

Effect of Branching on Rod-Coil Polyimides as Membrane Materials for Lithium Polymer Batteries

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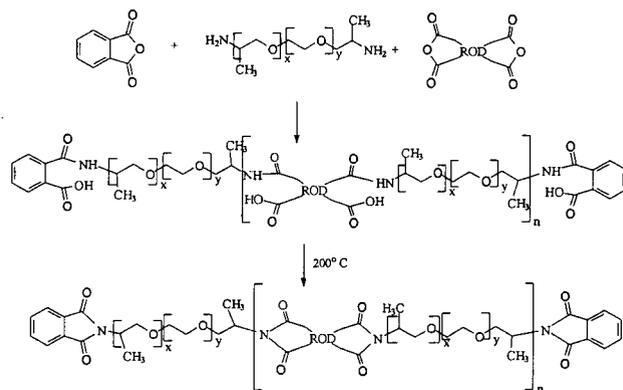
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ABSTRACT. This paper describes a series of rod-coil block co-polymers that produce easy to fabricate, dimensionally stable films with good ionic conductivity down to room temperature for use as electrolytes for lithium polymer batteries. The polymers consist of short, rigid rod polyimide segments, alternating with flexible, polyalkylene oxide coil segments. The highly incompatible rods and coils should phase separate, especially in the presence of lithium ions. The coil phase would allow for conduction of lithium ions, while the rigid rod phase would provide a high degree of dimensional stability. An optimization study was carried out to study the effect of four variables (degree of branching, formulated molecular weight, polymerization solvent and lithium salt concentration) on ionic conductivity, glass transition temperature and dimensional stability in this system.

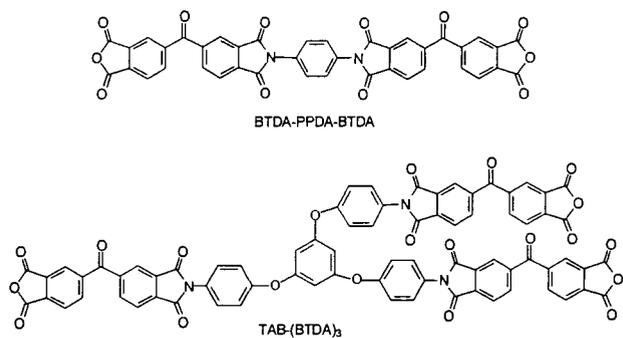
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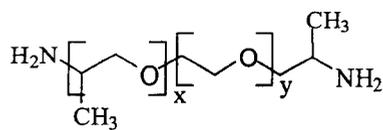
Scheme 1. Synthesis of rod-coil polyimide copolymers.



Rods



Coil



Jeffamine XTJ-502
 MW=2000, x=5, y=39.5

The coil block used in these polyimides is Jeffamine XTJ-502, a predominantly polyethylene oxide backboned, 2000 molecular weight polyether oligomer terminated at each end with amine. The rods are made with a central aromatic diamine or aromatic triamine capped on all ends with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). A diamine center produces a linear rod while a triamine center produces a branched rod.

Lithium trifluoromethane sulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) was purchased from 3M. The salt was vacuum dried for 24 hours at 115 °C before transfer to the glovebox. Poly(ethylene) oxide ($M_v=500,000$) was purchased from Aldrich® and used as received.

Ionic conductivity. Ionic conductivity was measured by electrochemical impedance techniques, using a Solartron/Schlumberger model 1250 FRA and model 1286 Electrochemical Interface. Samples of cured polymer electrolyte were cut from the parent sheet and carefully measured to determine thickness and area. Samples were mounted in a symmetric cell between 304 stainless steel blocking electrodes. Polyester shim material was used to maintain material thickness during the test and to keep the polymer sample from flowing at elevated temperature. Conductivity was measured over the range of 0°C to 80°C.

