New APTES Cross-Linked Polymers from Poly(ethylene oxide)s and Cyanuric Chloride for Lithium Batteries

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ABSTRACT: A new series of hyperbranched polymer electrolytes for use as membranes for lithium batteries are described. Electrolytes were made by polymerization between cyanuric chloride and diamino-terminated poly(ethylene oxide)s, followed by cross-linking via a sol−gel process. The cross-linking improves the mechanical integrity of the polymer films over other PEO-based electrolytes previously described without deleteriously affecting the ionic conductivity. Thermal analysis and lithium conductivity of free-standing polymer films were studied. The effects of several variables on conductivity were investigated, such as length of backbone PEO chain, length of branching PEO chain, extent of branching, extent of cross-linking, salt content, and salt counterion. Polymer films with the highest percentage of PEO were found to be the most conductive, with a maximum lithium conductivity of 3.9×10^{-5} S/cm at 25 °C, but more mechanically robust films with as much as 50% cross-linker were only slightly lower in conductivity (3.7×10^{-5} S/cm) at 25 °C.

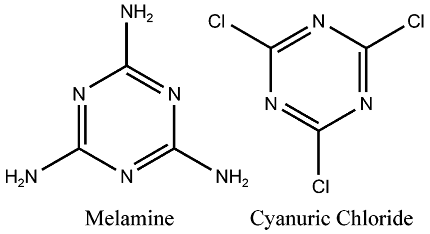
Introduction

Polymer electrolytes offer advantages in lithium batteries, such as design flexibility and the ease of polymer processing compared to solid crystalline and glassy materials.[1] However, low room temperature lithium ion conductivities of solid polymer electrolytes still hinders their use in commercial applications. For more demanding space applications such as the Mars rovers, astronaut suits, and manned surface vehicles, conductivities near 10^{-3} S/cm are desired down to −40 °C, along with adequate stability and cycle life over a broad temperature range.[2] Most polymeric materials that have been studied are based on poly(ethylene oxide) (PEO) because of their strong solvation of lithium ions.[3] However, at temperatures below 80 °C, PEO films tend to crystallize, dramatically decreasing conductivity.[4,5] Furthermore, for many battery applications even high molecular weight PEO has unacceptable mechanical properties, especially at higher temperatures.

Polymer electrolytes have been made that suppress crystallization by making hyperbranched random copolymers of PEO and poly(propylene oxide) (PPO) or PEO and poly[2-(2-methoxyethoxy)ethyl glycidyl ether] (MEEGE).[6−8] To provide dimensional stability, macromonomers of these materials have been capped with vinyl groups that are photocured to create a cross-linked network. These polymer electrolytes exhibit room temperature conductivities approaching 10^{-4} S/cm without losing their dimensional stability. However, the synthesis of these materials is rather cumbersome. The preparation of the macromonomer normally requires a pair of purification and isolation steps.

We recently reported a series of rod−coil hyperbranched copolymers for lithium batteries that illustrate a different approach to creating polymer electrolytes with both suppressed crystallinity and dimensional stability.[9] The polymers, consisting of PEO coil blocks and branched imide blocks, are completely amorphous at room temperature when doped with lithium trifluoromethane sulfonimide (LiTFSI). The rod segments consist of rigid linear or branched polyimides, and the coil segments are oligomeric alkylene oxide chains. It has been proposed that good mechanical and transport properties, as well as the amorphous nature of the alkylene oxide chains, are due to phase separation between the rod and coil segments.[10] It was also observed that increased branching and molecular weight lead to increased conductivity as well as dimensional stability.

Scheme 1



Herein, we discuss the properties of another type of hyperbranched copolymer made from inorganic siloxane and polyalkylene oxide units connected by melamine linkages (see Scheme 1). Melamine is chosen as the linking unit because it provides a branching site, cation binding sites to help ionic transport between polymer chains, and the opportunity for self-assembly through hydrogen bonding. In addition, the polymers are easily made by the reaction of cyanuric chloride with a series of amine-terminated alkylene oxides (Jeffamines, Huntsman Corp., shown in Scheme 2). A linear polymer is first made by reacting two of the aryl chlorides with the diamino-alkylene oxides (Scheme 3), followed by reaction of the third site on cyanuric chloride with varying ratios of monoamino-alkylene oxides and (3-aminopropyl)triethoxysilane (APTES). The APTES provides a cross-linking unit to increase the mechanical strength of the resulting film. The lithium trifluoromethane sulfonimide-doped polymers are cross-linked through a sol−gel process to form free-standing films.[11−13] Several parameters have been systematically varied in this study, including the oxygen-to-lithium ratio, molecular weight of the alkylene oxide diamine oligomers used in the backbone (MW = 600, 2000), molecular weight of the monoamine side chain oligomers (MW = 1000, 2620), and ratio of alkylene oxide oligomer to APTES in the

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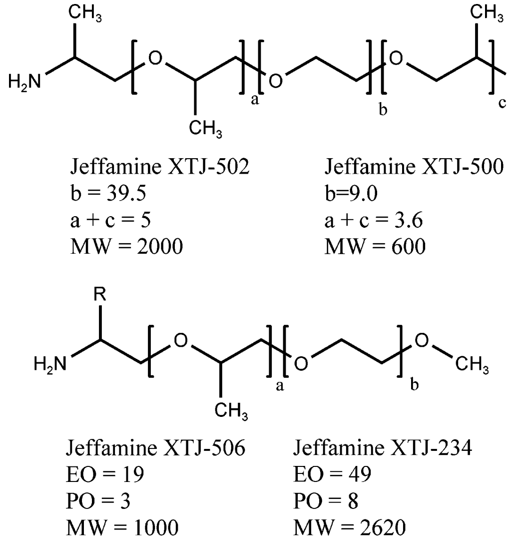
Scheme 2. Monoamine and Diamine-Capped Alkylene Oxide Oligomers That Were Used along with Their Approximate Molecular Weights and Ratios of Ethylene Oxide (EO) to Propylene Oxide (PO)



side chain to understand the effect of these variables on the ionic conductivity and other properties of the resulting polymer films.

