

# Novel Network Polymer Electrolytes Containing Fluorine and Sulfonic Acid Lithium Prepared by Ultraviolet Polymerization

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**ABSTRACT:** Novel gel network polymer electrolytes containing fluorine and sulfonic acid lithium were prepared by the ultraviolet polymerization of poly(ethylene glycol) dimethyl acrylate, 2-acrylamido-2-methyl propanesulfonic acid, and trifluoroethyl methacrylate. The network polymer was activated with 1.0M LiPF<sub>6</sub>/ethylene carbonate/dimethyl carbonate solutions (ethylene carbonate/dimethyl carbonate = 1 : 1 v/v) to prepare gel network polymer electrolytes. The characteristics of the polymer networks, including the gel fractions, thermal stability, liquid electrolyte uptake, and electrochemical properties, were studied. When the poly(ethylene glycol) dimethylacrylate/2-acrylamido-2-methyl propanesulfonic acid/trifluoroethyl methac-

rylate weight ratio was 60 : 35 : 5, the network polymer electrolytes showed the highest liquid electrolyte uptake (144%) and ionic conductivity (ca. 10<sup>-3</sup> S/cm) at room temperature (25°C). The network polymer electrolytes were electrochemically stable up to 5.0 V versus Li<sup>+</sup>/Li. The excellent performances of the network polymer electrolytes suggest that they are suitable for application in high-performance lithium-ion batteries. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2509–2514, 2008

**Key word:** photopolymerization; polymer electrolytes networks; electrochemistry; sulfonic acid lithium

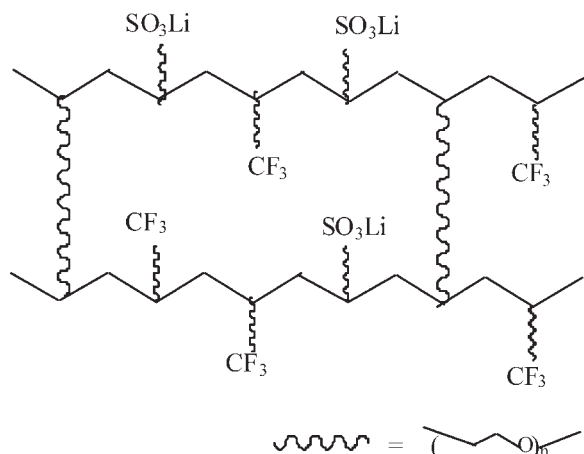
## INTRODUCTION

In the past few years, lithium-ion batteries using polymer electrolytes have been known as a preferred power source for various applications because of their high energy density, long life cycle, and memory-free effect.<sup>1–3</sup> The development of polymer electrolytes having high room-temperature ionic conductivity, excellent electrochemical stability, and good mechanical properties represents a crucial step in the evolution of polymer electrolytes for lithium-ion batteries. Solid polymer electrolytes typically show conductivities below 10<sup>-5</sup> S/cm at room temperature,<sup>4</sup> whereas the requirement for applications in lithium-ion batteries is at least 10<sup>-3</sup> S/cm. Conductivities in this range can be reached by the preparation of gel polymer electrolytes. Poly(ethylene oxide) (PEO) and poly(vinylidene fluoride) (PVDF) are two kinds of gel polymer electrolytes widely explored by many researchers.<sup>5–9</sup> A significant drawback of PEO-based polymer electrolyte systems is their insufficient mechanical properties. Various approaches involving the addition of ceramic fillers/additives and polar

plasticizers have been attempted.<sup>10–12</sup> PVDF-based polymer electrolytes have also been widely studied for rechargeable lithium-ion batteries because of their excellent mechanical and chemical stability.<sup>13,14</sup> However, their applications are limited by their poor ability to absorb the liquid electrolyte. One method has often been used to overcome this problem: trapping the solution in a microporous PVDF matrix.<sup>15</sup> However, developing dimensionally stable polymer electrolytes with high ionic conductivity, especially at room temperature, is still an important research topic.

