Synthesis and Characterization of Novel Semi-Interpenetrating Polymer Network Electrolyte Based on Crosslinked P(GMA-*co*-AN)/PEO

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ABSTRACT: A new solid polymer electrolyte based on semi-interpenetrating polymer networks (semi-IPN) of crosslinked poly(glycidyl methacrylate-*co*-acrylonitrile)/poly(ethylene oxide) (P(GMA-*co*-AN)/PEO) was synthesized with diethylenetriamine (DETA) as the crosslinking agent and characterized. Fourier transform infrared spectroscopy (FTIR) spectra suggested the formation of semi-IPN structure by crosslinking and revealed the interactions of Li$^+$ ions with both the ether oxygen in PEO chain and the nitrogen atom in AN segments. Differential scanning calorimetry (DSC) and X-ray diffraction pattern (XRD) measurements showed that crystallization of the semi-IPN polymer electrolyte was greatly impeded. Measurement of mechanical properties revealed that tensile strength of the polymer electrolyte was increased after crosslinking. Results of electrochemistry tests suggested that the new polymer electrolyte exhibited a high-ionic conductivity (10^{-4} S/cm) at room temperature, and an Arrhenius-like behavior of the conductivity was observed. And the semi-IPN polymer electrolyte with less content of PEO exhibited lower ion conductivity. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2095–2100, 2008

Key words: semi-IPN; crosslinking; crystallization; electrochemistry

INTRODUCTION

In the recent years, the design and synthesis of polymer electrolytes capable of transporting ions that utilized for fuel cells and lithium battery received great attention due to the increasing demand of portable, high-energy density, and safe power sources.[1] In a lithium secondary battery, polymer electrolytes function as separators as well as electrolytes.[2] An ongoing challenge in the design of polymer electrolytes is to combine in a single material the favorable electrochemical properties including high-ionic conductivity and interfacial compatibility at room temperature with the mechanical properties typical of thermoplastic.[3]

Although a large number of polymers satisfy the primary requisites for a host matrix in a battery, poly(ethylene oxide) (PEO)-based solid polymer electrolytes (SPEs) are the most widely studied.[4] However, the crystallinity of PEO below melting point is detrimental to the ion migration due to the reduction in the overall polymer flexibility, and PEO-based SPEs exhibited a low-ionic conductivity at ambient temperature.

Many valuable investigations have therefore focused on the enhancement of the room-temperature conductivity of PEO-based polymer electrolytes, via various approaches such as using blends,[5,6] copolymers, comb-branch polymers,[7] and crosslinked "networks."[8] All these enhancements have been achieved either by reducing the crystallinity of polymers or by lowering the glass transition temperature.[9]

Apart from PEO, poly(acrylonitrile) (PAN),[10] poly(vinylidene fluoride) (PVdF),[11] and poly(methyl methacrylate) (PMMA)[12] have also been used as host matrices for gel-type polymer electrolytes, which are fabricated by immobilizing lithium salts and nonaqueous solvents in a polymer matrix. Of these gel-type polymer electrolytes, the PAN-based system has been investigated extensively because of its high-ion conductivity at room temperature and dimensional stability.[13] However, the liquid phases in gel systems increase the ionic conductivity at the cost of the dimension stability of the polymer electrolytes.

Interpenetrating polymer networks (IPN) represent a unique class of materials in which two crosslinked polymers are held together by permanent topological entanglements.[14] The presence of three dimensionally interpenetrated networks radically improves the dimensional stability as well as reduces the crystallinity and phase separation.[15]

If only one component of the assembly is cross-linked leaving the other in linear form, the system is termed as a semi-IPN.[16] Specific noncovalent interactions between the linear and the crosslinked component can lead to a semi-IPN system in which the linear polymer is definitely trapped in the structure although not covalently crosslinked.[17]

Studies on the semi-IPN polymer electrolytes based on the PEO-PU/PAN[4] systems and poly(dimethyl siloxane-*g*-oligoethylene oxide) (SLX/EO)-poly(ethyleneoxide-*co*-propyleneoxide) triacrylate (EPTA) systems[18] previously showed good performance for lithium battery.