Experimental Section

Materials. Cyanuric chloride and (3-aminopropyl)triethoxysilane (APTES) were purchased from Aldrich Chemical Co. and used as received. Diisopropylethylamine was purchased from Aldrich in Biotech grade and used as received. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) was purchased from Aldrich in 99.95% purity, dried at 140 °C under vacuum for 10 h, and stored in a drybox. Monoamine- and diamine-capped polyalkylene oxide oligomers (Jeffamine XTJ-500, XTJ-502, XTJ-234, and XTJ-506) were obtained from Huntsman Corp. All glassware was oven-dried for at least 24 h prior to use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone prior to use.

Instrumentation. Polymers were characterized by differential scanning calorimetry (DSC) from −90 to 300 °C using a Q1000 calorimeter manufactured by TA Instruments. Thermal gravimetric analysis (TGA) was obtained using a TA Instruments high-resolution TGA2950 analyzer. ATR-FTIR spectra of polymer films were taken with a Nicolet Nexus 470 FTIR spectrometer equipped with a Smart Omni sample ATR accessory. Solid ^{13}C NMR spectra of the polymer films were obtained on a Bruker Avance 300 spectrometer using cross-polarization and magic angle spinning at 7 kHz. The acquisition also employed spinning sideband suppression using a CPSELTICS sequence. The solid ^{13}C spectra were externally referenced to the carbonyl of glycine (176.1 ppm relative to tetramethylsilane, TMS).

Ionic conductivity was measured by electrochemical impedance techniques, using a Solartron/Schlumberger model 1250 FRA and model 1286 electrochemical interface.[9] Conductivity was measured over the range of 0−80 °C. The cation transference number was estimated using steady-state current measurements with correction for interfacial impedance effects.[14] Symmetric, Li/SPE/Li, cells were constructed using coin cell hardware (National Research Council, Canada). A constant potential difference (10 mV) was applied and the current response monitored with time, until a steady-state value was achieved. The transference number was calculated from

$$t_+^{\text{dc method}} = \frac{I^S(\Delta V - I^0R^0)}{I^0(\Delta V - I^SR^S)}$$

