

# Ionic Conduction of Polyurethane/Sulfonated Polyether Blends

Xinling Wang, Weihua Zhu, Yunhang Liu, Xiaozhen Tang, Xiaohui Yang

School of Chemistry and Chemical Technology, Shanghai Jiaotong University, 800 Dongchuan Road, Shanghai 200030, People's Republic of China

Received 26 April 2002; accepted 3 June 2002

**ABSTRACT:** Sodium single-ion poly(ether urethane)/sulfonated polyether blends based on the synthesis of a series of poly(ethylene oxide)s with sodium sulfonate side chains (SPEO) with different molecular weights were prepared and characterized by Fourier transform infrared spectroscopy, elemental analysis, Fourier transform Raman spectroscopy, differential scanning calorimetry, and complex impedance analysis. The results showed that the molecular weight and content of SPEO significantly influenced the compatibility between the hard and soft segments of polyurethane (PU), the glass-transition temperature, and the ionic conductivities

of PU/SPEO complexes. The glass-transition temperature of the system obviously decreased and the ionic conductivities of PU/SPEO complexes progressively increased with an increase in the SPEO content. In a certain range of temperatures, the ionic conductivities of PU/SPEO complexes agreed with an Arrhenius equation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2369–2373, 2003

**Key words:** polyethers; blends; polyurethane; polymer electrolyte; conduction

## INTRODUCTION

Since Wright and coworkers<sup>1,2</sup> reported that ion conduction in complexes formed between poly(ethylene oxide) (PEO) and alkali metal salts and Armand et al.<sup>3</sup> suggested that an ion-conducting polymer could be used as a solid electrolyte in a high-energy-density battery, extensive studies on polymer-state electrolytes have been carried out.<sup>4–7</sup> Because of their high compliance, good adherence to electrodes, and excellent processability for being made into thin films, solid polymer electrolytes (SPEs) have a high potential for use in rechargeable lithium batteries and other electrochemical devices.<sup>8</sup>

Traditional SPE materials are based on complexes of polymers and alkali metal salts. An ion-conducting polymer can be viewed as a solid solution of alkali metal salts that dissociates into free ions under the coordinating effects of neighboring polymer segments containing polar groups. The segments can rearrange their position and configuration and, therefore, change the location of ions, and they can favor electrical conduction through ion transport. Most researchers have focused their efforts on finding an SPE system possessing both high ionic conductivity and good mechanical properties. Various polymers,<sup>9–15</sup>

such as PEO, poly(propylene oxide), poly(vinylidene fluoride), poly(vinyl alcohol), poly(methyl methacrylate), poly(acrylonitrile), and poly(bismethoxy ethoxy phosphazene), have been employed as polymer matrices in the investigation of SPEs. Polyurethanes (PUs) are used as host matrices of SPEs because of their good chemical stability, excellent mechanical properties, and low glass-transition temperature ( $T_g$ ).<sup>6,16–19</sup> However, most PU electrolytes consist of PU and inorganic salts and are called bi-ionic conductors. In bi-ionic conductors, the migration of anions toward the cathode can cause a serious decay of direct-current conductivity and a time-dependent increase in the cell impedance, which are harmful to rechargeable batteries.<sup>20</sup>

This article reports a polymer electrolyte system based on blends of PU and an organic sodium salt, poly(ethylene oxide) grafted with sodium sulfonate side chains (SPEO). We expected that the large size of the SPEO anion might hinder the migration of anions under an electric field and eventually overcome the disadvantages of bi-ionic PU electrolytes. The primary concern was the effect of the SPEO content and molecular weight on the ionic-conductivity properties of PU/SPEO complexes.

Correspondence to: X. Wang (shenxw@online.sh.cn).

Contract grant sponsor: National Natural Science Foundation of China.

## EXPERIMENTAL

### Materials

Poly(ethylene glycol) (PEG; number-average molecular weight = 100, 200, or 300; Aldrich Chemical Co.,

Milwaukee, WI) was dried at 70°C in a vacuum oven for 48 h before use. 4,4'-Diphenylmethane diisocyanate (Aldrich Chemical) was purified by vacuum distillation. 1,4-Butanediol (Riedel-de Haën Co., Seelze, Germany) was dried via refluxing over CaH<sub>2</sub> for 4 h for the exclusion of trace water and was then distilled under vacuum. The solvent *N,N'*-dimethylacetamide (DMA; Shanghai Solvent Factory, Shanghai, China) was dried and distilled before use. Dimethyl fumarate, sodium hydrogen sulfite (NaHSO<sub>3</sub>), dimethyl sulfoxide, and calcium hydride (all from Aldrich Chemical) were used without further purification.

