

# Novel Polymeric Aromatic Lithium Sulfonylimides as Salts for Polymer Electrolytes

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**ABSTRACT:** Three new polymeric aromatic lithium sulfonylimides were used as salts in high molecular weight poly(ethylene oxide) (PEO) electrolytes. Their conductivity and electrochemical stability behaviors were investigated. The electrolytes with lithium poly[4,4'-(hexafluoroisopropylidene)diphenoxy]sulfonylimide (LiPHFIPSI) showed a better conductive performance compared with the other two lithium salts. The best conductivity was obtained for PEO/LiPHFIPSI EO/Li = 16 ( $1.90 \times 10^{-4}$  S/cm at 60°C). Thermal analysis indicated that the salts effectively decreased the crystallinity of PEO. Moreover, the electrolytes also had good electrochemical stability and their oxidative potential was to 5.5 V versus Li/Li<sup>+</sup>. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1802–1805, 2002

**Key words:** polyaromatic; polyimide; polyether; blends; electrochemistry

## INTRODUCTION

In the last decade, many lithium salts with large anions such as lithium trifluoromethanesulfonyl imide (LiTFSI) and Li methide<sup>1–4</sup> have been used as charge carriers in polymer electrolytes. These lithium salts have a lower energy of salt dissociation due to their higher negative charge delocalization of the anions, which result in a lower interaction between cations and anions. Reibel et al.<sup>5</sup> designed a new aromatic lithium sulfonylimide, that is, lithium bis(4-nitrophenylsulfonyl)imide (LiNPSI), to provide a large delocalization of negative charge through the sulfonyl groups and aromatic groups fitted with strong electron-withdrawing substituents (—NO<sub>2</sub>) in the *para* position. However, LiNPSI, dissolved in a linear high molecular weight polyoxyethylene, would neither decrease the crystallinity of PEO nor slow down

the crystallization rate. Therefore, it gave poor conductivity at room temperature. In a later work,<sup>6</sup> they took an amorphous polyoxyethylene network, NPC1000, as a solvent for LiNPSI and better conductivity was obtained at ambient temperature ( $8 \times 10^{-6}$  S cm<sup>-1</sup> at 30°C).

Recently, we synthesized a new type of lithium sulfonylimides with bulky or polymeric polyfluorinated organic anions<sup>7,8</sup> and found that these lithium salts exhibited good conductivity in an organic solvent.<sup>8,9</sup> In this article, polymer–salt complexes of polymeric aromatic lithium sulfonylimides were made by choosing a linear high molecular weight polyoxyethylene (PEO,  $M_w = 9 \times 10^5$ ) to investigate their conductivity behaviors, and their electrochemical stability was also preliminarily investigated.

## EXPERIMENTAL

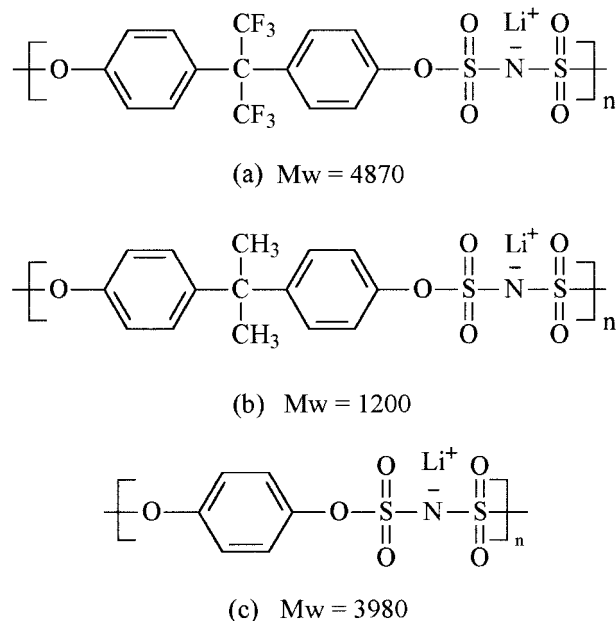
### Materials

Three polymeric aromatic lithium sulfonylimides, [lithium poly(4,4'-(hexafluoroisopropylidene)diphenoxy]sulfonylimide (LiPHFIPSI),