In the equation, I^S and I^0 are the steady state and initial current,

Scheme 3. Polymer Synthesis and Cross-Linking Reaction

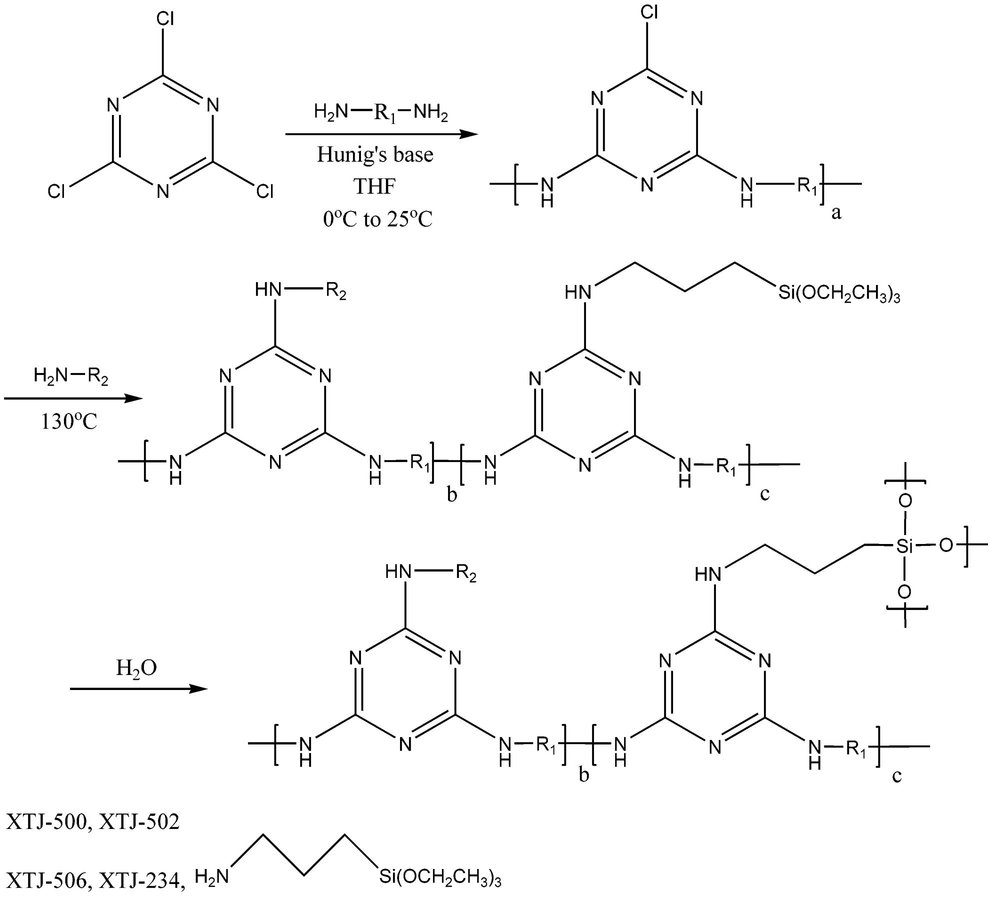


Table 1. Thermal and Conductivity Data

entry	linear segment diamine weight	monoamine weight	% monoamine	% APTES	O:Li ratio	*σ* (S/cm, 25 °C)	T_g	T_m	T_d	% PEO
1	2000	1000	75	25	21:1	3.3E−5[b]	−46.8		391	96
2	2000	1000	75	25	14:1	2.4E−5	−41.2		403	96
3	2000	1000	75	25	none		−56.3	27.4	340	96
4	2000	1000	50	50	21:1	2.1E-5	−46.5		355	95
5	2000	1000	50	50	14:1	1.6E-5	−42.5		386	95
6	2000	1000	50	50	7:1	*a*	−40.4		395	95
7	2000	1000	50	50	none		−52.7	26.6	357	95
8	2000	1000	25	75	21:1	2.0E-5	−50.9		349	93
9	2000	1000	25	75	14:1	1.6E-5	−46.9		390	93
10	2000	1000	25	75	7:1	*a*	−43.4		377	93
11	2000	1000	25	75	none		−53.6	24.4	332	93
12	2000	none	0	100	21:1	1.0E−5	−45.9		293	90
13	2000	none	0	100	14:1	9.7E−6	−40.9		297	90
14	2000	none	0	100	7:1	3.6E−6	−36.6		286	90
15	2000	none	0	100	none		−53.4	24.8	325	90
16	600	1000	75	25	21:1	1.1E−5	−47.9		375	92
17	600	1000	75	25	14:1	8.0E−6	−40.6		381	92
18	600	1000	75	25	7:1	*a*	−38.5		401	92
19	600	1000	75	25	none		−56.3	13.0	350	92
20	600	1000	50	50	21:1	4.5E−6	−37.7		371	88
21	600	1000	50	50	14:1	2.7E−6	−40.0		359	88
22	600	1000	50	50	7:1	1.7E−6	−38.5		369	88
23	600	1000	50	50	none		−53.4	8.4	339	88
24	600	1000	25	75	21:1	1.3E−6	−37.5		339	83
25	600	1000	25	75	14:1	*a*	−32.3		352	83
26	600	1000	25	75	7:1	*a*	−17.8		381	83
27	600	1000	25	75	none		−47.6	20.7	343	83
28	600	2620	75	25	21:1	2.6E−5	−54.0		406	96
29	600	2620	75	25	14:1	1.8E−5	−46.0		404	96
30	600	2620	75	25	none		−54.0	19.4	372	96
31	600	2620	50	50	21:1	1.4E−5	−52.0		377	93
32	600	2620	50	50	14:1	1.2E−5	−44.6		359	93
33	600	2620	50	50	none	1.2E−8	−51.5	19.6	349	93
34	600	2620	25	75	21:1	8.8E−6	−49.1		351	88
35	600	2620	25	75	14:1	4.3E−6	−42.3		358	88
36	600	2620	25	75	none	9.4E−9	−51.9	23.2	348	88
37	2000	2620	75	25	21:1	3.9E−5	−50.8		359	97
38	2000	2620	75	25	14:1	3.0E−5	−46.8		414	97
39	2000	2620	75	25	none		−59.5	23.9	380	97
40	2000	2620	50	50	21:1	3.7E−5	−52.2		395	96
41	2000	2620	50	50	14:1	3.0E−5	−46.2		403	96
42	2000	2620	50	50	none		−59.5	23.2	355	96
43	2000	2620	25	75	21:1	2.5E−5	−51.6		390	94
44	2000	2620	25	75	14:1	2.4E−5	−44.5		388	94
45	2000	2620	25	75	none		−56.9	24.8	355	94

[a] Films were too tacky to be removed from the substrate. [b] Read as 3.3×10^{-5}.

respectively, ΔV is the applied potential (10 mV), and R^S and R^0 are steady state and initial interfacial impedance, respectively.

Experimental analysis was carried out using RS/Series for Windows, including RS/1 version 6.01, and RS/Discover and RS/Explore Release 4.1, available from Domain Manufacturing Corp.

Polymer Synthesis. A typical synthesis of the polymer is given for a formulation containing Jeffamine diamine of MW 2000 in the linear backbone and 50% APTES, 50% Jeffamine (MW 2620) on the branching site (run 40 from Table 1).

XTJ-502 (13.40 g, 6.70 mmol) and diisopropylethylamine (3.6 mL, 21 mmol) were dissolved in 30 mL of THF. The reaction temperature was lowered to 0 °C in an ice bath. Cyanuric chloride (1.24 g, 6.70 mmol) dissolved in 2 mL of THF was then added to the solution. The solution immediately changed color from clear to yellow. The reaction was slowly warmed to room temperature and stirred overnight. The resulting viscous solution was filtered to remove a crystalline white solid (protonated base) that had formed during the course of the reaction. The filter cake was washed with THF, and the resulting filtrate was concentrated to the original reaction volume by rotary evaporation. The 2620 molecular weight monoamine, XTJ-234 (8.84 g, 3.37 mmol), and APTES (0.753 g, 3.40 mmol) were added to the filtrate, and the reaction was heated to 130 °C overnight. The resulting cloudy solution was then weighed and determined to be 55.2 wt % polymer assuming 100% yield.