In this article, a polymer electrolyte with semi-IPN structure was prepared by blending PEO with P(GMA-*co*-AN), which was then crosslinked by DETA. The structure of the polymer electrolyte was examined, and its conductivity behavior investigated.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA) (Acros) was used as received, acrylonitrile (AN) was distillated under reduced pressure, and both of them were stored under refrigerator at $-20°C$, reagent-grade diethylenetriamine (DETA) (Sinopharm Chemical), and PEO ($M_w \sim 10^5$) (Alfa Aesar) were used without further purification. Acetonitrile (Sinopharm Chemical) and *N,N*-dimethylformamide (DMF) (Sinopharm Chemical) were dehydrated using 4 Å molecular sieve. Lithium electrolyte (DMC : DEC : EC = 1 : 1 : 1(W/W)LiPF$_6$ 1.0*M*) (Zhangjiagang Guotai-Huarong New Chemical Materials) was stored in exsiccator before use.

Polymer synthesis

Copolymerization of GMA and AN was conducted at 60°C, using benzoyl peroxide (BPO) as initiator and DMF as medium in a single-necked flask under N$_2$ atmosphere for 6 h.[19] Upon cooling, the mixture was precipitated in ethanol, filtered, and washed with ethanol to obtain P(GMA-*co*-AN). The copolymer was further purified by Sorbite extraction for 24 h and dried under vacuum for 24 h to remove the residual solvents.

Elemental analysis result showed that the mole ratio of —CN and epoxy in the copolymer was 1 : 2.

Semi-IPN electrolyte preparation

Polymer electrolyte films of PEO ($M_w \sim 10^5$) blended with P(GMA-*co*-AN) copolymer were prepared by casting using acetonitrile as solvent. In a typical procedure, the solution of the mixture (0.1 g/mL) was stirred for 24 h to become homogeneous, then DETA

(equal mol to epoxy group of copolymer) was added, and the solution was heated at 70°C for 1 h for the reaction of DETA with epoxy group in the copolymer. Afterward, the mixture was cast into Teflon molders and evaporated slowly at room temperature, followed by vacuum drying at 70°C for 24 h for further crosslinking[20] (Scheme 1). The polymer film, so obtained, was soaked in lithium electrolyte to form polymer electrolyte.

Measurements

FTIR measurements were carried out on a BRUKER VECTOR-22 spectrometer. Thermal analysis of the semi-IPN polymer electrolytes was carried out in a TA DSC 2910 differential scanning calorimeter under N$_2$ atmosphere with a heating rate 10°C min^{-1} from -80 to 150°C.

Mechanical properties of the polymer were measured by use of a CMT4204 tension tester (SANS Group Company, Shenzhen China) at 10 mm min^{-1} stretching speed. The samples were kept in a desiccator before the experiment.

The ionic conductivity (σ) of the membrane-supported composite gel polymer electrolytes was determined by AC impedance spectroscopy (EG and G Model 273A potentiostat). The membrane was sandwiched between two parallel stainless steel (SS) discs ($d = 1.5$ cm). During the measurement, it was mounted in a sealed coin cell to prevent contamination of the sample. The frequency ranged from 100 KHz to 10 Hz at a perturbation voltage of 10 mV. The ionic conductivity was calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (l), and the electrode area (A) according to the equation $\sigma = l/AR_b$.

