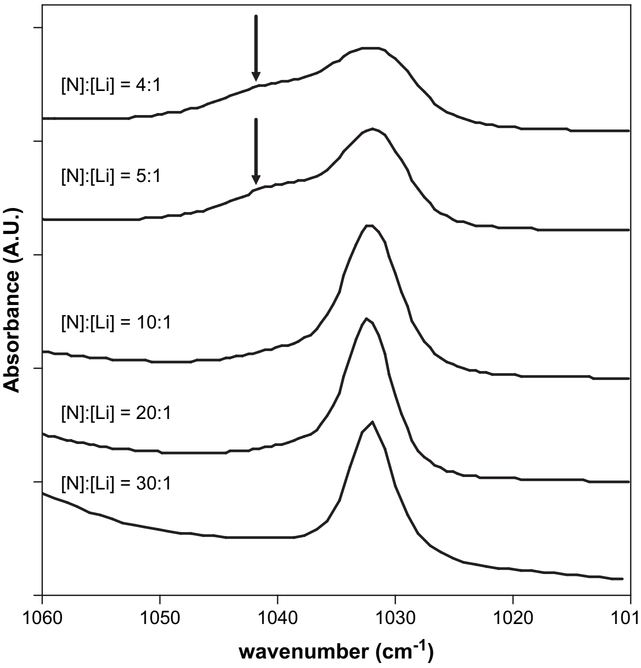

Fig. 2. FT-IR spectra (SO_3 symmetric stretch region) for non-crosslinked solution electrolytes (System I).

free mixtures of PEI/LiTf [47] and by Glatzhofer et al. in PEI gel electrolytes [44]. Thus, it is not surprising that Fig. 2 shows the fraction of free ions is highest at the lowest LiTf concentration.

Dielectric spectra of a non-crosslinked solution electrolyte having [N]:[Li] = 30:1 are presented in Fig. 3. Spectra were also collected for [N]:[Li] = 4:1, 5:1, 10:1, and 20:1. The dielectric loss $\varepsilon''(\omega)$ exhibits a linear dependence on ω at high frequencies, which is assumed to arise from the motion of Li^+ and Tf^- ions. At lower frequencies, electrode polarization screens the dielectric response of the material. The DC conductivity σ_0 determined by Eq. (2) is plotted vs. the [N]:[Li] ratio in Fig. 4, illustrating that σ_0 decreases strongly at low [N]:[Li] ratios. Some of the solution electrolytes exhibited ionic conductivity exceeding 10^{-3} S cm^{-1} at 20 °C, close to the desirable range for battery electrolytes. The lower values of σ_0 for samples having [N]:[Li] = 5:1 and 4:1 suggest that the concentration of "free" Li^+ ions available for conduction decreases at high LiTf concentrations due to formation of contact ion pairs and/or triple ions.