Polymers were also characterized by differential scanning calorimetry (DSC) from -90 °C to 300 °C using a Q1000 calorimeter manufactured by TA Instruments. Thermal gravimetric analysis (TGA) was obtained using a TA Instruments high resolution TGA2950 analyser. Fourier transform infrared spectroscopy was obtained from KBr pellets using a Nicole 5100 spectrometer. Solid nuclear magnetic resonance spectroscopy (NMR) was carried out on a Bruker Avance 300 spectrometer fitted with a solids subsystem capable of magic angle spinning at up to 7 kHz. Acquisition was obtained using cross polarization and a sideband suppression sequence. The spectra were externally referenced to the carbonyl of glycine (196.1 ppm relative to TMS). A Shore® Type-A hardness tester (BYK Gardener) was modified and applied to measure the depth of penetration for all the films.

Preparation of polymers. The polymers were prepared in the glove box under an argon atmosphere at <1 ppm water. Drying and final cure were carried out in a vacuum oven

approximately 4 hours until the entire solid was dissolved. The resulting yellow polyamic acid solution was 23.3% solids by weight. Enough of the solution to give a 2 g film (8.57g of solution) was cast into a 2 inch diameter aluminum boat. The solvent was removed by gentle heating on a hot plate overnight. Curing in the vacuum oven attached to the dry box at 200 °C resulted in an orange film. CP-MAS NMR: ^{13}C δ 15.13, 17.86, 47.78, 70.76, 75.27, 123.84, 128.21, 130.79, 135.04, 138.39, 164.79, 194.21. DSC: $T_g = -47.0$ °C, endotherm 23.8 °C. FT-IR (cm^{-1}): 2869.4, 1713.1, 1380.5, 1097.6.

Lithium trifluoromethane sulfonimide (0.0374 g,) was dissolved in enough of the 23.3% solid polyamic acid solution to give 3 g of polymer (10.87 g). This gives a 40:1 ratio of polyether oxygens to lithium ion in solution. The polymer-salt solution was cast onto stainless steel boats and submitted to the same drying and curing procedure used for the neat films. DSC: $T_g = -48.9$ °C. FT-IR (cm^{-1}): 2872.1, 1714.0, 1381.8, 1352.4, 1192.1, 1097.2.

Polyethylene oxide film.

Stock solutions of Poly(ethylene) oxide and lithium imide salt were prepared in acetonitrile (3 wt% and 21 wt% respectively). Solutions were mixed together in predetermined amounts by magnetic stirring for approximately 48 hours.

Polymer electrolyte films were prepared by casting. The polymer/salt solution was transferred to a Teflon Petri dish and vacuum de-gassed to disengage bubbles. The acetonitrile was allowed to evaporate for 48 hours at glove box temperature, ~ 25 °C. The dried films were further cured overnight at 40 °C under vacuum. This process produced flexible, 90 μm thick films with a 16:1 EO:Li salt content. DSC: $T_g = -40.8$ °C, $T_m = 50.3$ °C. FT-IR (cm^{-1}): 2886.5, 1467.0, 1353.8, 1341.8, 1192.5, 1098.0.

We used a statistical experimental design approach to evaluate the effects of these four variables on the polymer properties or responses. We wished to entertain a full quadratic model of the form:

$$\text{Response} = A + B*t + C*n + D*s + E*p + F*t^2 + G*n^2 + H*s^2 + I*t*n + J*t*s + K*t*p + L*n*s + M*n*p + N*s*p$$

where A through N are coefficients empirically derived from experimental data. The model contains terms for first order effects of all four variables, second order terms for t , n , and s , as well as all two-way interaction terms. To evaluate first and second order effects of t , n and s , a minimum of three levels of each variable must be considered. The three levels of t used are 0% TAB / 100% PPDA, 50% TAB / 50% PPDA, and 100% TAB / 50% PPDA. Three levels of s , based on the ratio of lithium ion to ether oxygen in the polymer (0.025, 0.05 and 0.075) were also studied. In addition, n was evaluated from 1.4 to 10.7 repeat units, corresponding to a formulated molecular weight of 6000 to 60,000 g/mole. Two levels of the discrete variable p , NMP and THF, were used to make the polymers.