RESULTS AND DISCUSSION

FTIR spectra of the polymer

The formation of the P(GMA-*co*-AN)-DETA/PEO semi-IPN was investigated by FTIR spectra. Figure 1(a) shows the IR spectrum of the copolymer P(GMA-*co*-AN). The peak at 907 cm^{-1} is indicative of epoxy group, and that at 2239 cm^{-1} is attributed to the nitrile (—CN) group in the copolymer. The 1728 cm^{-1} peak is due to the —C=O stretching vibration in GMA segments. Figure 1(b) presents the IR spectrum of the semi-IPN structured polymer thin film. The characteristic absorption peaks of the copolymer can be observed, and the peak at 1108 cm^{-1} is assigned to the ether (—C—O—C—) linkage in PEO system. Furthermore, it can be seen that the peak at 907 cm^{-1} nearly disappeared, indicating that the epoxy group of the copolymer P(GMA-*co*-AN) almost totally
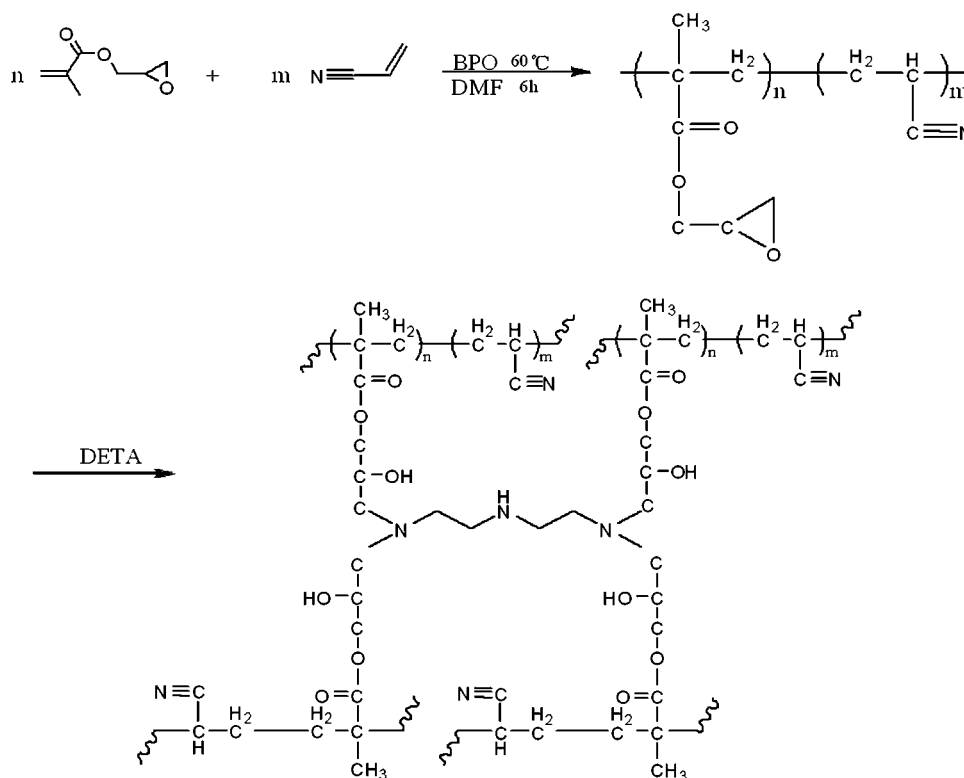
Scheme 1 Schematic representation of the crosslinking of P(GMA-*co*-AN) copolymer with DETA.

reacted with DETA. The IR spectrum suggest the formation of semi-IPN structure in which PEO was blended with the crosslinked P(GMA-*co*-AN). Figure 1(c) represents the IR spectra of the semi-IPN polymer in complexation with lithium salts. New peaks appeared in the spectroscopy, which can be seen more clearly in Figures 2 and 3, suggest the interaction between lithium ions and the semi-IPN polymer matrix. The weak shoulder peaks at around 1059 and 1147 cm^{-1} in Figure 2 indicate the interaction between (—C—O—C—) group in the PEO and lithium ions. Figure 3 depicts the FTIR spectra of —C≡N stretching in the absorption range of the —CN group for the semi-IPN structured polymer blends before and after interactions with lithium salt. The IR spectra reveal a weak shoulder at around 2272 cm^{-1} as a result of interaction between the Li$^+$ ions and —C≡N groups,[13] which is attributed to the formation of an associate involving the pair of unbonded electron on the nitrogen atom of the —C≡N groups.[21]

Thermal characteristics

The glass transition temperature (T_g) obtained from differential scanning calorimetry is a characteristic feature of amorphous phase. The thermograms of the semi-IPN systems are shown in Figure 4. The inflection point of the endothermic slope observed in the thermograms is taken as T_g, and the endothermic peak denotes the melting temperature (T_m).