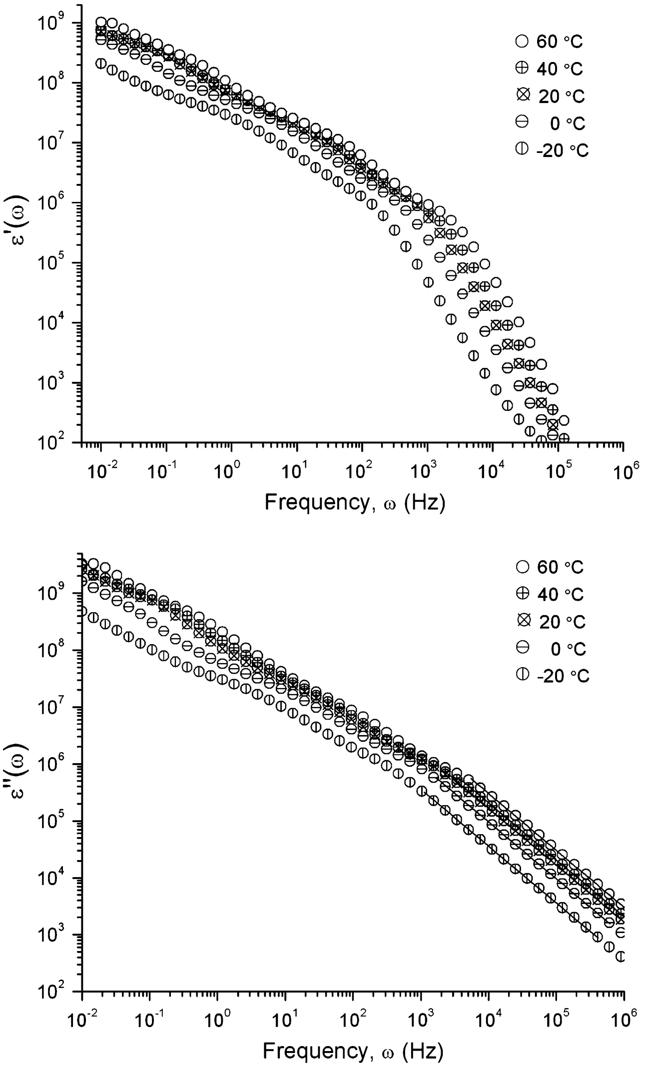

Fig. 3. Dielectric constant $\varepsilon'(\omega)$ and loss $\varepsilon''(\omega)$ for System I solution electrolyte with [N]:[Li] = 30:1. Lines are least squares fits to Eq. (2) (used to determine σ_0).

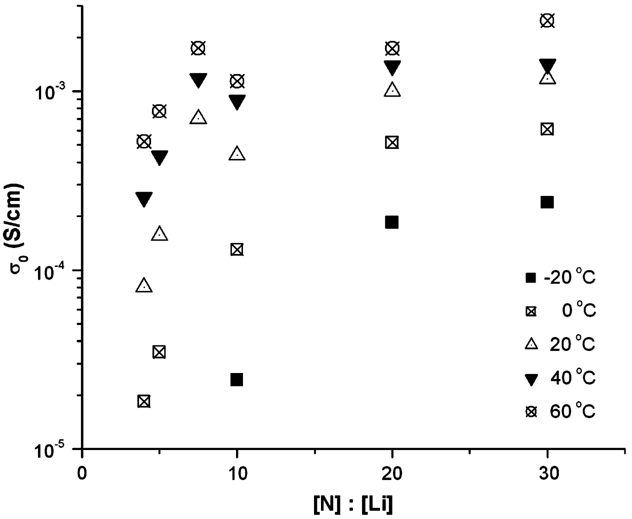

Fig. 4. Fitted values of DC conductivity (σ_0) for System I solution electrolytes.

3.3. Characterization of crosslinked gel electrolytes without LiTf (System II)

Gels were prepared via epoxide-amine random crosslinking in DMF, a simple and versatile reaction that produces stable covalent C–N bonds (Fig. 5). Only 1° and 2° amines can participate in the crosslinking reaction, and 1° amines can presumably react twice with epoxide groups [68]. The 1° amines are the least sterically hindered, and perhaps the most likely to undergo reaction with an epoxide group. Crosslinking is slow enough at ambient temperature to permit thorough mixing without gelation, but the gel point is reached within a few minutes at 100 °C. DMF is a good solvent for both PEI and DGEBA at 20 °C, and it offers a relatively high dielectric constant (38.3), which encourages separation of the Li^+ cations from the Tf^- counterions. Compositions of System II gel samples (designated A–I) are presented in Table 2. The ratio of PEI repeat units (moles –CH_2CH_2NH–) to moles DGEBA was varied from 190 (sample A, least densely crosslinked) to 32 (sample I, most densely crosslinked). All samples reached the gel point, producing optically transparent, slightly yellow, rubber-like networks. As DGEBA content increased, samples varied from pliable and tacky (sample A) to rubber-like and quite stiff (sample I). In no case did we observe any visual evidence of macroscopic phase separation or inhomogeneity after cure.

