Solid Polymer Electrolytes. VII. Preparation and Ionic Conductivity of Gelled Polymer Electrolytes Based on Poly(ethylene glycol) Diglycidyl Ether Cured with α,ω-Diamino Poly(propylene oxide)

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ABSTRACT: Crosslinked polymer electrolyte networks were prepared from poly(ethylene glycol) diglycidyl ether blended with an epoxy resin (diglycidyl ether of bisphenol A) in different ratios and then cured with α,ω-diamino poly(propylene oxide) in the presence of lithium perchlorate ($LiClO_4$) as a lithium salt. The ionic conductivities of these polymer electrolytes were determined by alternating current (AC) impedance spectroscopy. Propylene carbonate (PC) was used as a plasticizer to form gelled polymer electrolyte networks. The conductivities of the polymer electrolytes containing 46 wt % PC plasticizer were approximately 5×10^{-4} S cm^{-1} at 25°C and approximately 10^{-3} S cm^{-1} at 85°C. These polymer electrolytes were homogeneous and exhibited good mechanical properties. The effects of the polymer composition, plasticizer content, salt concentration, and temperature on the ionic conductivities of the polymer electrolytes were examined. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1264–1270, 2004

Key words: crosslinking; polyethers; networks

INTRODUCTION

During the past 2 decades, much research has been devoted to new fundamental and developmental amorphous polymer materials doped with lithium salts. These polymer materials have been identified as potential candidates for applications as electrolyte membranes in high-energy-density rechargeable lithium batteries.[1,2] Poly(ethylene oxide) (PEO) is the best host matrix for disassociating lithium salts. Besides PEO, several alternative systems, such as poly(methyl methacrylate),[3,4] polyacrylonitrile,[5,6] poly(vinylidine fluoride),[7] and polyurethane,[8–10] have been investigated. Because solid-state polymer electrolytes exhibit low ionic conductivity at ambient temperature, which prevents them from being used in further applications, organic plasticizers are used to swell the polymers and to enhance the ionic conductivity of the polymer electrolytes; in this way, gelled electrolytes are formed. These organic plasticizers, such as propylene carbonate (PC), ethylene carbonate, and γ-butyrolactone, generally have high dielectric constants to ensure high levels of ion dissociation. So that the gelled polymer electrolytes have sufficient mechanical properties, sometimes crosslinked networks are used as polymer components in gelled polymer electrolytes. The applications of electrolytes in lithium batteries require a combination of high ionic conductivity, good mechanical properties, good film-forming properties, and good chemical and electrochemical stability.

In an attempt to obtain polymer electrolytes with good film-forming properties, high ionic conductivity, and good mechanical properties, we prepared and studied a series of crosslinked siloxane/PEG copolymers in our previous work.[11] In this study, gelled crosslinked polymer electrolyte networks were prepared from poly(ethylene glycol) diglycidyl ether (PEGDE) blended with an epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] in different weight ratios with α,ω-diamino poly(propylene oxide)s used as curing agents. The conductivity behavior of these polymer networks doped with lithium perchlorate ($LiClO_4$) was investigated. The effects of the polymer composition, plasticizer content, salt concentration, and temperature on the ionic conductivity of the polymer electrolytes were examined.

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EXPERIMENTAL

Materials

PEGDE (Kyoeisha Chemical Co., Ltd., Japan) and DGEBA (Nan-Ya, Taiwan), epoxy monomers with epoxy group equivalent weights of 290 and 190 g/equiv,

respectively, and two α,ω-diamino poly(propylene oxide)s (Jeffamine D400 and Jeffamine D2000, Huntsman Corp., Utah) used as curing agents, with active hydrogen equivalent weights of 115 and 514 g/equiv, respectively, were dried at 80°C *in vacuo* for 24 h before use. LiClO$_4$ (Aldrich, Milwaukee, WI) was dried at 120°C *in vacuo* for 72 h. Acetone (Alps, Japan), PC (Acros, UK), and other chemicals were reagent-grade and were used without further purification.