The apparent enthalpies of melting (ΔH_m) are derived from the area under the endothermic peaks. The degree of crystallinity (χ) of the PEO fraction in the matrix is calculated from eq. (1):

$$\chi = \Delta H_m(\text{PEO})/\Delta H_m^0(\text{PEO}) \tag{1}$$

where ΔH_m^0 (PEO) = 205 J g^{-1} is the heat of melting per gram of 100% crystalline PEO and ΔH_m PEO is the apparent enthalpy of melting per gram of the PEO.
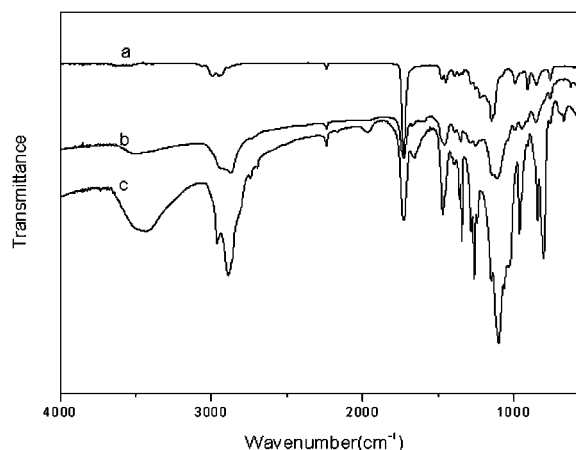

Figure 1 FTIR spectra of the formation of semi-IPN polymer electrolyte (a) P(GMA-*co*-AN); (b) semi-IPN based on P(GMA-*co*-AN)/PEO crosslinked by DETA; (c) semi-IPN doped with lithium electrolytes [EO]/[Li] = 10.
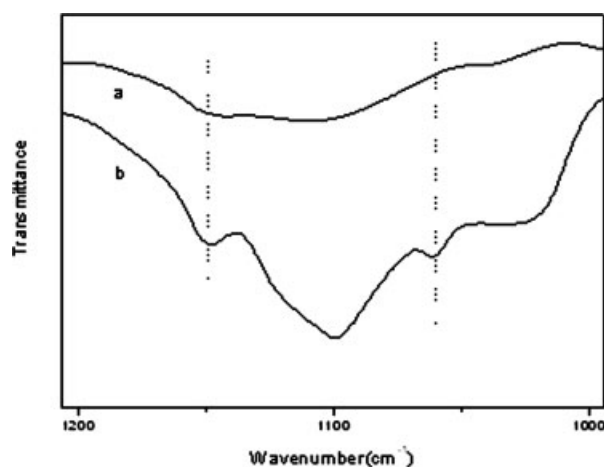
Figure 2 FTIR spectra for the —C—O—C group of PEO in semi-IPN polymer electrolyte chelated (a) without lithium ions; (b) with lithium ions [EO]/[Li] = 10.

The values of T_g, T_m, and χ for PEO and its blends with uncrosslinked and crosslinked copolymer as obtained from DSC measurements are summarized in Table I.

It can be seen that compared to pure PEO, the degree of crystallinity reduces dramatically with the addition of PAN and copolymer P(GMA-co-AN), especially after the copolymer formed a crosslinked structure with the addition of DETA. This is because that crosslinking of the copolymer greatly inhibited the chain mobility of another component PEO during crystallization. According to the value of χ of the semi-IPN system, some crystalline domains still exist, which suggests that the crosslinking degree of the copolymer is not very high. As a result, the dimension stability of the polymer system can be improved by crosslinking; at the same time, the polymer chains
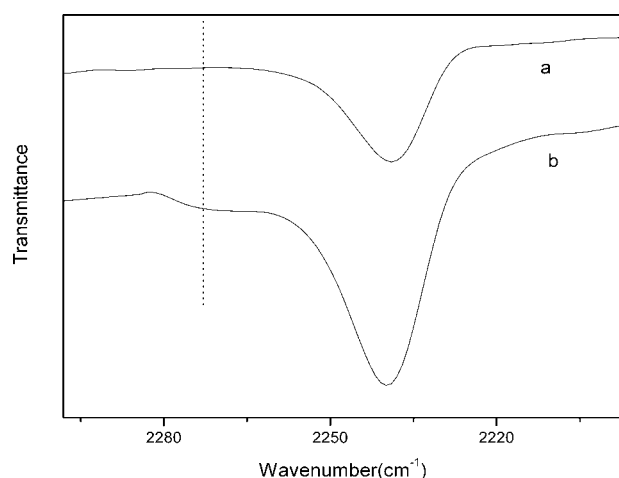