Equilibrium swelling experiments were conducted in pure DMF using System II gels without salt to verify that the gel point had been reached, and to provide a comparative measure of the effective crosslink density. All samples reached an equilibrium degree of swelling (DS) in DMF (Fig. 6), unlike the non-crosslinked PEI, which dissolved readily. The most weakly crosslinked gel (sample A) fragmented extensively during swelling, precluding accurate measurement of DS,

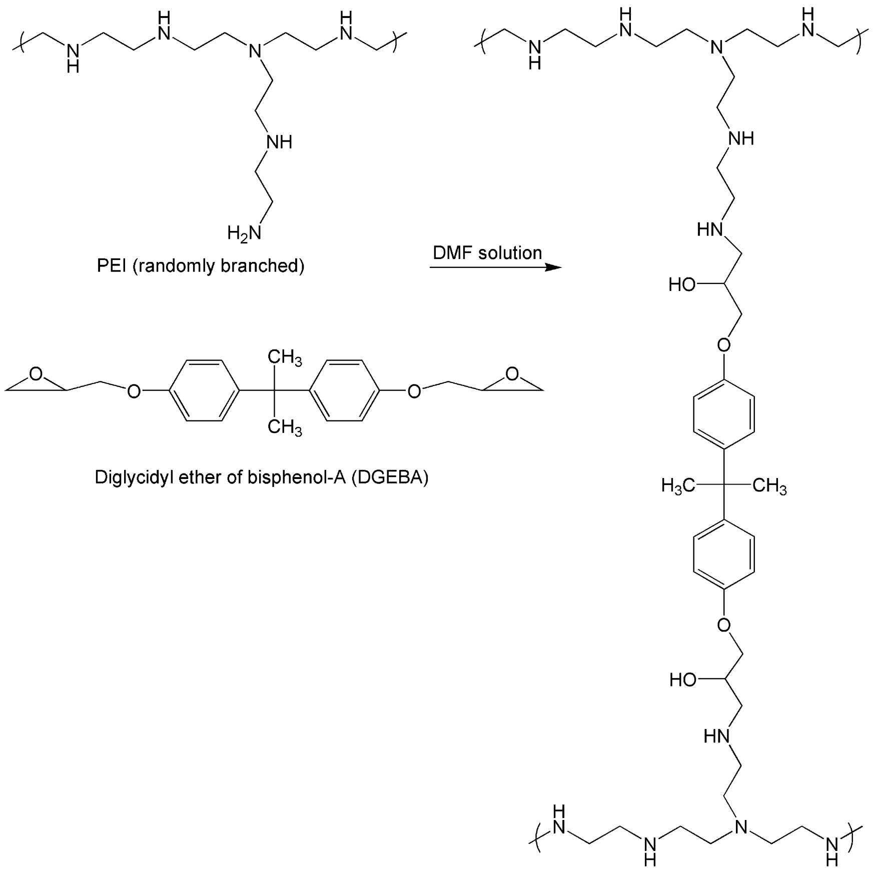

Fig. 5. Crosslinking reaction between DGEBA and PEI. Reaction of epoxides with secondary amines in the PEI backbone is also possible.

but all others remained intact. Sample A may closely approximate the minimum DGEBA concentration for gelation. DS is quite low (about 1.1 or less) for samples E, F, G, H, and I, which absorbed very little DMF beyond that already present at crosslinking. These densely crosslinked networks have very short elastic chains between junction points.