### Synthesis

The syntheses of poly(ether urethane) (PU), sulfonated dimethyl fumarate (SDMF), and SPEO have been reported previously.<sup>6</sup>

Films of PU/SPEO complexes were prepared with a solution-casting technique. In a typical procedure, appropriate amounts of PEG-PU and SPEO were dissolved in DMA, and the mixture was then poured onto a Teflon plate. After the solvent evaporated at 60°C in an oven for 24 h, the films were transferred to a vacuum oven and further dried at 60°C for at least 24 h for the removal of residual solvent.

### Characterization

IR spectra were recorded on a Nicolet 170 SX Fourier transform infrared (FTIR) spectrophotometer (WI) at a resolution of 2 cm<sup>-1</sup>. An elemental analysis was carried out on a PerkinElmer 240 elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) thermograms were recorded from -100 to 100°C with a PerkinElmer DSC2-C instrument at a heating rate of 10°C min<sup>-1</sup>. Fourier transform Raman spectra with a wave-number resolution of 2 cm<sup>-1</sup> were recorded at 25°C with a Bruker IFS66 (Ettlingen, Germany) with an FRA 106 Raman module and a near-infrared YAG laser with a wavelength of 1064 nm. Ionic-conductivity measurements with alternating current were conducted on a Hewlett-Packard 4192A impedance analyzer (Palo Alto, CA) in a frequency range of 10 to 10<sup>6</sup> Hz. The films were cut to a required size (10 mm in diameter and 0.2–0.3 mm

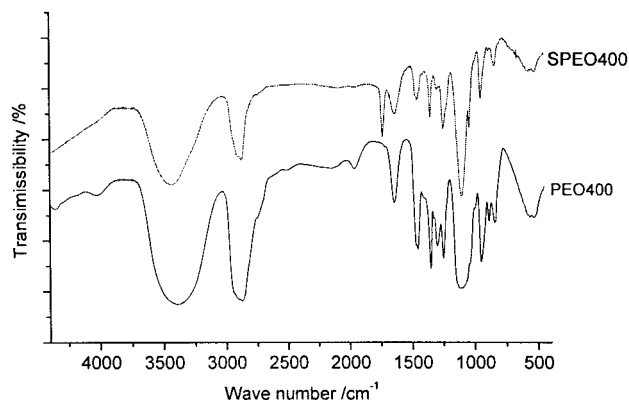


Figure 1 FTIR spectra of PEO400 and SPEO400.

thick) and were sandwiched between two copper electrodes.

The ionic conductivity ( $\sigma$ ) of the samples was calculated as follows:

$$\sigma = (1/R_B)L/A \quad (1)$$

where  $L$  is the thickness of the sample,  $A$  is the area of the copper electrode, and  $R_B$  is the bulk resistance of the sample.

### Composition of the SPE films

In this article, SPEO400 indicates SPEO with an average molecular weight of 400. PU/SPEO400-12 indicates a sample complex of PU with SPEO400, with the number 12 representing the molar ratio of ether oxygen groups to sodium cations, which is used to express the SPEO concentration in the system. Other samples are labeled similarly.

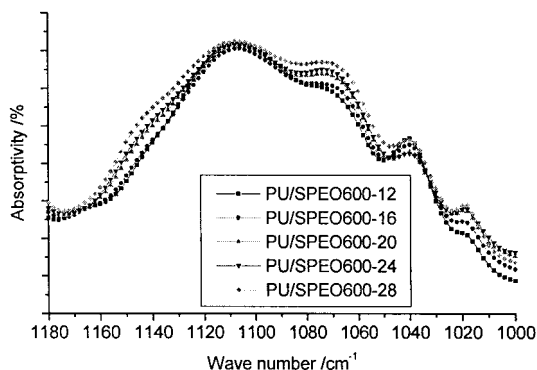
## RESULTS AND DISCUSSION

### FTIR spectral analysis

Figure 1 shows the FTIR spectra of PEO400 and SPEO400. An SO<sub>3</sub> stretching band at approximately 1040 cm<sup>-1</sup> and a carbonyl stretching band at approximately 1736 cm<sup>-1</sup> appear in the FTIR spectrum of SPEO400. This suggests that expected addition and