Figure 3 FTIR spectra for the acrylonitrile group of copolymer in semi-IPN polymer electrolyte chelated (a) without lithium ions; (b) with lithium ions [EO]/[Li] = 10.
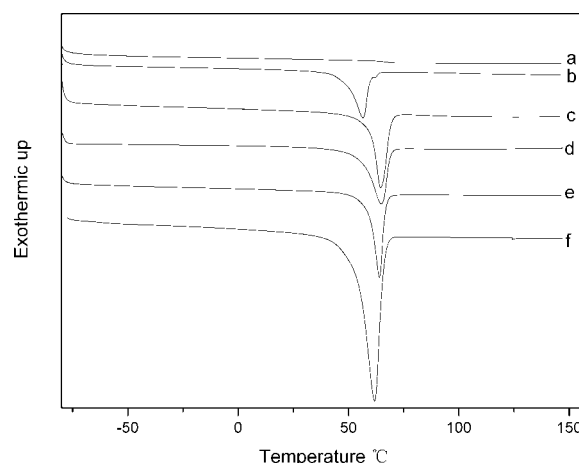
Figure 4 DSC thermograms of (a) P(GMA-co-AN); (b) P(GMA-co-AN)/PEO (50/50 wt) crosslinked by DETA; (c) P(GMA-co-AN)/PEO (60/40 wt) crosslinked by DETA; (d) P(GMA-AN)/PEO; (e) PAN-b-PEO; and (f) PEO.

remain flexible to transport ions. Furthermore, the semi-IPN polymer material exhibited a T_g well below room temperature, which is beneficial for the PEO-based material to obtain high-ionic conductivity at room temperature. The thermal analysis results revealed that the value of χ of the semi-IPN system was higher when the content of PEO was decreased, which led to a lower ion conductivity.

XRD characteristics

Figure 5 shows the XRD patterns of P(GMA-co-AN)/PEO before and after the crosslinking reaction with the addition of DETA. The XRD pattern of uncrosslinked P(GMA-co-AN)/PEO [Fig. 5(a)] reveals the crystalline peaks at 19.6° and 23.6°, respectively. Whereas these peaks nearly disappeared in the XRD pattern of crosslinked polymers [Fig. 5(b)]. The results indicated that the crosslinked system exhibited an

TABLE I
Effect of the Crosslinking and Blending on the Glass Transition Temperature (T_g), Crystalline Melting Temperature (T_m), Enthalpy Change (ΔH_m), and Degree of Crystalline (χ) of PEO

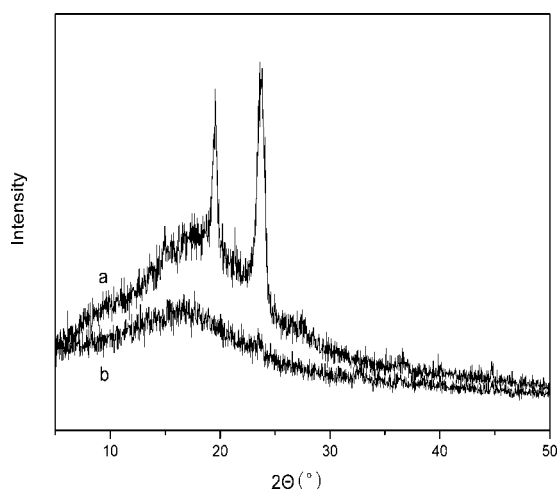| Samples	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	χ (%)
PEO	−62.90	61.79	136.5	66.6
PAN-b-PEO	−56.05	64.78	70.15	34.21
P(GMA-co-AN)/PEO	−54.04	64.00	60.04	29.28
P(GMA-co-AN)/PEO (60/40 wt %) crosslinked by DETA	−50.80	64.55	44.89	21.90
P(GMA-co-AN)/PEO (50/50 wt %) crosslinked by DETA	−48.21	61.51	32.80	16.0

Figure 5 X-ray diffraction patterns of P(GMA-*co*-AN)/PEO crosslinked (a) before DETA and (b) after DETA.

Figure 6 AC impedance spectrum of the SS/PE/SS cell at room temperature (25°C).

amorphous phase, which is consistent with the results of DSC measurements. It is known that amorphous morphology can greatly promote the motion of polymer chains and the diffusion of ions. Thus, the crosslinked semi-IPN system, which possesses an amorphous structure and low T_g, is expected to exhibit a high-ionic conductivity.