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**Figure 1** Structures of three polymeric aromatic lithium sulfonylimides: (a) lithium poly[4,4'-hexafluoroisopropylidene)diphenoxy]sulfonylimide (LiPHFIPSI); (b) lithium poly[4,4'-(isopropylidene)diphenoxy]sulfonylimide (LiPPIP SI); (c) lithium poly(hydroquinony)sulfonylimide (LiPHQSI).

lithium poly[4,4'-(isopropylidene)diphenoxy]sulfonylimide (LiPIP SI), and lithium poly(hydroquinony)sulfonylimide (LiPHQSI)], were synthesized by a previously reported method<sup>7,8</sup> and their structures are shown in Figure 1. The lithium salts were dried at 100°C under a vacuum for 24 h and stored in an argon-filled box (PEO,  $M_w = 9 \times 10^5$ ; Acros Organics, Beijing) was used as received. Tetrahydrofuran (THF, Aldrich) was dried over molecular sieves (type 4A, Merck) for several days before use.

### Sample Preparation

Lithium salts and PEO were each dissolved in THF at 60°C. Then, two solvents were mixed at 60°C with a magnetic stirrer and continuously stirred for 1 h. The solid electrolyte was obtained by completely evaporating THF at room temperature and the remainder was dried under a vacuum at 100°C for 48 h. Finally, the product was heated to 60–70°C in a home-made Teflon mold to acquire a translucent and flexible film (about 500- $\mu\text{m}$  thickness). The film was kept in desiccators under a vacuum with  $\text{P}_2\text{O}_5$  for the following measurements. All the procedures were carried out in a glove box filled with dry argon.

### Measurements

The conductivity of electrolytes was measured via the impedance method by sandwiching a given sample between two stainless-steel blocking electrodes (SS, area = 0.5 cm<sup>2</sup>). The measurements were performed using an SI 1250 frequency response analyzer and an SI 1286 electrochemical interface (Schlumberger Technologies) from 20 to 100°C over a frequency range from 5 mHz to 50 kHz.

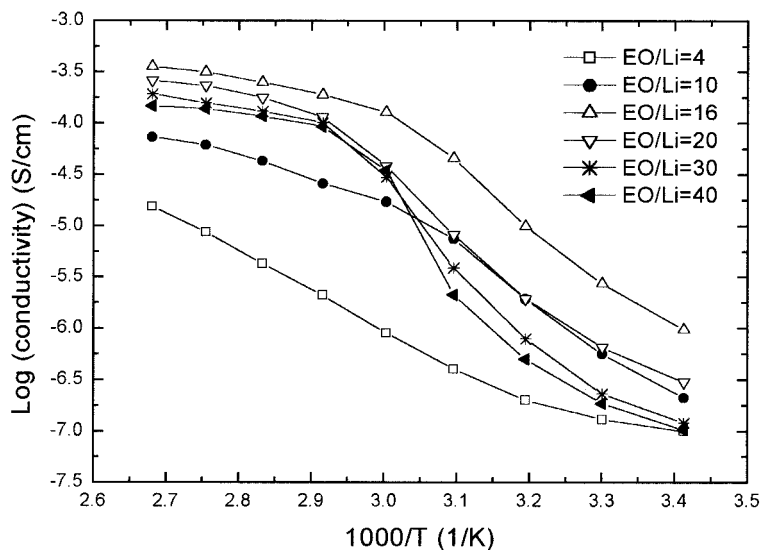
The melting temperature,  $T_m$ , and the thermal stability were measured in nitrogen using a Perkin-Elmer DSC-7 thermal analysis system. The samples were heated from 25 to 250 at 10°C min<sup>-1</sup>.