TABLE I  
Elemental Analysis Results for SDMF and SPEO

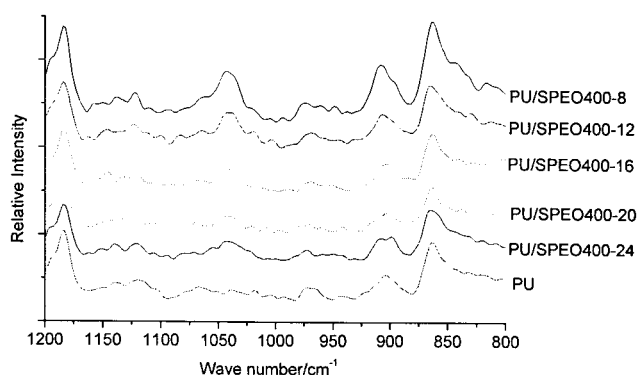
| Sample  | C%          |              | H%          |              | S%          |              |
|---------|-------------|--------------|-------------|--------------|-------------|--------------|
|         | Theoretical | Experimental | Theoretical | Experimental | Theoretical | Experimental |
| SDMF    | 29.04       | 29.83        | 3.69        | 4.10         | 12.90       | 12.63        |
| SPEO400 | 36.36       | 36.95        | 5.30        | 5.19         | 8.08        | 7.93         |
| SPEO600 | 41.50       | 42.01        | 6.37        | 6.47         | 5.80        | 6.12         |
| SPEO800 | 44.97       | 44.87        | 7.10        | 7.28         | 4.26        | 4.38         |



**Figure 2** IR spectra of PU/SPEO600 complexes in the ether oxygen stretching region.

transesterification reactions took place. The results of an elemental analysis (Table I) showed that experimental data were similar to theoretical data, and this consistent with the expected structure of SDMF and SPEO. This indicated that SPEO was synthesized successfully.

FTIR was used to investigate interactions between the organic sodium salt SPEO and the PU host matrix at room temperature. Two main IR spectral regions, 1660–1780-cm<sup>-1</sup> C=O stretching and 1000–1150-cm<sup>-1</sup> C—O—C stretching, are presented and studied. Figure 2 shows the 1000–1180-cm<sup>-1</sup> ether oxygen stretching region of the PU/SPEO400 series. The band centered around 1070 cm<sup>-1</sup> might be associated with the stretching vibrations of ether oxygen groups, involving coordination with sodium cations, whereas the bands at 1114 and 1146 cm<sup>-1</sup> were assigned to the stretching vibrations of nonbonded ether oxygen groups.<sup>21</sup> The stretching of free ether oxygen groups shifted from a higher frequency to a lower frequency when the SPEO concentration was increased. This shift to a lower frequency suggested that the ionic coordination between the ether oxygen groups and sodium cations increased with increasing SPEO contents in PU/SPEO systems. It was beneficial for the polymer electrolyte to enhance the ionic conductivity.



**Figure 3** Raman spectra of PU/SPEO400 complexes in the 1200–800-cm<sup>-1</sup> region.

**TABLE II**  
DSC data of PU/SPEO400 Complexes

| Sample        | [EO]/[Na <sup>+</sup> ] | $T_g$ (°C) |          | $\Delta C_p$ (J/g°C) |
|---------------|-------------------------|------------|----------|----------------------|
|               |                         | Onset      | Midpoint |                      |
| PU/SPEO400-8  | 8                       | -24.3      | -14.1    | 0.41                 |
| PU/SPEO400-12 | 12                      | -26.4      | -19.0    | 0.42                 |
| PU/SPEO400-16 | 16                      | -31.1      | -24.8    | 0.47                 |
| PU/SPEO400-20 | 20                      | -39.4      | -33.1    | 0.51                 |
| PU            | —                       | -40.7      | -34.9    | 0.46                 |

The same results were obtained from a study of PU/SPEO600.

### Raman spectral analysis

Figure 3 illustrates a typical Raman spectrum containing  $\nu_s$  ( $\nu$ : vibrational absorption band) ( $s$ : strong absorption band) ( $\text{SO}_3$ ) as a function of the SPEO concentration for the PU/SPEO400 series. The intensity of the 1040-cm<sup>-1</sup> band increased with increasing SPEO400 concentration. The 1040-cm<sup>-1</sup> band was assigned to the symmetric stretching vibration of the  $\text{SO}_3$  group. Figure 3 indicates that the intensity of the band of  $\nu_s(\text{SO}_3)$  gradually increased with a decrease in the molar ratio of ether oxygen to sodium cations or with an increase in the SPEO400 concentration.