Preparation of solvent-free and gelled crosslinked polymer electrolyte networks

All the polymer electrolyte networks were prepared as follows: Polymer electrolyte network films 100–150 μm thick were prepared through the dissolution of certain amounts of the epoxy monomers (PEGDE and DGEBA) and a stoichiometric amount of the curing agent in acetone, and then various amounts of LiClO$_4$ were dissolved in the as-prepared solutions. The concentration of LiClO$_4$ in the polymer network complexes was represented by the molar ratios of ether oxygens of PEGDE and α,ω-diamino poly(propylene oxide) to LiClO$_4$ ([O]/[Li$^+$]). After vigorous stirring, the mixtures were then poured onto aluminum plates; this was followed by the evaporation of the solvent at room temperature and curing at a temperature ranging from 150 to 185°C for different time intervals so that the completion of the curing was ensured. These specimens were dried *in vacuo* at 80°C for 72 h until no weight loss was observed, and then they were transferred into an argon-filled glove box (Vacuum Atmosphere, California) to prepare gelled polymer electrolyte networks and for cell assembly.

So that gelled polymer electrolyte networks would be obtained, the solvent-free polymer electrolyte films were soaked in the PC plasticizer for various periods at room temperature. The amount of the PC plasticizer was adjusted according to the total weight of each gelled polymer electrolyte network, which was composed of the solvent-free polymer electrolyte network and the liquid PC plasticizer.

Characterization

Differential scanning calorimetry (DSC; TA2010, DuPont, Wilmington, DE) measurements were conducted from −120 to +120°C at a heating rate of 10°C/min under a dry nitrogen atmosphere. The samples, sealed in aluminum pans, were first heated at 120°C for 10 min to remove the thermal history, and then they were cooled to −120°C and scanned. All the thermograms were baseline-corrected and calibrated against indium metal. The glass-transition temperature (T_g) was reported as the onset of the curve.

Alternating current (AC) impedance measurements of the polymer electrolytes were performed with as-prepared thin films about 200 μm thick with an area of 0.785 cm^2. The ionic conductivities of the films sandwiched between two polished stainless steel blocking electrodes were obtained with a model 604A electrochemical analyzer (CH Instruments, Inc., Texas) under an oscillation potential of 10 mV from 100 kHz to 100 Hz. The ionic conductivities were calculated as follows: $\sigma = l/(R_b \times S)$, where R_b is the bulk electrolyte resistance determined from AC impedance and l and S are the film thickness and the surface area of the electrode, respectively.
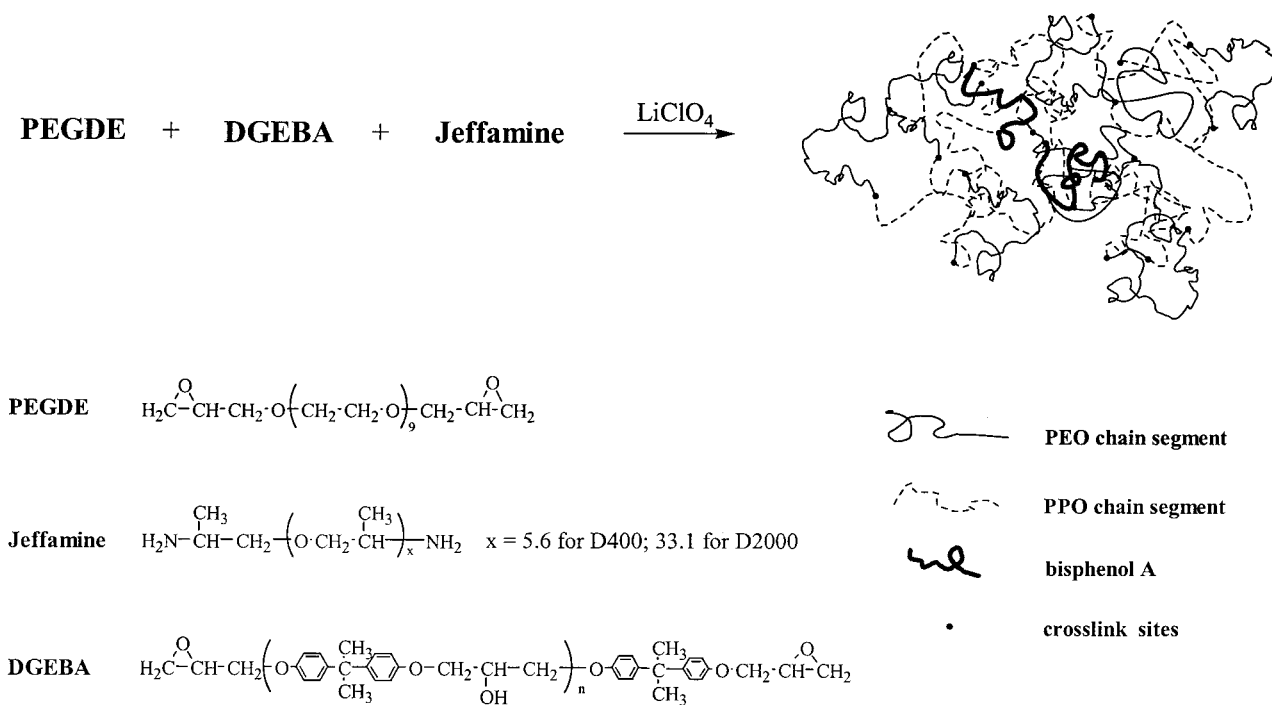
RESULTS AND DISCUSSION