In this study, a simple method of ultraviolet (UV) polymerization was used to synthesize network polymer electrolytes having segments with high solvent retention. Poly(ethylene glycol) dimethyl acrylate (PEGDMA) was used as a chemical crosslinker to improve the dimensional stability of the polymer electrolyte. Generally, the ability of a polymer to absorb and retain the electrolyte solution is crucial for gel polymer electrolytes. Therefore, 2-acrylamido-2-methyl propanesulfonic acid lithium (AMPS–Li), which has a good affinity for liquid electrolytes, was incorporated into the networks to achieve high ionic conductivity.<sup>16</sup> Trifluoroethyl methacrylate (TFEM) was chosen to increase the mechanical properties and chemical stability.<sup>17,18</sup> This is illustrated in Scheme 1.

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**Scheme 1** Schematic representation of the network based on the polymerization of the dimethyl acrylate crosslinker and acrylate comonomers.

## EXPERIMENTAL

### Materials

PEGDMA (number-average molecular weight  $\approx 536$ ) was obtained from Yantai YK Chemical Engineering Co., Ltd. (Shandong Province, China). 2-Acrylamido-2-methyl propanesulfonic acid (AMPS) was purchased from Shandong SQ Chemical Engineering Co., Ltd. (Shandong Province, China). TFEM was purchased from Xeogia Fluorine-Silicon Chemical Co., Ltd. (Heilongjiang Province, China). The UV initiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was provided by Runtecchem Co., Ltd. (Jiangsu Province, China). The other reagents were local commercial products. All the materials were used without purification. The chemical structures of PEGDMA, AMPS, and TFEM are shown in Scheme 2.

### Network polymer electrolyte preparation

PEGDMA, AMPS, TFEM, and DMPA (DMPA accounted for 5 wt % of the total weight of PEGDMA, AMPS, and TFEM) were first dissolved in a solvent (acetone/distilled water = 1 : 0.1 v/v), and a homogeneous solution was obtained. The homogeneous solution was cast onto two pieces of a glass sheet, and UV light (Osram, Germany, Ultra-Vitalux; 300 W, 10-cm distance) was irradiated onto the cast film for 10 min. The obtained freestanding networks were immersed in a LiOH/ethanol solution to exchange protons for lithium ions, and this was followed by washing with ethanol three times and drying *in vacuo* at 80°C for 2 days. Then, the dry polymer networks were activated in the 1.0M LiPF<sub>6</sub>/ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte (EC/DMC = 1 : 1 v/v).

### Network polymer electrolyte characterizations

#### Gel fraction analysis

To estimate the gel fractions of the different network polymers, weighed amounts of the network polymers were extracted with acetone as the extracting solvent for 24 h with Soxhlet extractors. After extraction, the gelled polymer was dried to a constant mass, and then the weight of the polymer was measured again. The gel fraction was calculated according to the following equation:

$$G = (B/A) \times 100\% \quad (1)$$

where  $G$  is the gel fraction and  $A$  and  $B$  are the weights of the network polymers before and after the extraction, respectively.

#### Thermogravimetric analysis (TGA)

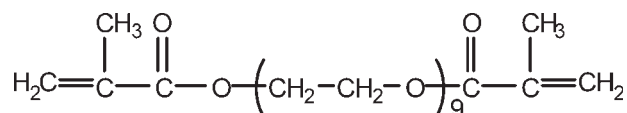
A PerkinElmer thermogravimetric analyzer (TGA-7) was used to investigate the thermal stability of the network polymer electrolytes. The samples (ca. 10 mg) were heated from the ambient temperature to 800°C in a nitrogen atmosphere, and the heating rate of 10°C/min was used in all cases.

#### Measurements of the swelling properties

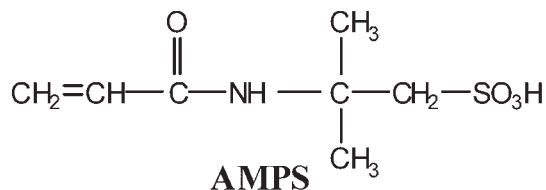
The uptake amount of EC and DMC (1 : 1 v/v) was determined as follows:

$$\text{Uptake} = (M - M_0)/M_0 \times 100\% \quad (2)$$

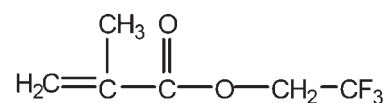
where  $M_0$  and  $M$  represent the weights of the samples before and after immersion in the liquid electrolyte, respectively.