A full-factorial design to evaluate this model would contain 54 experiments. To minimize the number of experiments in the study, we used a d-optimal experimental design strategy. In this type of non-classical design, a set of runs is computer-generated from the 54 candidate runs to evaluate the desired model most efficiently. The scope of the design can be described as a box (shown in Figure 1) with each of the three axes representing three continuous variables (n , s and t). The symbols in the box represent each of the runs. Runs in the design synthesized in NMP are shown as shaded squares, and those in THF are shown as open circles. The total number of unique experiments in the d-optimal design is 23. In addition, 4 runs from across the design are

Table 1. Data from experimental design study.

Run	FMW	<i>n</i>	<i>t</i> , %	<i>s</i>	<i>p</i>	Log cond, room temp	T _g , w/Li salt	T _g , neat	Penetration depth, %
1	20000	4.40	0.5	0.05	THF	-4.96	-43.3	-50.9	54
2	20000	4.40	0.5	0.075	THF	-5.20	-38.2	-50.3	45
3	10000	2.89	0	0.075	THF	-5.05	-37.9	-53.5	61
4	20000	4.40	0.5	0.025	THF	-5.31	-48.7	-49.9	38
5	20000	3.29	1	0.05	THF	-4.97	-42.3	-49.0	42
6	20000	4.40	0.5	0.05	THF	-4.98	-41.4	-50.3	39
7	20000	6.62	0	0.05	THF	-5.11	-42.9	-53.0	49
8	30000	10.35	0	0.075	THF	-5.20	-36.4	-51.7	52
9	30000	5.15	1	0.025	THF	-5.05	-47.8	-50.5	45
10	10000	1.92	0.5	0.05	THF	-5.03	-44.4	-52.0	63
11	20000	4.40	0.5	0.05	THF	-5.11	-42.8	-47.3	48
12	10000	1.44	1	0.075	THF	-5.08	-37.3	-47.6	55
13	10000	1.44	1	0.025	THF	-4.98	-48.4	-47.4	58
14	30000	5.15	1	0.075	THF	-5.11	-37.6	-49.3	36
15	20000	4.40	0.5	0.05	THF	-5.25	-42.4	-51.3	52
16	10000	2.89	0	0.025	THF	-5.04	-48.9	-49.3	52
17	30000	10.35	0	0.025	THF	-5.07	-47.6	-50.3	37
18	10000	1.44	1	0.03	NMP	-5.04	-45.5	-51.9	63
19	10000	1.44	1	0.075	NMP	-5.17	-37.2	-52.0	71
20	30000	10.35	0	0.03	NMP	-5.04	-45.9	-54.2	34
21	30000	10.35	0	0.075	NMP	-5.22	-36.4	-53.9	52
22	10000	2.89	0	0.05	NMP	-4.91	-45.4	-52.8	45
23	30000	5.15	1	0.05	NMP	-4.91	-45.4	-50.3	52
24	10000	1.44	1	0.075	THF	-5.06	-38.5	-52.8	54
25	60000	10.72	1	0.025	NMP	-4.72	-53.7	-55.9	42
26	6000	1.40	0	0.025	NMP	-4.67	-53.1	-59.1	86
27	60000	10.72	1	0.075	NMP	-4.75	-45.5	-55.6	54

Typical DSC traces for films with and without lithium salt are shown in Figure 2. The neat films typically have two reversible transitions, a glass transition temperature (T_g) between -60 and -45 °C and a transition at approximately 18 to 25 °C which is due to crystallization of the

Terms not statistically significant (<90 % confidence) were dropped from the model one at a time by the stepwise modeling technique.

A response surface model for T_g is shown in Figure 3. Significant terms in the model included first order effects of salt concentration and triamine concentration, and a second order effect of n -value, with salt concentration being the most dominant. An interactive/synergistic effect of triamine concentration with n -value was also significant. This interaction can be clearly seen in Figure 3. When $t = 0$ (100% linear polymers), T_g increases with increasing n -value (higher molecular weight). When $t = 1$ (100 % branched polymers), T_g decreases with increasing n -value. No terms containing solvent were significant in the model. Standard error of regression for the model was 1.05 °C with an $r^2 = 0.95$.