Mechanical properties

The tensile strength testing results for the polymer films are presented in Table II. The pure PEO film exhibited a critical stress of 3.78 MPa. After blending with P(GMA-*co*-AN), the critical strength of the film was 3.22 MPa, which was lower than that of the pure PEO film. The decreased critical strength of blended film might be related to the incompatibility of PEO and copolymer. The critical strength of film the of P(GMA-*co*-AN)/PEO crosslinked by DETA showed a critical strength twice higher than that of uncrosslinked P(GMA-*co*-AN)/PEO. This indicates that the crosslinking apparently contributes to the improvement in the mechanical property. It was noticed that after doping with lithium electrolytes (DMC : DEC : EC = 1 : 1 : 1 (W/W)LiPF$_6$ 1.0M), the critical strength of polymer electrolyte was 2.04 MPa, higher or similar in comparison with the results observed by others.[22]

Electrical properties

The ionic conductivity of the gel-type polymer electrolytes was measured using two SS electrodes plates at different temperatures to study the conduction behavior of the charge carriers in the plasticized semi-IPN system. Figure 6 shows the AC impedance spectrum of SS/PE/SS cell (PE, polymer electrolyte) measured at 25°C. The absence of semicircle at high frequency in the impedance spectrum suggests that only the resistive component of polymer electrolyte could be considered in presence of plasticizer.[23] And the constant phase element (CPE) behavior is mainly attributed to the diffusion response between the polymer electrolyte and the electrode.[24] The intercept of the spectrum on the real axis gives the electrolyte

Figure 7 log σ versus 1000/T plots for semi-IPN polymer electrolyte based on P(GMA-*co*-AN)/PEO (50/50 wt) (a) and P(GMA-*co*-AN)/PEO (60/40 wt) (b) crosslinked by DETA.

TABLE II
Critical Strength of Films of (a) PEO, (b) P(GMA-*co*-AN)/PEO, (c) P(GMA-*co*-AN)/PEO Crosslinked by DETA, and (d) P(GMA-*co*-AN)/PEO Doped with Lithium Electrolytes

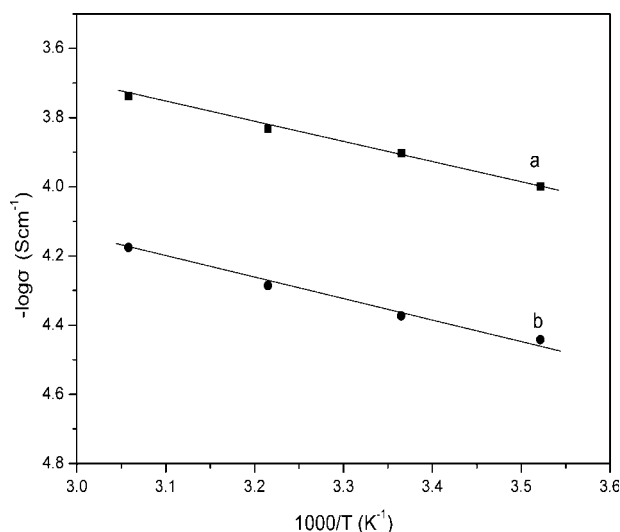| Samples	a	b	c	d
Critical strength (MPa)	3.78	3.22	6.31	2.04

resistance, and the ionic conductivity was calculated to be 10^{-4} S/cm. It is believed that the high-ionic conductivity of the polymer electrolyte results from the amorphous structure. In addition, it was found that the polymer electrolyte film was robust enough to handle after doping with lithium electrolytes (DMC : DEC : EC = 1 : 1 : 1(W/W) LiPF$_6$ 1.0M), which is attributed to the improved dimensional stability resulted from the crosslinking structure.

The effect of temperature on the conductivity of the semi-IPN polymer electrolytes were investigated and $\log -\sigma$ versus $1000/T$ was depicted in Figure 7. It is found that $\log \sigma$ changed linearly with $1/T$, indicating an Arrhenius-like behavior of conductivity according to eq. (2).

$$\sigma = \sigma_0 \exp(-E_a/kT) \tag{2}$$

where σ_0 is a constant, E_a the activation energy, and k the Boltzmann constant.