**PEGDMA**

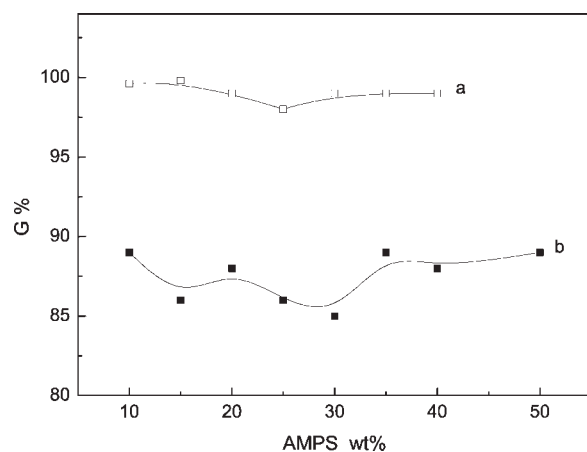


**AMPS**



**TFEM**

**Scheme 2** Chemical structures of PEGDMA, AMPS, and TFEM.



**Figure 1** Gel fraction ( $G$ ) of the network polymer electrolytes as a function of the PEGDMA and AMPS contents at 25°C: (a) 60 wt % PEGDMA and (b) 50 wt % PEGDMA.

#### Ionic conductivity measurements

The network polymer electrolytes [immersion of the dry polymer networks into a 1.0M LiPF<sub>6</sub>/EC/DMC (1 : 1 v/v) solution at room temperature for 24 h] were sandwiched between two stainless steel blocking electrodes. The ionic conductivities of the polymer electrolytes were obtained from the bulk resistance ( $R_b$ ), which was measured by alternating-current complex impedance analysis with a Solarton 1287 frequency response analyzer over a frequency range of 10 Hz to 1 MHz at an amplitude of 5 mV. The ionic conductivity ( $\sigma$ ) of the polymer electrolyte was determined as follows:

$$\sigma = t/(R_b A) \quad (3)$$

where  $t$  is the thickness of the network polymer electrolytes and  $A$  is the surface area of the networks.

#### Electrochemical stability window measurements

The electrochemical stability of the swelled network polymer electrolytes [immersion of the dry polymer networks into a 1.0M LiPF<sub>6</sub>/EC/DMC (1:1 v/v) solution at room temperature for 24 h] was evaluated by sweep voltammetry at 20°C. Discs of the network polymer electrolytes were sandwiched between lithium metal and stainless steel (with a 10-mm diameter) and then placed inside a Teflon cell holder. Stainless steel was used as a working electrode, and lithium metal was used both as a counter electrode and as a reference electrode. A sweeping voltage (1 mV/s) was applied to the cell starting from the open circuit voltage. When decomposition of the network polymer electrolytes took place, a large current passed through the cell. The decomposition voltage was evaluated as the onset of the current increase on voltage/current plots. The measurements were car-

ried out with a Solarton 1287 electrochemical interface.