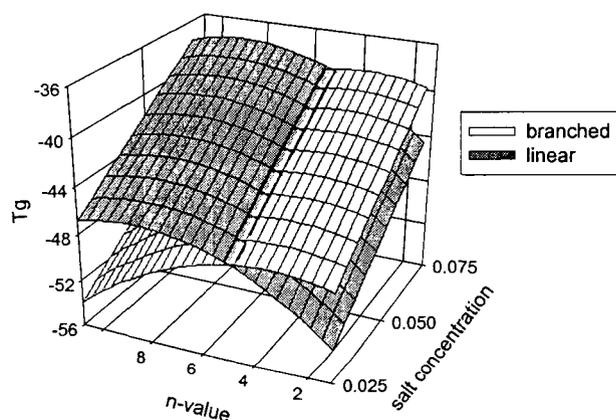


Figure 3. Response surface model of T_g vs. n -value and salt concentration.

Ionic conductivity measured by electrochemical impedance is shown in Figure 4 for a sampling of the films. The conductivity was measured from 0 °C to 80 °C for all of the films in the design. For the films with salt concentrations from 0.05 to 0.075, a second order linear regression plot fit the data quite well through the whole range. The films with salt concentration at 0.025 exhibited a slight drop off in conductivity at approximately 20 °C, corresponding to the

in excellent agreement with the predicted optimum. Including this run in the model increases r^2 to 0.83 and reduces the standard error to 0.079.

A predicted response surface model for log ionic conductivity vs. salt concentration and n , and broken down into branched and linear polymer, is shown in Figure 5. From this figure, it is clear that the optimum salt concentration for any level of the other two variables is the mid-level of the design range. Also, this figure illustrates the strong interaction between number of repeat units,

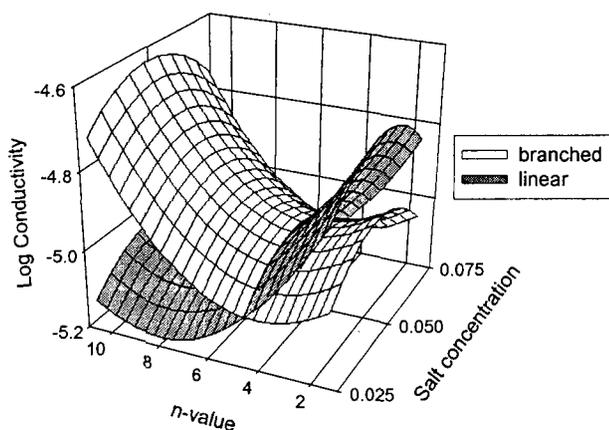


Figure 5. Response surface model of ionic conductivity versus salt concentration and n .

n , and triamine concentration, t (or extent of branching). The linear polymers ($t = 0$), shown as the shaded surface, decrease in conductivity with increasing n , while the branched polymers ($t = 1$) increase in conductivity with increasing n . This is probably due to the fact that the coils at the end of the polymers in the linear systems dominate the conductivity. In the branched polymers, there is essentially a chain end in every repeat unit.

The response surface with salt concentration held constant at the optimum value of 20:1, is shown in Figure 6. This also shows the strong effect of increased branching (increased triamine concentration) especially in conjunction with increasing number of repeat units in the polymer.

monitor residual solvent. In all cases, less than 4% NMP remained in the films and had no significant effect on either the conductivity or the T_g . Also of concern was dissolution of lithium salt in NMP. However, this also proved not to be a problem. Even though the salt dissolves in NMP only sluggishly, it readily dissolves in polymer solutions in NMP or THF equally well.

Polymer films made from the optimum conditions for ionic conductivity also look to have the best physical properties. The highest molecular weight films with the most branching were robust, flexible and quite elastic. Films from the higher molecular weight, linear formulations were also quite robust and flexible, but not nearly as elastic as the fully branched films. As expected, films at the other extreme—the low molecular weight, linear films—were quite soft and tore easily. As a way of quantifying the physical properties of the films, a simple hardness test was done. A Shore® Type-A hardness tester (BYK Gardener) was modified and applied to measure the depth of penetration was measured for all the films.