The shear storage moduli (G') of System II gels were measured by DMA at a frequency of 1 Hz immediately after crosslinking (Fig. 6). Measured values of G' ranged from 0.018 MPa (sample B) to 0.31 MPa (sample I). Increasing the DGEBA concentration strongly enhances the storage modulus, as expected for a random crosslinking process. The average molar mass between crosslink junctions (M_c) decreases with increasing chemical crosslink density. The modulus of a rubber-like network with short elastic chains is expected to scale as $(G/RT) \sim \nu \sim (1/M_c)$, where ν is the number density of elastically effective network chains. (G/RT) is approximately proportional to the concentration of chemical crosslinks for a densely crosslinked network where entanglement effects are not significant. Note that the total crosslink density in a given sample may exceed the concentration of DGEBA units due to the presence of 3° amines in the original PEI, which can potentially serve as additional effective crosslink junctions.

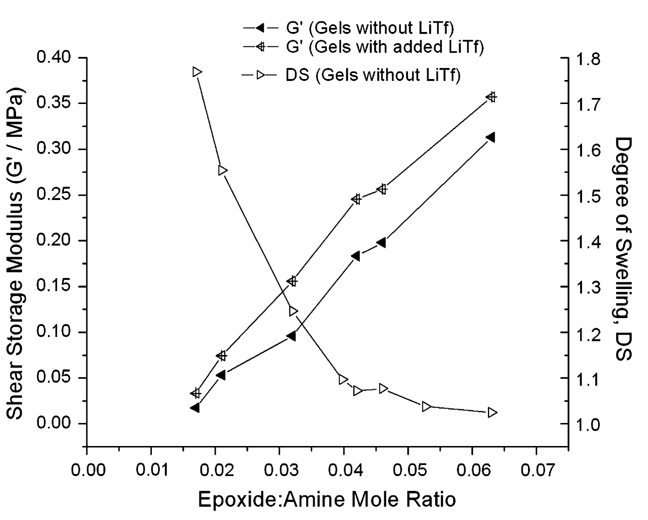

Fig. 6. Shear storage moduli of System II and System III gels measured at 30 °C and $\omega = 1$ Hz, and equilibrium swelling of System II gels in DMF at 23 °C.

3.4. Characterization of crosslinked gel electrolytes containing LiTf (System III)

Based upon the measured DC conductivities of the solution electrolytes and the evidence of contact ion pair formation from FT-IR spectroscopy, crosslinked gels having [N]:[Li] = 30:1 were chosen for further study. Gel formulations (A′ through I′), described in Table 3, were identical to formulations (A through I) described in Table 2, except LiTf salt was added prior to crosslinking. The shear storage moduli determined by DMA for System III gels are plotted in Fig. 6 for comparison to System II gels. The storage moduli of the System III gels are generally higher than the corresponding System II gels. This apparent enhancement of the storage modulus at $\omega = 1$ Hz may be attributed to the interactions of Li^+ cations with PEI segments, which may function as transient physical crosslinks. Addition of LiTf salt (≈ 5 mass%) did not adversely affect macroscopic gelation or mechanical properties for any of the samples studied.

Fig. 7 presents dielectric spectra for gel I′ (most densely crosslinked). The spectra are qualitatively similar to those of the non-crosslinked solution electrolyte having [N]:[Li] = 30:1 (Fig. 3). Fig. 8 is a plot of the fitted values of σ_0 for both non-crosslinked liquids and crosslinked gels as a function of the mole ratio of epoxides to amines, illustrating that σ_0 decreases strongly with increasing DGEBA content. The most densely crosslinked gel, sample I′, had σ_0 less than 1% of the value measured for the non-crosslinked solution. Thus, from an engineering standpoint, a trade-off exists between maintaining high conductivity and achieving high storage modulus by crosslinking for this system. Fig. 9 plots the dependence of conductivity on inverse temperature for the same group of samples. The downward trend of σ_0 with increasing $(1/T)$ is similar for all samples studied, but the conductivity is substantially attenuated as crosslink density increases.