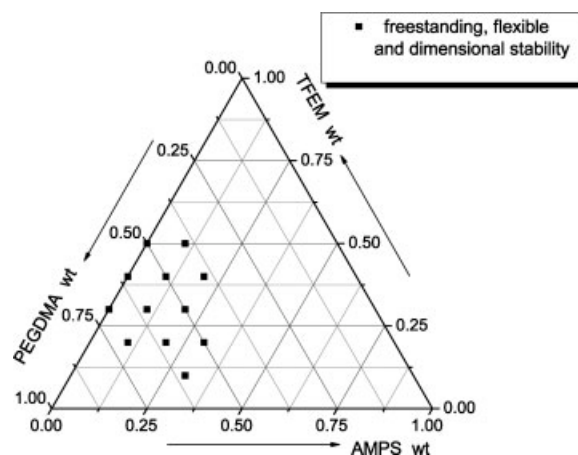
## RESULTS AND DISCUSSION

### Gel fraction

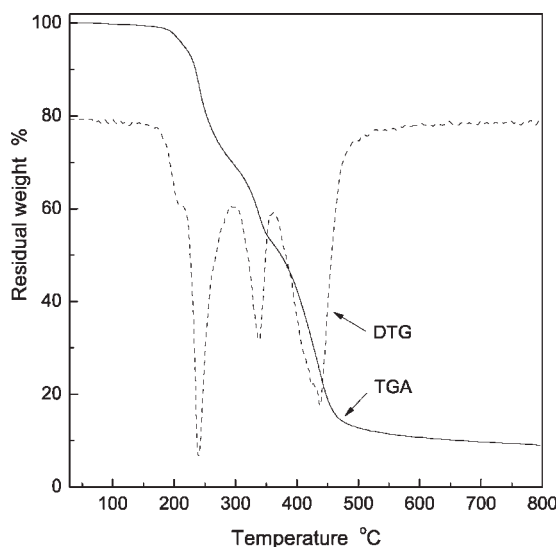
Gel fraction analysis was performed to assess the effectiveness of AMPS and TFEM incorporated into the network polymer electrolytes. The gel fraction of the networks was calculated with eq. (1) and is presented in Figure 1. The average gel fractions were 98 and 87% when the PEGDMA contents were 60 and 50 wt %, respectively. The gel fraction increased with an increase in the PEGDMA content because of the crosslinking effect of PEGDMA containing two terminal double bonds. A change in the gel fraction can be observed with different ratios of AMPS to TFEM in Figure 1. Therefore, the gel fraction of the polymer networks was determined by the content of PEGDMA.

### Visual appearance

The visual appearance of polymer networks activated by the 1.0M LiPF<sub>6</sub>/EC/DMC liquid electrolyte is shown in Figure 2 (the liquid electrolyte uptake behavior is discussed later). The freestanding, flexible, and dimensionally stable networks were obtained in a range of suitable weight percentages of PEGDMA, AMPS, and TFEM, as shown in the phase diagram (Fig. 3). The results indicated that chemical crosslinking by PEGDMA greatly improved the network dimensional stability. To obtain better mechanical properties for gel network polymer electrolytes, a quantitative amount of poly(trifluoroethyl methacrylate) should be added.



**Figure 2** Effect of the PEGDMA, AMPS, and TFEM weight ratios on the visual appearance of the polymer electrolyte networks activated by the 1.0M LiPF<sub>6</sub>/EC/DMC liquid electrolyte at 25°C.



**Figure 3** TGA thermogram of the network polymer electrolyte with a PEGDMA/AMPS/ $C_6H_7O_2F_3$  weight ratio of 60 : 35 : 5.

### TGA

The TGA curves and corresponding first derivative thermogravimetry (DTG) curves for the network polymer electrolytes are shown in Figure 3. The crosslinking networks showed three-step decomposition processes at 170–290°C, at 300–360°C, and above 470°C due to the degradation of PEGDMA,<sup>19</sup> AMPS–Li, and TFEM<sup>20</sup> in the PEGDMA/AMPS–Li/TFEM copolymer, respectively. The decomposition temperature of the poly(2-acrylamido-2-methyl propanesulfonic acid) homopolymer was about 210°C;<sup>21</sup> however, the decomposition temperature of AMPS–Li in the copolymer started at 300°C because the sulfonic acid group was neutralized by LiOH. These results indicated that the presence of AMPS–Li and TFEM in the networks enhanced the heat resistance. The thermal stability of the network was high enough for it to be applied in lithium-ion batteries.