Lithium trifluoromethane sulfonimide (0.711 g, corresponding to a 21:1 O to Li ratio) was then dissolved in a 4.55 g aliquot (2.51 g of polymer) of this solution. The solution was poured into a 60 mm diameter Teflon dish and air-dried in a fume hood for 24 h. The resulting sticky solid was then dried under vacuum at room temperature to 80 °C until bubbling within the film ceased, followed by further curing at 160 °C under vacuum overnight. The film was immediately transferred into a drybox, cooled, removed from the Teflon dish, and sealed in an airtight bag. Films that were made in entries 1, 2, 37, and 38 in Table 1 were too sticky to remove from the Teflon dish and were cast into aluminum pans instead. Lithium conductivities of these films were measured while attached to the aluminum backing.

The infrared spectrum of this polymer is dominated by peaks that correspond to the alkylene oxide units. Peaks were observed at 2887 (CH stretch), 1349 (CH_2 scissors), 1099, and 1059 cm^{-1} (C−O−C asym stretch). Solid ^{13}C NMR of the polymer films include a broad resonance at 70.7 ppm that can be assigned to all of the methylene and methyne carbons in the alkylene oxide units in the diamine and monoamine portions of the polymers. The methyl carbons from the propylene oxide units appear at 17.6 ppm, while a peak at 47.2 ppm can be assigned to the nitrogen substituted carbons at the termini of the diamines and monoamines. Solid ^{13}C NMR of the sticky precursor shows peaks that are more narrow

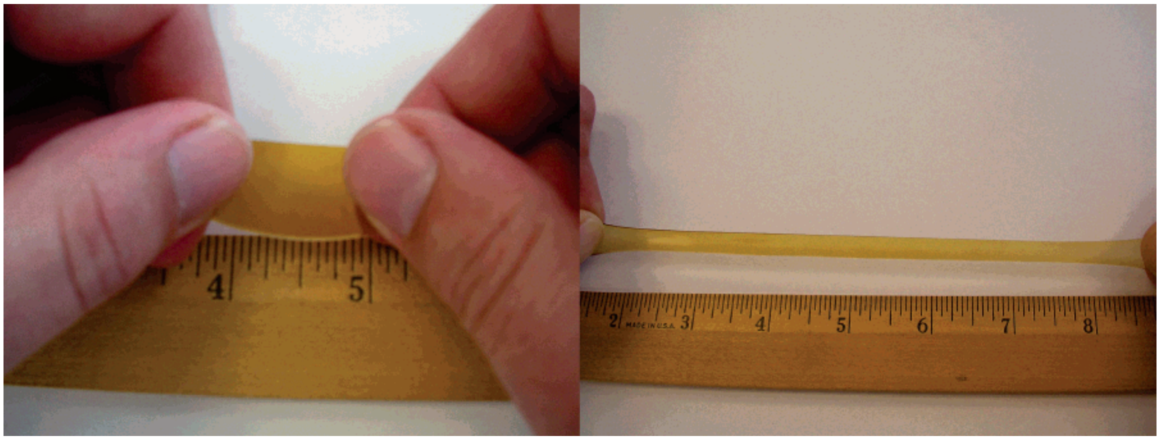


Figure 1. Polymer entry 42 before and after stretching.

and defined than the stretchy cured film. The precursor also shows resonances at 58 and 17 ppm that correspond to the siloxane ethoxy groups prior to hydrolysis, which also disappear after the cross-linking reaction. The melamine carbons in the spectra of the fully cured polymers appear as a small broad peak at 163.6 ppm not very different from their chemical shift in the starting melamine, while the three carbons in the propyl group of APTES appears at 11, 22, and 42 ppm in both the polymer and precursor.

Results and Discussion

Polymer Synthesis and Characterization. The reaction of cyanuric chloride with various alkyl and aromatic amines has been reported previously.[15] Simanek and co-workers have recently reported the synthesis of dendrimers in which melamine is the core unit.[16−18] They also demonstrated the chemoselective reactivity of the three reactive sites on cyanuric chloride at various temperatures. Reaction of one site takes place at 0 °C, the second site at room temperature, and the third site above 70 °C. Jan and co-workers have used similar methodology to synthesize linear poly(alkylene oxide)s by the reaction of various Jeffamines with two of the reactive sites of cyanuric chloride in the presence of base.[19] Through gel permeation chromatography analysis, they found M_w's of 38 000 and 28 700 using Jeffamine D-2000 (poly(propylene oxide) (PPO)) and Jeffamine D-2001 (PEO), respectively. Unfortunately, they report that these polymers exist as viscous liquids and semisolids. We show that through the addition of APTES to the third reactive site the polymers become cross-linked and behave as elastomeric solids.

Scheme 2 shows the synthesis of lithium bis(trifluoromethane)-sulfonimide-doped PEO's that can be cast into free-standing films. First, the linear polymer was made by the reaction of equimolar amounts of cyanuric chloride with diamines XTJ-500 (MW = 600) or XTJ-502 (MW = 2000) in THF at room temperature. These diamines contain a mixture of ethylene oxide and propylene oxide units in the chain. The ethylene oxide promotes lithium ion conductivity while the propylene oxide units help suppress crystallization.[20] Diisopropylethylamine (Hünig's base) was added to remove HCl generated in the reaction medium. The ammonium salt precipitates during the reaction and is removed by filtration. No gel formation was observed during the reaction, which gives evidence that the polymer is not cross-linking prematurely via reaction of the third reactive site on cyanuric chloride. Once the linear polymer is made, the third site is reacted with monoamines XTJ-506 (MW = 1000) or XTJ-234 (MW = 2620) at 130 °C. In addition, APTES in varying amounts is also added to the reaction to provide for a cross-linked network once films are cast. Polymer solutions are doped with lithium salts and cast into films in Teflon dishes. Three different lithium salt concentrations measured by the ratio of Jeffamine oxygen to lithium were evaluated (21:1, 14:1, 7:1). Films are typically air-dried overnight in a fume hood, followed by drying and further curing under full vacuum at 160 °C overnight. The resulting films are immediately transferred into a drybox and sealed into airtight bags to avoid any absorption of water.