### Thermal analysis of the PU/SPEO complexes

$T_g$  of the PU/SPEO system was measured so that we could evaluate the compatibility between the hard and soft segments after the introduction of SPEO into the PU matrix. DSC thermograms of the PU/SPEO400 series are shown in Table II.  $T_g$  of PU decreased (from ca. -14 to -33°C) with an increase in the [EO]/[Na<sup>+</sup>] molar ratio from 8 to 28 (where [EO] is the ethylene oxide concentration). (In each sample the ethylene oxide units or concentration can be calculated because weight of SPEO is accurately added). According to the conventional ionic transport mechanism based on polymer/salt complexes, sodium cations can coordinate with the polar ether oxygen groups of PU. Therefore, the solvation of the sodium cations by the PEG soft segment partially blocked the local motion of the polymer segment through the formation of transient crosslinking and resulted in a stiffening of the polymer chains or a higher  $T_g$ .

Table III lists DSC data for PU/SPEO400-24, PU/SPEO600-24, PU/SPEO800-24, and PU/SDMF-24 samples. The results indicate that  $T_g$  of the PU/SPEO series was lower than that of the PU/SDMF sample. The main reason was the compatibility of PU/SPEO being better than that of PU/SDMF. In the PU/SPEO blends, both the soft segments of PU and SPEO possessed the same repeat units, ethylene oxide, and enhanced the compatibility between PU and SPEO.

**TABLE III**  
DSC data of PU/SPEO Complexes

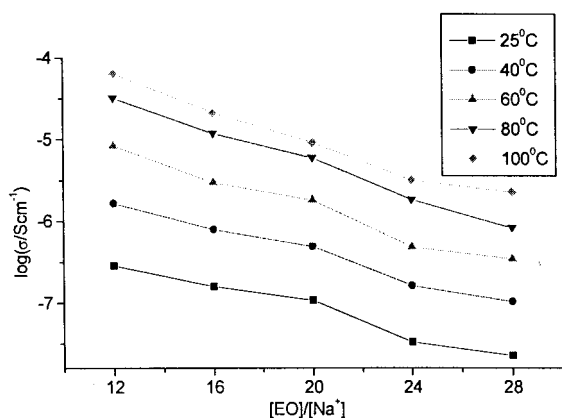
| Sample        | [EO]/[Na <sup>+</sup> ] | T <sub>g</sub> (°C) |          | ΔC <sub>p</sub> /J/(g°C) |
|---------------|-------------------------|---------------------|----------|--------------------------|
|               |                         | Onset               | Midpoint |                          |
| PU/SPEO400-24 | 24                      | -31.1               | -25.1    | 0.47                     |
| PU/SPEO600-24 | 24                      | -40.2               | -33.2    | 0.51                     |
| PU/SPEO800-24 | 24                      | -50.6               | -43.2    | 0.68                     |
| PU/SDMF-24    | 24                      | -29.5               | -20.2    | 0.48                     |
| PU            | —                       | -40.7               | -34.9    | 0.46                     |

ΔC<sub>p</sub> refers to heat capacity at constant pressure.

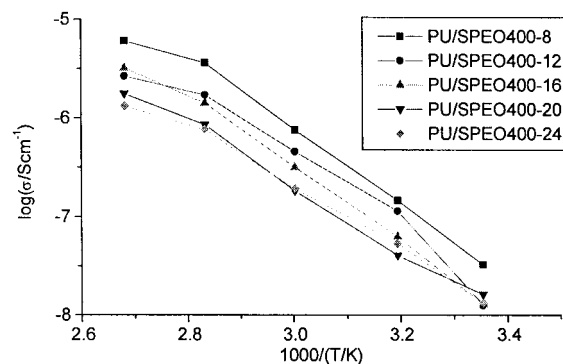
Moreover, the molecular weight of SPEO significantly influenced T<sub>g</sub> values of PU/SPEO complexes: T<sub>g</sub> decreased with an increase in the molecular weight of SPEO in the PU/SPEO blends. SPEO acted as a plasticizer in PU/SPEO blends and showed better compatibility when its molecular weight was higher. Meanwhile, at a certain [EO]/[Na<sup>+</sup>] ratio, the weight fraction of high molecular weight SPEO far exceeded that of low molecular weight SPEO in the PU/SPEO complexes investigated. Therefore, T<sub>g</sub> decreased dramatically because the mobility of the PEG soft segment was enhanced with the molecular weight of SPEO.