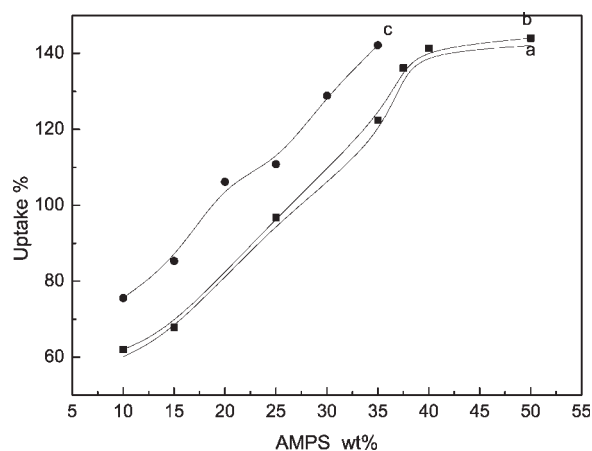
### Liquid electrolyte uptake and electrochemical properties

The ionic conductivity of a polymer electrolyte is dependent on the number of movable ions in the network and the interconnectivity of the ionic channels. Because ion transport takes place primarily in the region of the plasticizing polymer and organic solvent in gel polymer electrolytes, liquid electrolyte uptake is an important parameter for ionic conductivity. The liquid electrolyte uptake was measured with eq. (2) and is shown in Figure 4. The neutralization of AMPS had only a small enhancing effect on the liquid electrolyte uptake capacity [Fig. 4(a,b)]. However, the neutralization was necessary. On the

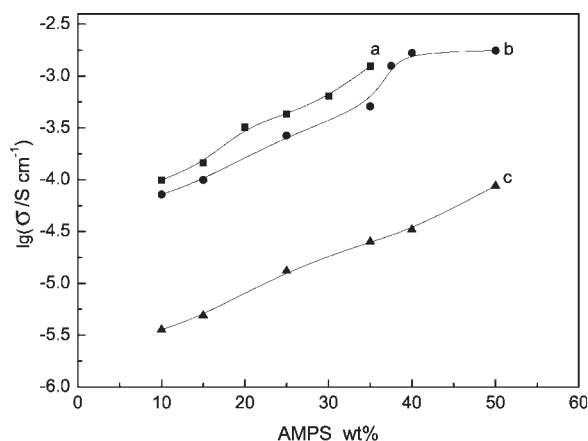
one hand, it was an approach to increase the effective  $Li^+$  content in gel network polymer electrolytes; on the other hand, it could prevent the negative influence of sulfonic groups on the electrode. It is well known that a high crosslinking density will lead to low liquid uptake. However, the liquid uptake of the polymer networks containing 60 wt % PEGDMA [Fig. 4(c)] was higher than that of the networks containing 50 wt % PEGDMA [Fig. 4(b)]. This could be ascribed to the oxyethylene group (good affinity for the liquid electrolyte) and the relatively long chain (number-average molecular weight  $\approx 536$ ) in PEGDMA. As also shown in Figure 4, the uptake increased with an increase in the AMPS content. This result indicated that the liquid uptake content in the network was more dependent on the AMPS content than on the PEGDMA content.

The room-temperature ionic conductivity of the PEGDMA/AMPS–Li/TFEM copolymer electrolytes is shown in Figure 5. It is evident that the trend of the ionic conductivity of the electrolytes is analogous to that of their liquid uptake. The conductivity of  $10^{-3}$  S/cm was obtained at an AMPS weight ratio above 35, which is high enough for practical applications in lithium-ion batteries. The 50 wt % PEGDMA sample without  $LiPF_6$  [Fig. 5(c)] showed ionic conductivity of about  $10^{-5}$  S/cm due to the dissociative  $Li^+$  in the AMPS–Li chain. However,  $LiPF_6$  should be added to provide more current carriers because the conductivity is lower.