The electrochemical stability of electrolytes was determined by cyclic voltammetry (CV). It was carried out using a three-electrode cell: a stainless-steel block as the working electrode (area = 0.5 cm<sup>2</sup>), a lithium metal disc as the counterelectrode, and a lithium strip interposed between two adjacent layers as the reference electrode. The current-potential curves were recorded using an HB-104 function generator and an HA-501 potentiostat/galvanostat (Hokuto Denko Ltd.) at a 10 mV/s scan rate and a potential range from 0.0 to 6.0 V versus Li/Li<sup>+</sup>.

## RESULTS AND DISCUSSION

### Ionic Conductivity

Three lithium polymeric aromatic sulfonylimides blends with the PEO matrix with different salt concentrations and the conductivity behaviors of the electrolytes are discussed below. Figure 2 shows Arrhenius conductivity plots for PEO/LiPHFIPSI complexes with various salt concentrations. The plots indicate that most of the electrolytes contain a different amount of crystals at the turning points, and the melting peaks of the crystals in the electrolytes were found. The melting temperature decreased with an increasing salt concentration, according to thermal analysis. However, in the case of the EO/Li = 4 electrolyte, the turning point was not observed. The DSC data also exhibited that no melting peak was found in this system from ambient to 250°C. The most conductive system was obtained for the EO/Li = 16 electrolyte in the whole temperature range (from 20 to 100°C) and the value of the conductivity was found to be over 10<sup>-4</sup> S/cm above 60°C. Although the EO/Li = 4 electrolyte was amorphous, its conductivity was the lowest, which can

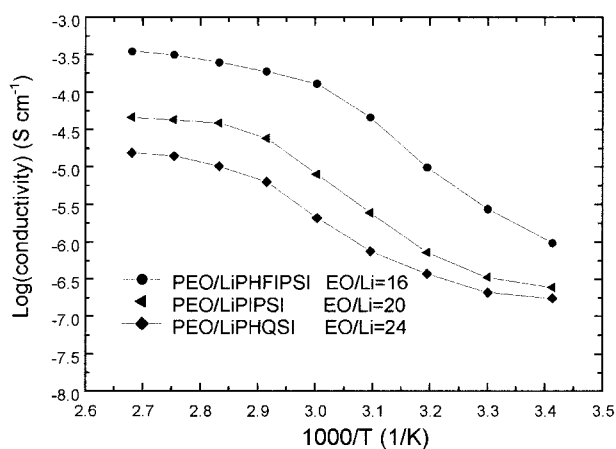


**Figure 2** Arrhenius conductivity plots for PEO ( $M_w = 9 \times 10^5$ ) containing LiPHFIPSI at salt concentrations of EO/Li = 4, 10, 16, 20, 30, and 40.

be attributed to the existence of small salt particles in the electrolyte, which handicap the transportation of cations. For all electrolytes except for EO/Li = 4, the conductivities were close to each other at high temperatures because the electrolytes were amorphous to 70°C and the conductivity only depended on the salt concentration at this time. On the other hand, hysteresis effects were observed in the conductivity measurements. When the systems were cooled from 100°C to room temperature, the ion conductivity became slightly higher. This result was in agreement with that of Reibel et al.'s work, which indicated some retardation to recrystallization.<sup>5</sup>

The conductivity of LiPIPSI and LiPHQSI was also measured with various salt concentrations (EO/Li = 10, 16, 20, 24, and 30 for LiPIPSI and EO/Li = 10, 16, 20, and 24 for LiPHQSI). The most conductive systems were found to be EO/Li = 20 and EO/Li = 24 for LiPIPSI and LiPHQSI, respectively. The results of conductivity for the most conductive polymer electrolytes of the three salts are shown in Figure 3. It can be seen that all the electrolytes under the experimental conditions are classic semicrystalline systems. The PEO/LiPHFIPSI (EO/Li = 16) electrolyte appears to have the best conductivity in the whole temperature range, LiPIPSI is second, and LiPHQSI exhibits the least conductivity. On the other hand, with corresponding salt concentrations, the results have a similar sequence as that shown in Figure 3. It is obvious that these results should be related to the different structures of the three lithium salts.