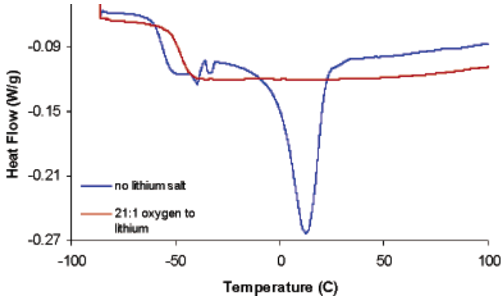


Figure 2. DSC analysis of polymer entries 16 and 19. Entry 16 contains lithium salt while entry 19 does not.

The cross-linked polymer films are strong and highly elastic in nature. Figure 1 shows an example of the flexibility of an undoped film that contains 2000 MW Jeffamine diamine in the main polymer chain and a 1:1 ratio of 2620 Jeffamine monoamine to APTES in the branching site. This film contains the lowest amount of cross-linking and highest conductivity of all free-standing films studied in the doped form. Moreover, the film is strong and flexible enough to be stretched to over seven times its initial length and completely relax back to its original shape. Tensile properties of these films could not be measured since the films, thinned out by elongating up to 650−750%, failed in the grips before breaking. 100 000 MW PEO has been measured previously to have a modulus of 0.510 and an elongation at break of only 5%.[21]

A summary of room temperature conductivity for the lithium-containing films, differential scanning calorimetry (DSC) data, and thermal gravimetric analysis (TGA) data for the films is given in Table 1. TGA data show that all the polymer films have an onset of decomposition (T_d) in excess of 350 °C. DSC analysis shows a strong melt transisition (T_c) around room temperature for films that are not doped with lithium salt. However, with the addition of lithium salt, this transition disappears (Figure 2). It has been shown previously that the addition of LiTFSI increases the amorphous nature of PEO due to the size of the imide ion hindering alignment of the polymer chains.[22] Thermal studies have shown the PEO−salt complex to be completely amorphous when the O:Li ratio <12 and semicrystalline at O:Li >12. In this system, the polymer−salt complex stays amorphous even at O:Li > 20, most likely because of the addition of small amounts of PPO to the polymer backbone. These results are advantageous since most systems tend to show maximum conductivity around an O:Li ratio of 20:1. As is the case in most other solid polymer electrolytes, glass transition temperature (T_g) tends to increase with an increase in salt concentration. In addition, lithium conductivity tends to decrease with increasing polymer T_g. The most conductive samples have T_g's between −40 and −60 °C. Less conductive samples have T_g's that are higher than −40 °C.

The salt-containing films from Table 1 can be considered as an experimental design[23] in four variables: diamine type (*d*, molecular weights of 600 and 2000 g/mol), monoamine type (*m*, molecular weights of 1000 and 2620 g/mol), percent APTES replacing the monoamine in the third reactive site (*s*, 25−75%), and O to Li ratio (*l*, 7 to 1, 14 to 1, or 21 to 1). Diamine type and monoamine type are discrete (nonnumerical) variables evaluated at two levels while salt concentration and % APTES are continuous (numerical) variables evaluated at 3 or 4 levels each. This allows an empirical model to be derived to describe the relationship of room temperature ionic conductivity to each of the variables. Modeling in this way provides the ability to predict optimum parameters to maximize conductivity. Also, it allows evaluation of interactive/synergistic effects among variables. In addition, the model graphically shows significant relationships between variables which are difficult to discern by looking at a data table. In this type of analysis, a quadratic model of the form

$$\text{response (log conductivity)} = A + Bm + Cd + Ds + El + Fs^2 + Gl^2 + Hmd + Ims + Jml + Kds + Ldl + Nsl$$

is typically entertained where *m* is monoamine molecular weight, *d* is diamine molecular weight, *s* is % APTES, and *l* is O:Li ratio and A through N are coefficients empirically derived from modeling the experimental data. A quadratic model allows the ability to model nonlinear effects of the variables efficiently. The full model contains first-order effects of all four variables and second-order terms for *s* and *l* as well as all possible two-way interaction terms. (Owing to the discrete nature of variables monoamine type and diamine type, there is no physical meaning to a second-order term in these variables.)

Values for the room temperature ionic conductivity shown in Table 1 were analyzed using linear least-squares regression. The conductivity was normalized using a log transform before modeling. All independent variables were orthogonalized (transformed to the −1 to 1 range) prior to modeling. Terms not deemed to be statistically significant (<90% confidence) were dropped from the model one at a time using a stepwise modeling technique. In this case, significant terms include all main effects and three interactive/synergistic terms: *dm*, *ms*, and *ds*. All terms in the model were greater then 98.5% significant. Standard error of the regression was 0.071 with an $R^2 = 0.98$.

A three-dimensional graph of the resulting response surface model for log ionic conductivity plotted vs lithium-to-oxygen ratio and APTES percent is shown in Figure 3. Four separate surfaces are shown for the four combinations of monoamine and diamine used in the formulations. Overall, the films containing 2000 MW diamine and 2620 MW monoamine (green surface) have the highest conductivities, followed by those made with 2000 MW diamine and 1000 MW diamine (blue surface), and those with 600 MW diamine and 2620 MW monoamine (yellow surface). The films made with 600 MW diamine and 1000 MW monoamine (red surface) have the lowest overall conductivities.