### Ionic-conductivity properties of the PU/SPEO complexes

Figure 4 shows the isotherm curves of the ionic conductivity against the SPEO concentration from an [EO]/[Na<sup>+</sup>] ratio of 8 to 28 for the electrolytes based on the PU/SPEO600 complex. In Figure 4, the ionic conductivity is shown to have increased with a decrease in the [EO]/[Na<sup>+</sup>] molar ratio. For the PU/SPEO complexes, there existed an interaction between the sodium cations and polar oxygen atoms in the ether units of the PU soft segments. As the polymer chain segments rearranged their configuration and position under an electric field, the location of the



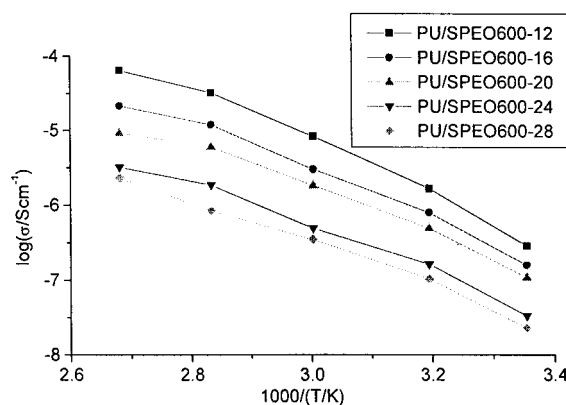
**Figure 4** Ion concentration dependence of the ionic conductivity for PU/SPEO600 complexes.



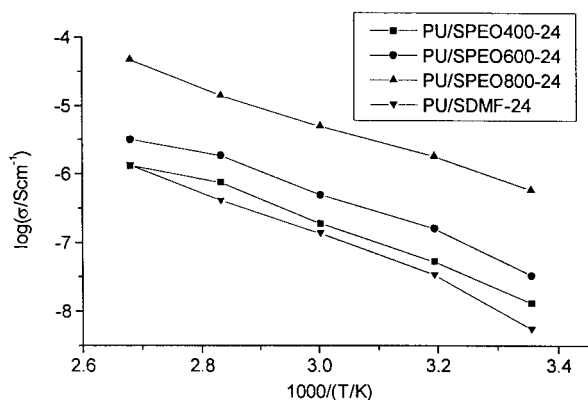
**Figure 5** Temperature dependence of the ionic conductivity for PU/SPEO400 complexes.

charge carriers was changed, and ionic transport was achieved accordingly. With respect to the PU/SPEO blend system, the amount of SPEO increased with the decrease in the [EO]/[Na<sup>+</sup>] ratio; therefore, the number of charge carriers was naturally increased. More sodium cations might be involved in the ion-transport process, which was favorable for an enhancement in the ionic conductivity of the PU/SPEO complexes investigated.

Figures 5 and 6 illustrate the temperature dependence of the ionic conductivity for PU/SPEO400 and PU/SPEO600 complexes, respectively. The ionic conductivities of PU/SPEO increased with an increase in the temperature because salt dissociation and ion mobility became easier at high temperatures. However, when the temperature was increased, the mobility of the polymer chain segments and the fraction of the free volume also apparently increased. All these factors resulted in an increase in the ionic conductivity of the PU/SPEO complexes. Furthermore, Figures 5 and 6 reveal five straight lines with different slopes for PU/SPEO400 and PU/SPEO600 complexes. It was inferred that the ionic conductance behavior of the PU/SPEO complexes followed the Arrhenius equation in the temperature region under investigation.



**Figure 6** Temperature dependence of the ionic conductivity for PU/SPEO600 complexes.



**Figure 7** Temperature dependence of the ionic conductivity for PU/SPEO600 complexes at an [EO]/[Na<sup>+</sup>] ratio of 24.