LiPHFIPSI has the highest charge delocalization of an anion due to the mesomeric effect of the sulfonyl groups and the negative inductive effect of the aromatic group. Especially, the strong electron-withdrawing fluorinated methyl groups have a very important role in charge delocalization compared with the results of LiPIPSI. LiPHFIPSI has the lowest ion-ion interaction among the three salts, which has a higher percentage of salt dissociation and the highest conductivity. LiPHQSI has the smallest anion and only one aromatic group in every chain, which provides less negative charge delocalization. The conductivity of the three polymeric lithium salts was higher than that of LiNPSI in



**Figure 3** Arrhenius conductivity plots of the most conductive systems for PEO ( $M_w = 9 \times 10^5$ ) containing LiPHFIPSI (EO/Li = 16), LiPIPSI (EO/Li = 20), and LiPHQSI (EO/Li = 24).

same polymer matrix below 50°C,<sup>5</sup> which might be due to that their polyanions decrease the crystallinity of PEO so that the cations could transport in the electrolytes easily. In the whole temperature range (from 20 to 100°C), the conductivity of the PEO/LiPHFIPSI (EO/Li = 16) electrolyte was approximately over one magnitude more than that of PEO/LiNPSI (EO/Li = 30), which indicated that more aromatic groups and strong electron-withdrawing groups, for example, fluorine atoms in a lithium salt molecule, were very useful for increasing the conductivity of a polymer electrolyte. On the other hand, LiPIPSI and LiPHQSI had a lower conductivity than that of LiNPSI above 50°C, which might be attributed to the stiffness of their polyanions, which hinder the segmental mobility of PEO at high temperature.

### Electrochemical Stability

The electrochemical stability of the electrolytes was carried out via cyclic voltammetry at a 10 mV/s scan rate and with a potential range from 0.0 and 6.0 V versus Li/Li<sup>+</sup> by sandwiching the polymer electrolytes between a blocking working electrode (SS) and a lithium counterelectrode, plus a lithium strip as the reference electrode. The anodic and the cathodic voltages at which the current was observed to flow at high values (higher than 0.1 mA/cm<sup>2</sup>) were taken as the breakdown limits of the electrolytes.

The oxidative potentials of three categories of electrolytes with the most conductive systems were measured. One can assume that the anodic breakdown voltage was above 5.5 V versus Li/Li<sup>+</sup> for all samples at 50°C. These results show that the solid electrolytes have good electrochemical stable windows, which suggest that they could be safely used for lithium or lithium ion batteries.

On the other hand, lithium ion transference numbers ( $t_+$ ) close to unity in the PEO-based polymer electrolytes are expected due to the polymeric aromatic lithium sulfonylimides having bulky polyanions. A preliminary work has been done concerning the measurements of the lithium ion transference number and the results have shown that the polymer electrolytes with these lithium salts had the characteristic of a single lithium ion conductor.<sup>10</sup>

### CONCLUSIONS

The polymeric aromatic lithium sulfonylimides, especially the polymeric aromatic lithium sulfonylimide that contains fluorinated methyl groups, gave better conductivity in polymer electrolytes, not only due to their large negative charge delocalization but also to the better hindrance to the crystallization of linear high molecular weight PEO by their large polyanions. Nevertheless, all electrolytes showed good electrochemical stability (>5.5 V versus Li/Li<sup>+</sup>). In further work, we will try to find a suitable polymer matrix as a solvent for these salts and the preparation of a nanocomposite polymer electrolyte with these salts might be another way to enhance the room-temperature conductivity of the polymer electrolytes.<sup>11</sup> The polymeric aromatic lithium sulfonylimides might be of potential use as a new type of polymer electrolyte salt for a lithium ion battery or other electrochemical devices.

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