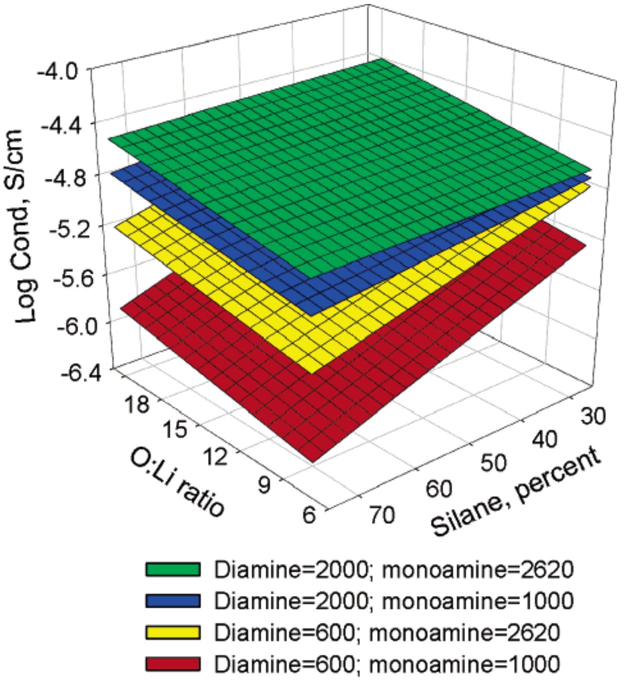


Figure 3. Response surface model predicting conductivities for four series of polymers.

The synergistic/interactive effect of diamine with monoamine MW (*dm*) is illustrated by the surfaces in Figure 3. Comparing the red surface to the blue surface (both representing films containing the 1000 MW monoamine) and the green surface to the yellow surface (both representing films containing the 2620 MW monoamine), it is evident that films having the 2000 MW diamine in the polymer backbone have as much as a 10-fold increase in conductivity over films with the 600 MW diamine in the polymer backbone. This trend can not only be explained by the fact that films containing 2000 MW diamine have longer chains of alkylene oxides within the films and therefore lower T_g, but the 2000 MW diamine also has a higher percentage of ethylene oxide to propylene oxide than the 600 MW diamine (∼7.9:1 vs ∼2.5:1). Poly(propylene oxide) is a poorer conductor of ions.

By comparing the blue surface to the green surface (both representing films containing the 2000 MW diamine) and the red surface to the yellow surface (both representing films containing the 600 MW diamine), it is evident that increasing the MW of the monoamine side chain from 1000 to 2620 increases the conductivity, although the effect is larger for the 600 MW diamine. For polymers with a 600 MW backbone, there is as much as a 7-fold increase in conductivity when increasing the side chain MW from 1000 to 2620. For films that contain 2000 MW PEO in the polymer backbone, increasing the MW of the PEO branch from 1000 to 2620 has a less dramatic effect on the conductivity. In this case, the conductivity is increased by at most a factor of 2.

The synergistic/interactive effects of both monoamine and diamine type with percent APTES (*ms* and *ds*, respectively) is also illustrated by the surfaces shown in Figure 3. Within each surface (having the same diamine and monoamine combination), conductivity decreases with the amount of cross-linking APTES added. This effect is most dramatic for the films containing 600 MW diamine and 1000 MW monoamine (red surface) which shows nearly a 10-fold change in conductivity over the range of percent APTES modeled. For polymers with the 600 MW diamine and 2620 diamine (yellow surface), there is only a 2-fold change in conductivity over the same range. For films

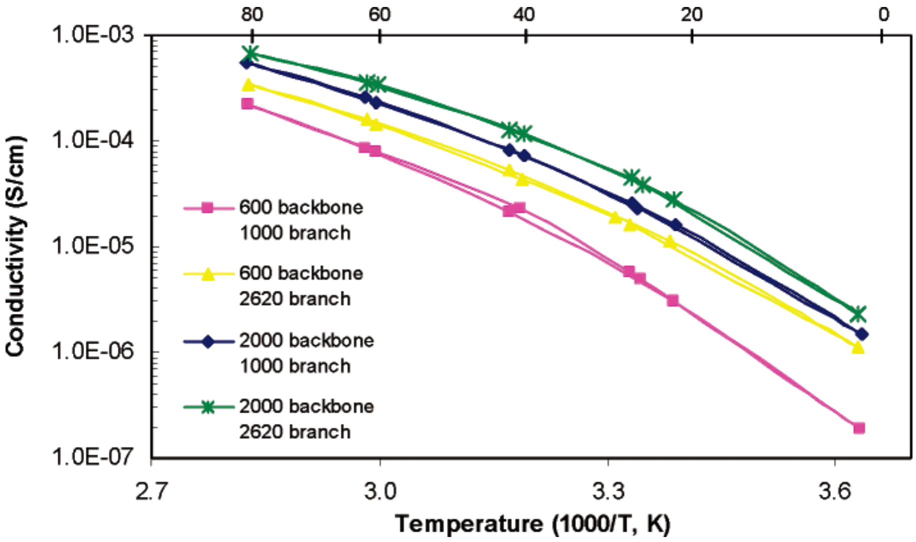


Figure 4. Temperature dependence of ionic conductivities for a series of polymers in which the branching site contains 50% APTES and 50% monoamino Jeffamine. The oxygen-to-lithium ratio is 21:1 in each case.

made with 2000 MW diamine (blue and green), the decrease in conductivity with increasing APTES content is very small.