In this study, in an attempt to obtain a high-ionic-conductivity electrolyte with good mechanical properties, we prepared gelled crosslinked polymer electrolyte networks from PEGDE blended with an epoxy resin (DGEBA) in different ratios with α,ω-diamino poly(propylene oxide)s (Jeffamine D400 and D2000) as curing agents in the presence of LiClO$_4$ as a lithium salt and a PC solvent as a plasticizer. According to IR spectra of these crosslinked polymer networks, the characteristic epoxide absorption peak at 915 cm^{-1} disappeared, and this indicated the complete reaction of the epoxide on PEGDE and DGEBA. All the polymer films were transparent and elastic. The schematic structure of the polymer networks is shown in Scheme 1.

Ionic conductivity measurements and DSC studies

Figure 1 shows the temperature dependence of the ionic conductivity for PEGDE–DGEBA–D400 solvent-free polymer electrolytes with different concentrations of DGEBA (wt %) at the LiClO$_4$ concentration of [O]/[Li$^+$] = 10. The concentration of DGEBA was based on the weight of DGEBA to the total weight of the epoxy precursors, including PEGDE and DGEBA. As shown in Figure 1, the ionic conductivity increased as the temperature increased, and the conductivity data followed the Vogel–Tamman–Fulcher (VTF) equation:

$$\sigma(T) = AT^{-1/2} \exp[-B/\kappa_B(T - T_0)]$$

where A is a constant proportional to the number of carrier ions, B is the pseudoactivation energy related to polymer segmental motion, κ_B is the Boltzmann constant, and T_0 is a reference temperature at which the configurational entropy of the polymer becomes zero and is close to T_g. The application of the VTF form to ion transport in polymer electrolytes requires the coupling of mobile charge carriers to the segmental motion of the polymer host.[1] Furthermore, the introduction of DGEBA segments to the polyether-based networks resulted in a reduction of the ionic conductivity, which was attributed to the higher crosslinking

PEGDE + DGEBA + Jeffamine $\xrightarrow{\text{LiClO}_4}$

PEGDE $\underset{\text{O}}{H_2C-CH\text{-}CH_2\text{-}O}\left(\text{CH}_2\text{-}CH_2\text{-}O\right)_9 CH_2\text{-}\underset{\text{O}}{CH\text{-}CH_2}$

Jeffamine $H_2N-\underset{CH_3}{CH}-CH_2\left(O\text{-}CH_2\text{-}\underset{CH_3}{CH}\right)_x NH_2$ x = 5.6 for D400; 33.1 for D2000

DGEBA $H_2C\text{-}CH\text{-}CH_2\left(O\overset{\text{}}{\underset{CH_3}{\overset{CH_3}{C}}}O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\right)_n O\overset{CH_3}{\underset{CH_3}{C}}O\text{-}CH_2\text{-}CH\text{-}CH_2$

PEO chain segment

PPO chain segment

bisphenol A

• crosslink sites

Scheme 1   Schematic structure of the polymer networks.