To illustrate the influence of the SPEO molecular weight on the ionic conductivity of the PU/SPEO complexes, we performed impedance measurements to determine the conductivity of four PU/SPEO samples with SPEO samples of different molecular weights. Figure 7 shows the effect of the SPEO molecular weight on the ionic conductivity of PU/SDMF and PU/SPEO complexes at an [EO]/[Na<sup>+</sup>] ratio of 24. The ionic conductivity of the PU/SPEO complexes clearly and monotonically increased with an increase in the molecular weight of SPEO within the whole temperature range investigated. The PU/SDMF-24 sample showed the lowest ionic conductivity, whereas the PU/SPEO800-24 sample exhibited the highest ionic conductivity, about  $6.0 \times 10^{-7} \text{ S cm}^{-1}$  at room temperature and  $4.8 \times 10^{-5} \text{ S cm}^{-1}$  at 100 °C, respectively. This feature was consistent with the DSC results previously presented. As expected, SPEO could act as an ionic resource and as a plasticizer in the PU/SPEO electrolytes. With an increase in the SPEO molecular weight, the plasticizing effect of SPEO became pronounced, allowing a high mobility of the charge carriers and providing a desirable ion-conductivity environment in the polymer electrolyte system. At a certain salt concentration, the amount of SPEO in the PU/SPEO800 system was higher than that in other systems containing low molecular weight SPEO, and there was a higher mobility of ion and polymer chain segments, which eventually led to a decrease in  $T_g$  and an increase in the ionic conductivity for the PU/SPEO complexes.

## CONCLUSIONS

The PU/SPEO complexes exhibited good film-forming abilities, low  $T_g$ 's, and certain ionic conductivities. The system might be viewed as a single-ion conductor. The concentration and molecular weight of SPEO greatly influenced the compatibility,  $T_g$ 's, and ionic conductivities of the PU/SPEO complexes. The compatibility of PU and SPEO increased with an increase in the content and molecular weight of SPEO, but  $T_g$  decreased sharply. Eventually, the ionic conductivities of the PU/SPEO complexes progressively increased. Moreover, the ionic conductance behavior obeyed the Arrhenius equation in the temperature range investigated.

## References

- Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* 1973, 14, 589.
- Wright, P. V. *J Polym Sci Polym Phys Ed* 1976, 14, 965.
- Armand, M. B.; Chabagho, J. M.; Duclot, M. I. In *Fast Ion Transport in Solids*; Vashishta, J. N., Ed. Elsevier: Amsterdam, 1979; p 131.
- MacCallum, J. R.; Vincent, C. A. *Polymer Electrolyte Reviews*; Elsevier: London, 1987; p 39.
- Wright, P. V. *Electrochim Acta* 1998, 43, 1137.
- Wang, X. L.; Li, H.; Tang, X. Z.; Chang, F. C. *J Polym Sci Part B: Polym Phys* 1999, 37, 837.
- Allcock, H. R.; O'Connor, S. J. M.; Olmeijer, D. L. *Macromolecules* 1996, 29, 7544.
- Lee, H. S.; Yang, X. Q.; Breen, J. M. *J Electrochem Soc* 1994, 141, 886.
- Zea Bermudez, V. D.; Alcácer, L.; Acosta, J. L.; Morales, E. *Solid State Ionics* 1999, 116, 197.
- Sreekanth, T.; Reddy, M. J.; Ramalingaiah, S.; Subba Rao, U. V. *J Power Sources* 1999, 79, 105.
- Huang, B. Y.; Wang, Z. X.; Li, G. B. *Solid State Ionics* 1996, 85, 79.
- Le Nest, J. F.; Gandini, A.; Charadame, H. *Macromolecules* 1988, 21, 1117.
- Fauteux, D.; Lupien, M. D.; Robitaille, C. D. *J Electrochem Soc* 1987, 134, 2761.
- Greenbaum, S. G.; Pak, Y. S.; Wintersgill, M. C.; Fontanella, J. J.; Schultz, J. W. *J Electrochem Soc* 1988, 135, 235.
- Greenbaum, S. G.; Ademic, K. J.; Pak, Y. S.; Wintersgill, M. C.; Fontanella, J. J. *Solid State Ionics* 1988, 28, 1042.
- Wei, X.; Yu, X. H. *J Polym Sci Part B: Polym Phys* 1997, 35, 225.
- Robila, G.; Ivanoin, M.; Buruiana, E. C. *J Appl Polym Sci* 1993, 49, 2025.
- Ding, Y.; Register, R.; Yang, C.; Cooper, S. *Polymer* 1989, 30, 1213.
- Wen, T. C.; Luo, S. S.; Yang, C. H. *Polymer* 2000, 41, 6755.
- Onishi, K.; Matsumoto, M.; Nakacho, Y. *Chem Mater* 1996, 8, 469.
- Ferry, A.; Jacobasson, P.; Heumen, J. D. V.; Stevens, J. R. *Polymer* 1996, 37, 737.