For all surfaces, conductivity decreases as the amount of lithium relative to oxygen is increased. Furthermore, since there is no interactive term with salt in the model, this relationship is the same for all combinations of diamine and monoamine used. Increasing the lithium-to-oxygen ratio also had an adverse effect on the mechanical properties of the polymer films. The films become softer and stickier.

The least conductive (600 MW diamine and 1000 MW monoamine) series has the largest drop-off in ionic conductivity as temperature is decreased as shown in Figure 4 for formulations containing 50% APTES and 21:1 O to Li. This is most likely because polymers with shorter PEO chains require an increase in temperature to activate the transport of ions between chains. The other three formulations show nearly identical trends with temperature.

The values for T_g from Table 1 were also modeled using multilinear regression (Figure 5). Significant terms for the T_g model include all main effects and three interactive terms: *dm*, *ml*, and *ds*. All terms in the model were greater then 98.3% significant. Standard error of the regression was 2.1 °C with an $R^2 = 0.87$. It is easiest to view the surfaces as two distinct pairs: those with the 600 g/mol diamine in the backbone and those with the 2000 g/mol diamine in the backbone. Those with 600 MW diamine in the backbone show a large increase in T_g with increasing silane concentration, and those with 2000 MW diamine in the backbone show a much flatter response to silane concentration.

In general, the T_g is lower in films that contain the longer monoamine (MW = 2620 g/mol) as a side chain. At −54 °C, the film that has the lowest T_g is that made from 600 g/mol diamine in the backbone and 75% 2620 MW monoamine (25% APTES) with 21 to 1 O to Li ratio. This is probably because with the 600 g/mol diamine in the backbone, there is a higher frequency of branching sites along the backbone, leading to a lower T_g. However, this film is not as conductive as the film with 2000 g/mol diamine and 75% 2620 g/mol monoamine with the same salt concentration ($T_g = -51.4$ °C). This is most likely due to the 600 g/mol diamine having a higher percentage of PPO than the 2000 MW backbone, which counteracts the improved freedom of movement from having more branching PEO sites.

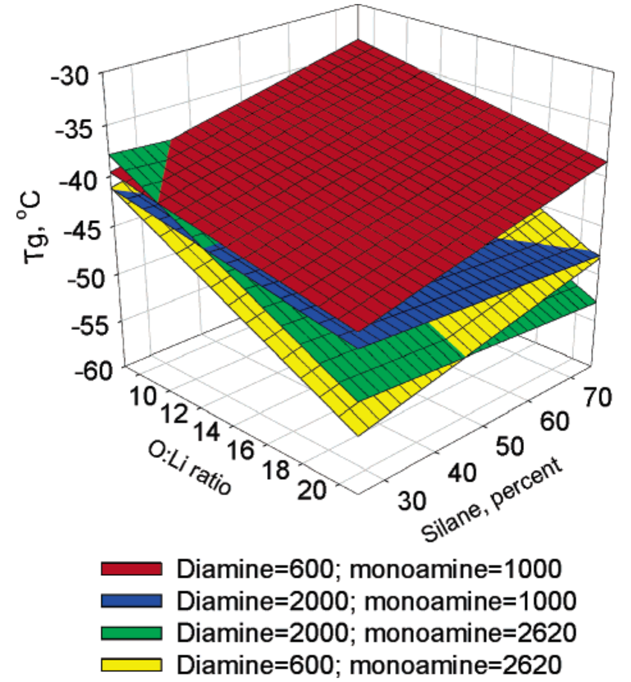


Figure 5. Response surface model predicting glass transition temperatures for four series of polymers. Note that the values of the percent silane are reversed compared to Figure 3 to provide the best viewing angle for all four surfaces.

Table 2. Effects of Counterion and Plasticizer on the T_g and Lithium Conductivity of Polymer 40

salt	% propylene carbonate added	T_g	σ (S/cm, 25 °C)	T_+
$LiN(SO_2CF_3)_2$	none	−52.2	3.6E−5[b]	0.21
$LiN(SO_2CF_3)_2$	10		6.8E−5	0.21
$LiN(SO_2CF_3)_2$	20		2.2E−4	*a*
$LiN(SO_2CF_3)_2$	60		6.0E−4	0.04
$LiN(SO_2CF_3)_2$	220		1.7E−3	*a*
$LiSO_3CF_3$	none	−50.0	1.7E−5	*a*
$LiClO_4$	none	−49.1	1.2E−5	*a*

[a] Not measured. [b] Read as 3.6 × 10^{-5}.

Two samples were tested for conductivity in which no lithium salt was added (entries 33 and 36 in Table 2). These samples both had ionic conductivities of about 1 × 10^{-8} S/cm, or 3 orders of magnitude less than the lithium-doped samples. The