The steady increase in conductivity with temperature is interpreted as a hopping mechanism between coordinating sites, accompanied by local structural relaxation and segmental motion of the polymer. It is thus concluded that the temperature dependence of conductivity for the semi-IPNs of (PGMA-PAN)-DETA/PEO/LiPF$_6$ follows an Arrhenius relationship in the measurement temperature range. The fact that the semi-IPN polymer electrolyte with less content of PEO exhibited lower ion conductivity is mainly attributed to the higher degree of crystallinity elucidated by DSC results. In addition, less content of PEO in the system resulted in the decreased concentration of coordinated lithium ions, which is responsible for ion transportation.

CONCLUSIONS

Semi-IPN polymer electrolyte of P(GMA-*co*-AN)/PEO was synthesized by means of the crosslinking of P(GMA-*co*-AN) in the presence of DETA. The formation of semi-IPN structure greatly impeded the crystallization of PEO and promoted the dimensional stability of the material. The polymer electrolyte exhibited a room temperature conductivity of 10^{-4} S/cm, and the temperature dependence of its conductivity follows Arrhenius behavior in the measured tempera-

ture range. And the semi-IPN polymer electrolyte with less content of PEO exhibited lower ion conductivity. The semi-IPN structured material is promising as a SPE with good room temperature conductivity and desirable mechanical and thermal properties.

References

1. Dias, F. B.; Plomp, L.; Veldhuis, J. B. J. J Power Source 2000, 88, 169.
2. Hou, X. P.; Siow, K. S. Polymer 2001, 42, 4181.
3. Liu, G.; Reinhout, M.; Mainguy, B.; Baker, G. L. Macromolecules 2006, 39, 4726.
4. Basak, P.; Manorama, S. V. Solid State Ionics 2004, 167, 113.
5. Rajendran, S.; Mahalingam, T.; Kannan, R. Solid State Ionics 2000, 130, 143.
6. Choi, B. K.; Kim, Y. W.; Shin, H. K. Electrochim Acta 2000, 45, 1371.
7. Cowie, J. M. G.; Spence, G. H. Solid State Ionics 1999, 123, 233.
8. Kang, K. Y.; Cheong, K.; Noh, K.-A.; Lee, C.; Seung, D.-Y. J Power Source 2003, 119–121, 432.
9. Song, J. Y.; Wan, C. C. J Power Source 1999, 77, 183.
10. Tatsuma, T.; Taguchi, M.; Iwakr, M.; Sotomura, T.; Oyama, N. J Electroanal Chem 1999, 472, 142.
11. Cheng, C. L.; Wan, C. C.; Wang, Y. Y. J Power Source 2004, 134, 202.
12. Georén, P.; Lindberg, G. Electrochim Acta 2004, 49, 3497.
13. Liang, Y. H.; Wang, C. C.; Chena, C.-Y. J Power Source 2005, 148, 555.
14. Kim, H. K.; Wang, X. S.; Fujita, Y.; Sudo, A.; Nishida, H.; Fujii, M.; Endo, T. Macromol Rapid Commun 2005, 26, 1032.
15. Basak, P.; Manorama, S. V. Eur Polym J 2004, 40, 1155.
16. Kim, S. J.; Lee, C. K.; Lee, Y. M.; Lee, K. B.; Park, Y. D.; Kim, S. I. J Appl Polym Sci 2003, 90, 3922.
17. Vidal, F.; Popp, J.-F.; Plesse, C.; Chevrot, C.; Teyssie, D. J Appl Polym Sci 2003, 90, 3569.
18. Noda, K.; Yasuda, T.; Nishi, Y. Electrochimica Acta 2004, 50, 243.
19. Brar, A. S.; Dutta, K. Macromolecules 1998, 31, 4695.
20. Casalbore-Miceli, G.; Chen, Y. S.; Girotto, E. M.; Li, Y.; Rinaldi, A. W.; Zanelli, A. Sensors Actuators B 2006, 119, 577.
21. Hou, W. H.; Chen, C. Y. Electrochim Acta 2004, 49, 2105.
22. Kim, S. H.; Choi, J. K.; Bae, Y. C. J Appl Polym Sci 2001, 81, 948.
23. Yang, M. J.; Li, W. L.; Wang, G. G.; Zhang, J. Q. Solid State Ionics 2005, 176, 2829.
24. Belmonte, G.; Bueno, P.; Longo, E.; Bulhões, L. O. S. J Electroanal Chem 1998, 452, 229.