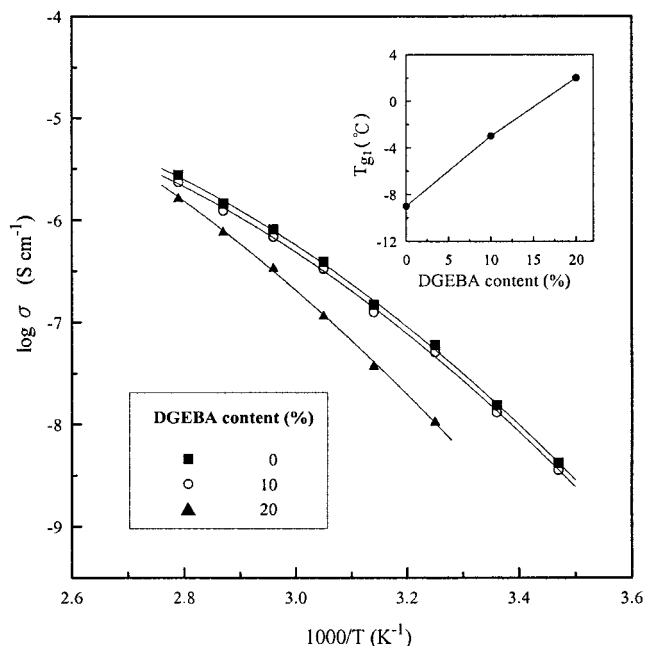degree. In comparison with the PEGDE oligomer, the DGEBA oligomer had a lower molecular weight. Consequently, a greater DGEBA content in the polymer network caused a higher crosslinking degree, and this led to an increase in the glass-transition temperature of the polymer electrolytes (T_{g1}) as a result of the reduction of the free volume of the polymers (see the inset in Fig. 1). T_{g1} was attributed predominantly to the motion of the polyether segment of the network (see the discussion in Fig. 2). The application of the free-volume theory proposed by Cohen and Turnbull[12] to polymer electrolytes revealed that the average free volume of the polymer host was one of the
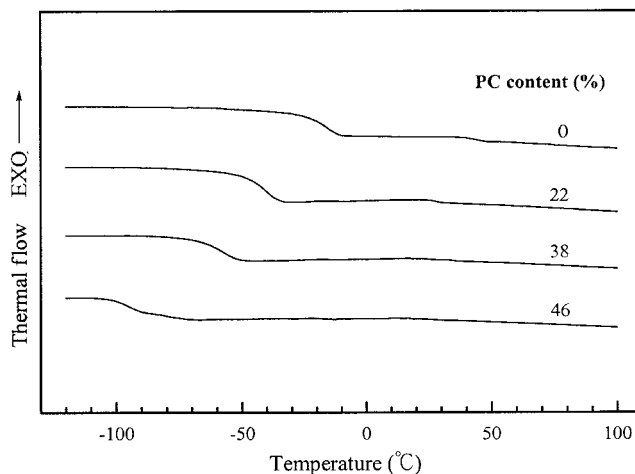

Figure 1   Temperature dependence of the ionic conductivity (σ) for solvent-free polymer electrolytes (PEGDE–DGEBA–D400) with different contents of DGEBA (wt %) at the LiClO$_4$ concentration of [O]/[Li$^+$] = 10. The inset shows the variation of T_{g1} with the DGEBA content.

Figure 2   DSC thermograms of PEGDE–D400–10 wt % DGEBA at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 and at PC concentrations of 0–46 wt %.

determinants of the ionic conductivity of the electrolytes. Therefore, the higher T_{g1} value, a result of the lower segmental motion (the lower fraction of the free volume) of the polymer chain, resulted in a reduction of the ionic conductivity. Figure 1 shows that the ionic conductivity decreased slightly at a DGEBA concentration of 10 wt %; however, the mechanical properties of the polymer electrolyte network were remarkably improved.