Figure 6 illustrates the temperature dependence of the conductivity for network polymer electrolytes with the PEGDMA/AMPS/ $C_6H_7O_2F_3$  weight ratio of 60:35:5. The plot of the logarithm of the ionic conductivity versus the reciprocal of the temperature is



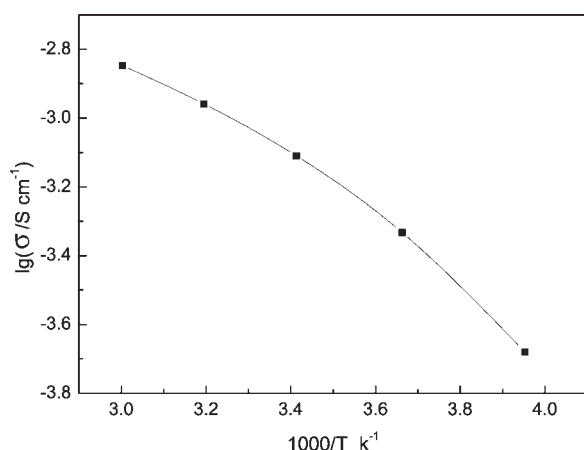
**Figure 4** Effect of the PEGDMA and AMPS contents on the liquid electrolyte uptake of the network polymer electrolytes at 25°C: (a) 50 wt % PEGDMA with AMPS not neutralized by LiOH, (b) 50 wt % PEGDMA with AMPS neutralized by LiOH, and (c) 60 wt % PEGDMA with AMPS neutralized by LiOH.



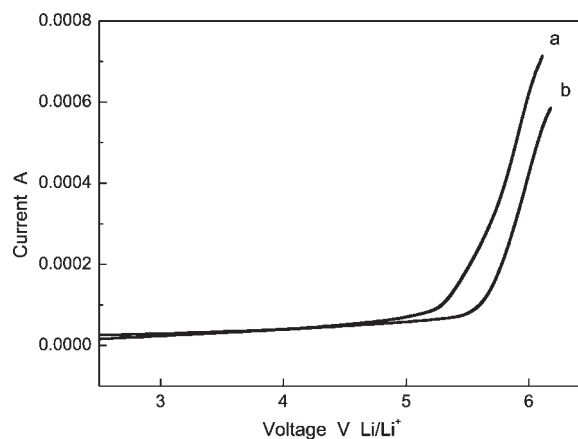
**Figure 5** Room-temperature ionic conductivity ( $\sigma$ ) of the network polymer electrolytes as a function of the PEGDMA and AMPS contents at 25°C: (a) 60 wt % PEGDMA, (b) 50 wt % PEGDMA, and (c) 50 wt % PEGDMA without  $\text{LiPF}_6$ .

curved rather than linear. Thus, the ionic conduction mechanism of our newly synthesized network polymer electrolytes seems to obey the Vogel–Tammann–Fulcher (VTF) rule.<sup>22</sup>

The electrochemical windows of the PEGDMA/AMPS/TFEM system at room temperature are given in Figure 7. The current responses of samples a and b were negligible below 5.0 V, indicating no decomposition of any components in this potential region. The electrochemical windows were higher than the requirements of practical applications (4.5 V). As shown in Figure 7, the electrochemical window of sample b (5.5 V) was wider than that of sample a (5.1 V); this may be because the fluoride content (TFEM) in sample b was higher than that in sample a and the carbon–fluoride group was beneficial to the electrochemical stability of the PEGDMA/AMPS/TFEM system.



**Figure 6** Arrhenius plots of the ionic conductivity ( $\sigma$ ) of the network polymer electrolyte with a PEGDMA/AMPS/ $\text{C}_6\text{H}_7\text{O}_2\text{F}_3$  weight ratio of 60 : 35 : 5.



**Figure 7** Electrochemical stability window of the gel polymer electrolytes with PEGDMA/AMPS/TFEM weight proportions of (a) 60 : 35 : 5 and (b) 50 : 35 : 15 by a linear sweep voltammogram at 20°C.