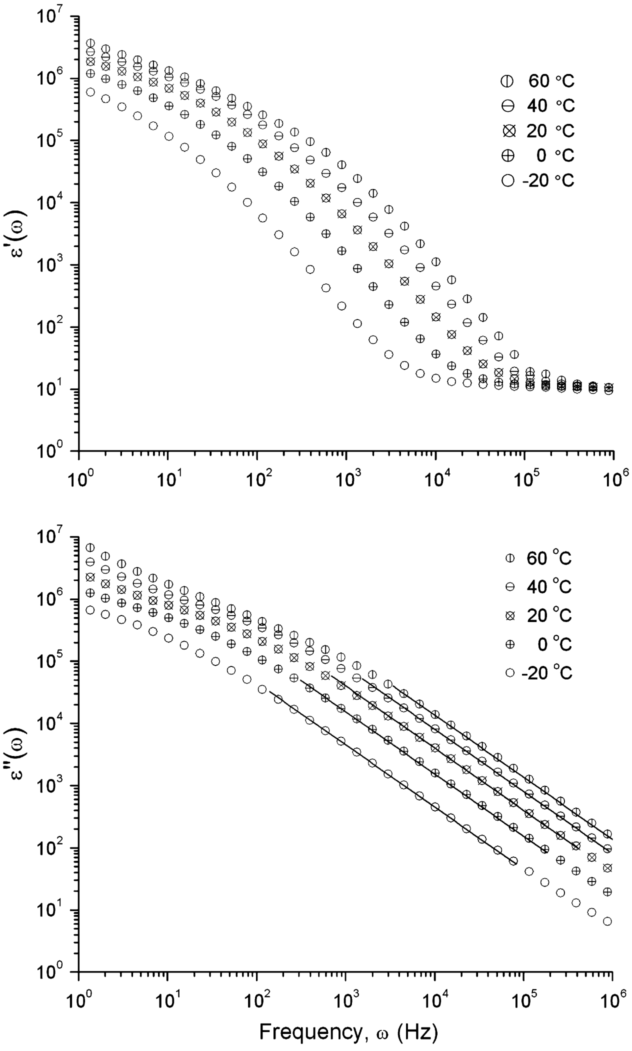

Fig. 7. Dielectric constant $\varepsilon'(\omega)$ and loss $\varepsilon''(\omega)$ for gel electrolyte (System III, Gel I′) having [N]:[Li] = 30:1. Lines are least squares fits to Eq. (2) (used to determine σ_0).

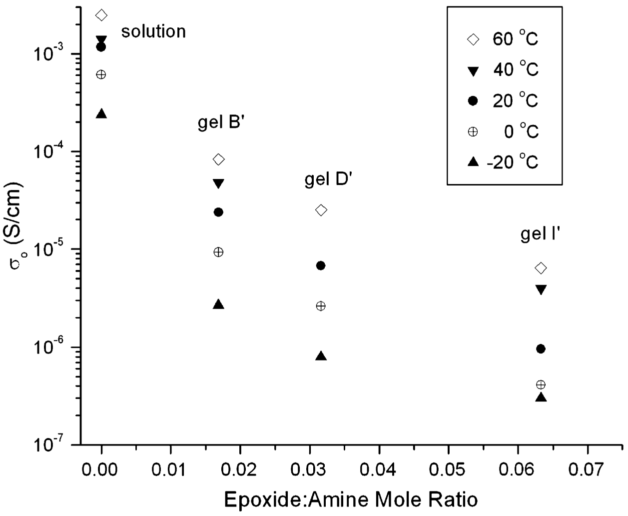

Fig. 8. Fitted values of the DC conductivity (σ_0) for System I solution electrolyte and System III gel electrolytes, all of which have [N]:[Li] = 30:1.