Response surface modeling for percent penetration showed the most dominant effect to be n -value as shown in Figure 9. Though minor, effects of triamine fraction and salt concentration were also significant. Triamine fraction was also present in the model as a two-way interaction with n -value.

At low n , percent penetration decreases with increasing triamine concentration, whereas at high n , there is no effect. Increasing salt concentration has the effect of softening the film and increasing penetration to a minor extent (approximately 5% across the whole range). Since this is such a minor effect, it is not shown. Salt concentration is held constant at a 0.05 lithium to oxygen ratio for the graph in Figure 9, and.

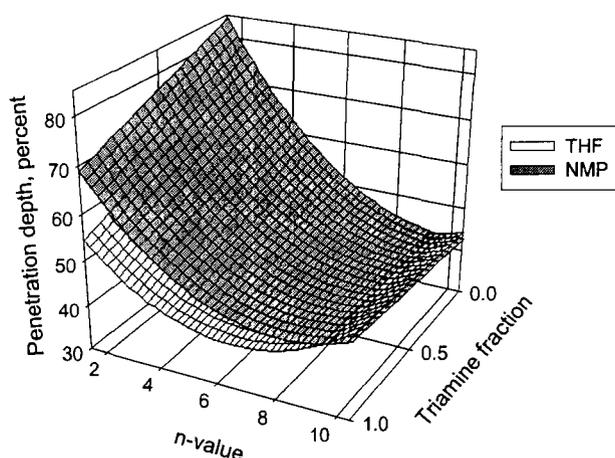


Figure 9. Plot of response surface model for percent penetration with salt at optimum ratio of 20.5:1 oxygen to lithium.

For the first time, solvent is also significant in the model, but only as a two-way interaction with n -value. The graph in Figure 9 demonstrates this significant, synergistic effect of solvent with n -value on the percent penetration. For lower n -values, the small amount of residual NMP (0 to 4%) must plasticize the polymer to some extent raising the percent penetration as much as 15% whereas at higher n -values there is no difference in penetration between NMP and THF. Standard error of regression for the model was 5.4% with an $r^2 = 0.86$. All terms in the model were greater than 91.5% significant.

CONCLUSIONS. This paper describes a series of rod-coil block co-polymers that produce easy to fabricate, dimensionally stable films with good ionic conductivity down to room temperature for use as electrolytes for lithium polymer batteries. The polymers consist of short, rigid rod polyimide segments, alternating with flexible, polyalkylene oxide coil segments. The highly incompatible rods and coils should phase separate, especially in the presence of lithium ions. The coil phase would allow for conduction of lithium ions, while the rigid rod phase would

REFERENCES

1. Summer Intern, 2001.
2. Employed by QSS Group, Inc.
3. Kim, Y. T.; Smotkin E. S. *Solid State Ionics* **2002**, *149*, 29-37.
4. Nishimoto, A.; Agehara, K.; Furuya, N.; Watanabe, T.; Watanabe, M. *Macromolecules* **1999**, *32*, 1541-1548.
5. Croce, F.; Persi, L.; Scrosati, B.; Serraino-Fiory, F.; Plichta, E.; Hendrickson, M. A. *Electrochimica Acta* **2001**, *46*, 2457.
6. Soo, P. P.; Huang, B.; Sadoway, D. R.; Mayes, A. M.; *J. Electrochem. Soc.* **1999**, *146*, 32.
7. Yoshino, M.; Ito, K.; Kita, H.; and Okamoto, K. *J. Poly. Sci: B Polymer Physics* **2000**, *38*, 1707-1715.
8. Eby, R. K., private communications. This is under further investigation and will be reported elsewhere.
9. Michot, C.; Baril, D.; and Armand, M. *Solar Energy Materials and Solar Cells*, **1995**, *39*, 289-299.