DSC thermograms of PEGDE–D400–10 wt % DGEBA at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 with a PC concentration of 0–46 wt % are shown in Figure 2. For the PC-free polymer electrolyte, two thermal transitions were observed at very different temperatures. The lower temperature (T_{g1}) was attributed predominantly to the motion of the polyether segments coordinated with Li$^+$ ions of the network, and the slight inflection at about 40°C (T_{g2}) corresponded to T_g of the network, above which chain motion took place.[13] Also, no melting transition existed for any of the samples in the range of analyzed temperatures, and this indicated no existence of a crystalline structure in the polymer networks.

In comparison with the PC-free sample, a significant decrease in T_g with increasing PC content was observed, particularly for T_{g1} from −15.2 to −92.8°C at a PC concentration of 46 wt %. This indicated that the solvation degree of Li$^+$ by ether oxygens in the soft segment decreased. The reduced T_g was due to the enhanced segmental mobility by the PC solvent, and this led to an increase in the ionic conductivity of the polymer electrolytes (as discussed later).

Figure 3 shows the AC impedance spectra for the PEGDE–D400·LiClO$_4$ polymer electrolyte network, at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 and at the PC concentration of 38 wt %, attached to stainless steel cells as a function of the temperature from 15 to 85°C. The resistance (R_b) of the polymer electrolyte obtained from the intercept on the real axis decreased as the temperature increased, indicating the increase in the ionic conductivity of the polymer electrolyte due to the enhancement of the ionic mobility. Generally, Nyquist plots present a semicircle in the higher frequency region and an inclined straight line at a lower frequency for solvent-free polymer electrolytes. The migration of ions may occur through the free volume of the polymer matrix, which acts as a resistor. The immobile polymer chains become polarized in the alternating field and act as capacitors. The ionic migration and bulk polarization are physically parallel, and so the semicircle in the high-frequency region can be observed. Figure 3 shows that the semicircle observed at a high frequency disappeared when the polymer electrolyte network contained 38 wt % PC plasticizer; this suggests that only the resistive component of the polymer electrolyte can be considered.
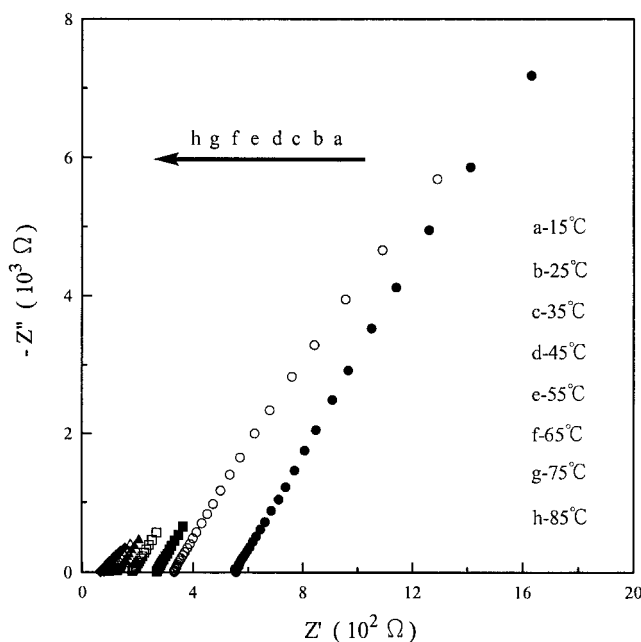

Figure 3 AC impedance spectra for the PEGDE–D400 · LiClO$_4$ polymer electrolyte network, at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 and at the PC concentration of 38 wt %, attached to stainless steel cells as a function of the temperature range from 15 to 85°C.