The observed depression in σ_0 with increasing crosslink density may be attributed to a reduction in the mobility of charge carriers following crosslinking. Reaction of terminal 1° amines of PEI with DGEBA to produce crosslink junctions reduces the overall concentration of PEI chain ends, and segments in chain ends lose translational degrees of freedom. Dangling chains are known to enhance Li^+ ion mobility in (solvent-free) polyether networks [69,70]. It is plausible that the concentration of chain ends may also affect ion mobility in PEI gel electrolytes, assuming the motion of charge carriers is coupled to the segmental motions of the network chains. Although segmental motion in the crosslinked gels is

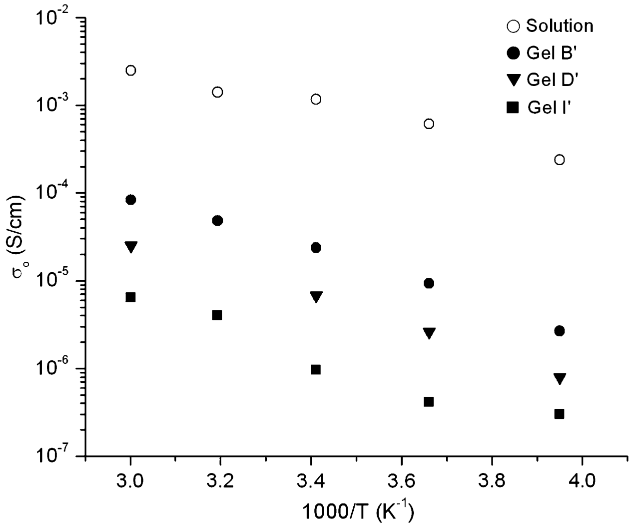

Fig. 9. Dependence of DC conductivity (σ_0) on inverse temperature for System I solution electrolyte and System III gel electrolytes, all of which have [N]:[Li] = 30:1.

increasingly restricted as crosslink density increases, the resulting depression of σ_0 cannot be directly ascribed to an increase in the glass transition temperature following crosslinking. The measured values of T_g (by DMA at $\omega = 1$ Hz) were quite close to $T = -30\,^\circ\text{C}$ for all samples (Table 3). This apparent lack of variation in T_g is most likely due to the high solvent content of the gels. Despite the lack of variation in T_g, the loss of fast segmental motions associated with numerous chain ends, which become tethered to the network upon crosslinking, may be responsible for the observed drop in conductivity. The concentration of chain ends does not necessarily have a measurable effect on T_g in a crosslinked electrolyte, especially in the presence of a solvent. In addition to arguments based upon changes in the mobility of charge carriers, one must also consider the possibility that crosslinking with DGEBA reduces the concentration of charge carriers in some capacity. However, it seems unlikely that the addition of DGEBA units at an overall mass fraction of 10% or less would cause a drastic change in the dissociation of LiTf, especially given the high concentration of DMF. Unfortunately, a strong absorbance near 1036 cm^{-1} in the FT-IR spectrum of DGEBA overlaps the SO_3 symmetric stretch band of the Tf^- anion, preventing direct comparison with the FT-IR spectra for System I solution electrolytes presented in Fig. 2.

4. Conclusions

Random crosslinking of branched, low molar mass PEI with a difunctional epoxide (DGEBA) is a simple and effective means to obtain gel electrolytes with high solvent content, high ionic conductivity, and rubber-like mechanical properties. DGEBA crosslinking provides a simple means to obtain rubber-like electrolytes with adjustable storage modulus. However, a trade-off exists between high storage modulus and low ionic conductivity with DGEBA as crosslinker. The reduction in conductivity upon crosslinking is attributed in part to a reduction of segmental mobility by tethering of chain ends to the network, which reduces the mobility of charge carriers. From the standpoint of battery applications, this system might be optimized by selecting the lowest chemical crosslink density that provides desirable mechanical behavior. We did not quantitatively characterize impact resistance and energy of failure, mechanical properties which are important for battery electrolyte applications, but the gels were mechanically robust and could survive routine mechanical testing without fracturing. It may also be possible to further increase the conductivity of these gels by increasing the solvent content and optimizing the [N]:[Li] mole ratio. With suitable optimization and testing of electrochemical and thermal stability, PEI gel electrolytes are promising materials for battery electrolytes that may be competitive with the more widely studied systems based upon other polymers.

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