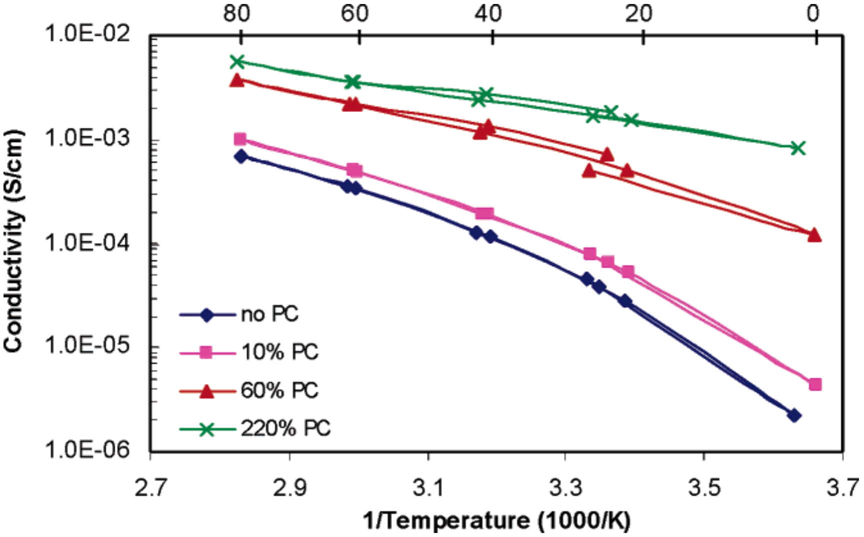


Figure 6. Temperature dependence of ionic conductivities for polymer 40 with propylene carbonate added.

ammonium salt that is formed by protonation of diisopropylethylamine during the course of the reaction precipitates and is removed by filtration after the reaction with the second site on cyanuric chloride. The reaction has to be filtered at this point because the precipitate disappears after reaction with APTES. The conductivity data suggest that any remaining dissolved ammonium salt is subsequently incorporated into the polymer film, although it has a minor effect on conductivity. If needed, the residual ammonium salt can be removed by filtering the polymer solution through basic alumina prior addition of lithium salt. The alumina is then washed with THF until the filtrate is no longer UV active.

Effects of Salt and Plasticizer. A brief study was performed to observe the effects of adding propylene carbonate (PC) as a plasticizer to these polymers. Kim and Smotkin have shown previously that the addition of only 10% PC to high MW PEO films doped with lithium trifluoromethanesulfonimide increases lithium conductivity by a factor of 2 between 50 and 80 °C.[24] A polymer having 2000 MW diamine, 2620 MW monoamine, and 50% APTES (same formulation as entry 40 in Table 1) was chosen for the study. Formulations with 10, 20, and 60 wt % PC were added to the film after curing as well as a film in which PC was added to the point of saturation (220 wt %).

Similar to the previously reported results with PEO, adding 10% PC doubles the conductivity, as shown in Table 2 and Figure 6. When PC is increased to 60%, the conductivity is increased by over an order of magnitude. However, unlike PEO, even with as much as 60% PC added to the polymer film, the film maintains excellent mechanical strength. Cation transference numbers were obtained for films that contain 0%, 10%, and 60% PC. There does not appear to be any significant change in transference number when only 10% PC is added. However, the addition of 60% PC increases anion transport more significantly than cation transport. This is not surprising since the ether oxygen lone pairs can bind to the lithium cation, but not the TFSI anion. Glass transitions were not observed down to −90 °C for any of the films in which PC was added.

Experiments were also run in which lithium trifluoromethanesulfonimide was replaced with lithium perchlorate and lithium trifluoromethanesulfonate. Films that were made with the latter two salts were slightly less conductive. Surprisingly, these two salts also had adverse effects on the film's mechanical properties. These films are much stickier compared to the parent films doped with lithium trifluoromethanesulfonimide, even though films doped with lithium trifluoromethanesulfonimide are expected to have less mechanical strength since the trifluoromethanesulfonimide counterion is known to have a plasticizing effect on polymer films.[25]

Conclusions

This paper describes a new, hyperbranched polymer system that has been synthesized as an alternative to PEO for use as a solid electrolyte for lithium batteries. The polymer is made by the reaction of diamino-terminated alkylene oxides with cyanuric chloride, followed by reaction with monoamino-terminated alkylene oxides and (3-aminopropyl)triethoxysilane (APTES). The latter reagent serves of the cross-linking agent to provide dimensional stability to the polymer film, while the addition of the alkylene oxide side chains provides higher conductivity. The resulting polymer films show significant improvements in both ionic conductivity and mechanical properties over PEO itself.

A systematic study was performed, in which oxygen-to-lithium ratio, molecular weight of the PEO backbone (MW = 600, 2000), molecular weight of the side chains (MW = 1000, 2620), and percent APTES as cross-linker were varied. Films were characterized using ac impedance to measure lithium conductivity, TGA, and DSC. Films that were found to be the most conductive contained a 21:1 oxygen:lithium ratio, a 2000 g/mol Jeffamine diamine in the polymer backbone, 75% 2620 g/mol Jeffamine monoamine and 25% APTES in the side chain, and lithium trifluoromethanesulfonimide as the lithium salt. The conductivity at 25 °C for this optimum formulation is 3.9×10^{-5} S/cm. Lithium conductivity decreases with increasing amounts of cross-linking agent, but the film strength increases. Slightly higher conductivities may be obtained with polymers having less than 25% APTES cross-linker. However, dimensional stability is compromised as APTES percent approaches zero.

The optimum conductive films containing 2000 g/mol Jeffamine diamine, 2620 g/mol Jeffamine monoamine, and 21:1 O:Li in the backbone and only 25% APTES were too weak to be produced as free-standing films. However, increasing APTES to 50% in polymers with the same combination of diamine and monomer shows only a slight drop-off in room temperature conductivity (3.7×10^{-5} S/cm) but much better mechanical integrity. Using this formulation, the lithium counterion was varied and propylene carbonate (PC) was added as a plasticizer. Films were found to have both the highest conductivity and best dimensional stability when trifluoromethanesulfonimide was chosen as the counterion. Addition of 10−60 wt % PC increased lithium conductivity by almost an order of magnitude without compromising the mechanical integrity of the films. However, the addition of PC increases anion transport more significantly than cation transport.

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