## CONCLUSIONS

A simple approach to preparing novel gel network polymer electrolytes containing fluorine and sulfonic acid lithium was studied. Liquid electrolyte uptake measurements indicated that the liquid uptake content in the network was mainly dependent on the AMPS–Li content. The thermal stability of the polymer networks was enhanced by AMPS–Li and TFEM. Good mechanical and electrochemical properties of the polymer networks could be achieved by the proper choice of the PEGDMA/AMPS/TFEM ratio. The optimum PEGDMA/AMPS/TFEM weight ratio in this study was 60:35:5. When the polymer electrolyte networks were activated by the 1.0M  $\text{LiPF}_6/\text{EC}/\text{DMC}$  liquid electrolyte, freestanding, flexible, and dimensionally stable networks were obtained. The highest liquid electrolyte uptake was 144%, and the maximum ionic conductivity was higher than  $10^{-3}$  S/cm at room temperature. The ionic conduction mechanism of the network polymer electrolytes was in agreement with the VTF rule. The gel polymer electrolytes were electrochemically stable up to 5.0 V. These results indicate that gel network polymer electrolytes containing fluorine and sulfonic acid lithium are suitable for applications in high-performance lithium-ion batteries.

## References

- Xue, J. S.; Wise, R. D.; Zhang, X. L.; Manna, M. E.; Lu, Y. X.; Ducharme, G.; Cuellar, E. A. *J Power Sources* 1999, 80, 119.
- Choi, Y. S.; Bae, Y. C.; Sun, Y. K. *J Appl Polym Sci* 2005, 98, 2314.
- Anonymous. *Am Ceram Soc Bull* 2006, 85, 6.
- Zhang, H. J.; Kulkarni, S.; Wunder, S. L. *J Phys Chem B* 2007, 111, 3583.
- Elmer, A. M.; Wesslen, B.; Sommer-Larsen, P.; West, K.; Hassander, H.; Jannasch, P. *J Mater Chem* 2003, 13, 2168.

6. Kim, K. M.; Park, N. G.; Ryu, K. S.; Chang, S. H. *J Appl Polym Sci* 2006, 102, 140.
7. Xi, J. Y.; Qiu, X. P.; Cui, M. Z.; Tang, X. Z.; Zhu, W. T.; Chen, L. Q. *J Power Sources* 2006, 156, 581.
8. Cha, E. H.; Lim, S. A.; Lee, C. W.; Macfarlane, D. R. *J Power Sources* 2006, 163, 269.
9. Sannier, L.; Bouchet, R.; Santinacci, L.; Grugeon, S.; Tarascon, J. M. *J Electrochem Soc* 2004, 151, A873.
10. Byrne, N.; Efthimiadis, J.; MacFarlane, D. R.; Forsyth, M. *J Mater Chem* 2004, 14, 127.
11. Morita, M.; Noborio, H.; Yoshimoto, N.; Ishikawa, M. *Solid State Ionics* 2006, 177, 715.
12. Rajendran, S.; Sivakumar, M.; Subadevi, R.; Wu, N. L.; Lee, J. Y. *J Appl Polym Sci* 2007, 103, 3950.
13. Nicotera, I.; Coppola, L.; Oliviero, C.; Ranieri, G. A. *Ionics* 2005, 11, 87.
14. Kim, J. R.; Choi, S. W.; Jo, S. M.; Lee, W. S.; Kim, B. C. *Electrochim Acta* 2004, 50, 69.
15. Wang, H. P.; Huang, H. T.; Wunder, S. L. *J Electrochem Soc* 2000, 147, 2853.
16. Tiyaiboonchaiya, C.; Pringle, J. M.; MacFarlane, D. R.; Forsyth, M.; Sun, J. Z. *Macromol Chem Phys* 2003, 204, 2147.
17. Ishigure, T.; Hirai, M.; Sato, M.; Koike, Y. *J Appl Polym Sci* 2004, 91, 410.
18. Lazzari, M.; Chiantore, O.; Castelvetro, V. *Polym Int* 2001, 50, 863.
19. Ha, J. C.; Kim, S. Y.; Lee, Y. M. *J Controlled Release* 1999, 62, 381.
20. Raihane, M.; Ameduri, B. *J Fluorine Chem* 2006, 127, 391.
21. Alonso, A.; Catalina, F.; Salvador, E. F.; Peinado, C. *Macromol Chem Phys* 2001, 202, 2293.
22. Kao, H. M.; Chao, S. W.; Chang, P. C. *Macromolecules* 2006, 39, 1029.