Figure 4 illustrates the temperature dependence of the ionic conductivity for the PEGDE–D400–10 wt % DGEBA–PC complexes with different PC contents at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15. In Figure 4(a), the ionic conductivity data can be approximately described by the Arrhenius equation in the analyzed temperature range, in which the ion transport is decoupled from the polymer host and occurs through activated hopping. It is also clear that a higher content of PC solvent results in a higher ionic conductivity and a lower activation energy for ion transport. This is coupled with the conducting pathway in the polymer electrolytes. At a higher content of the PC plasticizer, the plasticizer can form a local solvent channel for ionic conduction.[14]

The temperature dependence of the ionic conductivity for PEGDE–D400–10 wt % DGEBA doped with various LiClO$_4$ concentrations at a PC concentration of 38 wt % is shown in Figure 5(a). The dependence of the ionic conductivity on the temperature did not fully obey the Arrhenius equation. Figure 5(b) shows the LiClO$_4$ concentration dependence of the ionic conductivity at various temperatures. The maximum conductivity was obtained at the concentration of [O]/[Li$^+$] = 15. The free-volume theory was also useful to clarify the ion-transport mechanism and to understand the mobility of the polymer segment. As the concentration of LiClO$_4$ increased, the number of charge carriers also increased, but the average free volume decreased because of the increase in T_g (as a result of the interaction
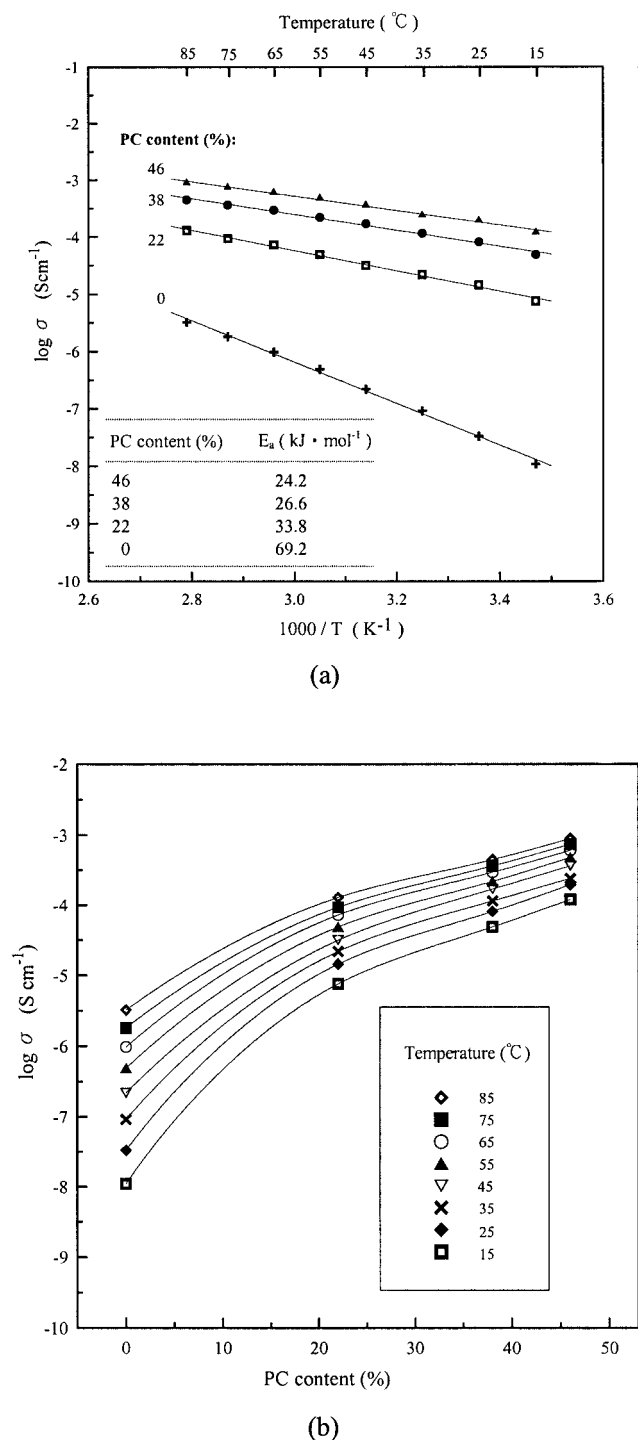
Figure 4 Temperature dependence of the ionic conductivity (σ) for PEGDE–D400–10 wt % DGEBA–PC complexes with different PC contents at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15.

of Li$^+$ with ether oxygens). At a low salt concentration level, the increase in the number of charge carriers dominated, and the decrease in free volume was compensated by the larger increase in the number of charge carriers. Hence, the conductivity increased

with the LiClO$_4$ concentration at the lower concentration level. When the LiClO$_4$ concentration reached the concentration of [O]/[Li$^+$] $\geq$ 15, the decrease in the free volume became more prominent than the increase in the number of charge carriers. At this stage, the lower fraction of the free volume was no longer compensated by the continuous increase in the number of charge carriers. Consequently, the conductivity decreased with the increase in the salt concentration at high LiClO$_4$ concentration levels.
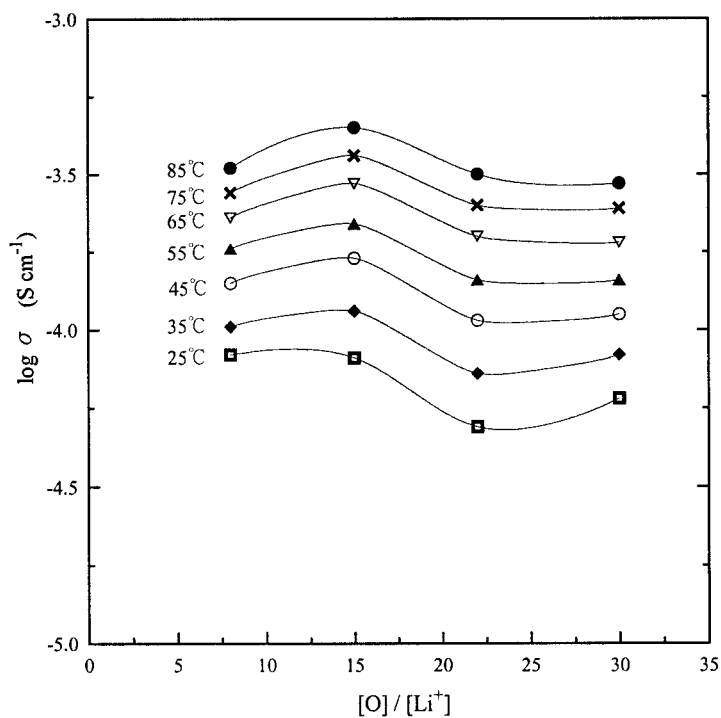
Figure 6 shows the Arrhenius plots of the ionic conductivities for PEGDE–D400–10 wt % DGEBA · LiClO$_4$ and PEGDE–D2000–10 wt % DGEBA · LiClO$_4$ complexes at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 and at the PC concentration of 38 wt %. A higher ionic conductivity and a lower activation energy for ion transportation can be observed in the polymer electrolyte network with the longer poly(propylene oxide) (PPO) segment. This was attributed to the longer PPO segment possessing a higher fraction of the free volume of the polymer electrolyte network; this enabled easier ionic transportation and agreed with our previous work on epoxy–siloxane polymer networks complexed with LiClO$_4$.[15] Because the D2000 oligomer had a higher molecular weight than the D400 oligomer, with the same composition, the polymer electrolyte network with D2000 as a curing agent had a lower crosslinking degree (i.e., a higher fraction of the free volume) than the network with D400.

CONCLUSIONS

Crosslinked polymer electrolyte networks were prepared from PEGDE blended with an epoxy resin (DGEBA) in different ratios and then cured with α,ω-diamino poly(propylene oxide)s in the presence of LiClO$_4$ as a lithium salt with a simple film-forming technique. T_g of the soft segments of these polymer networks varied with the DGEBA content and decreased significantly with the PC solvent. The mechanical properties of these gelled polymer electrolytes were remarkably enhanced by the introduction of DGEBA segments. The ionic conductivities of these polymer electrolyte networks were dependent on the polymer composition, salt concentration, PC content, and temperature. The higher temperature and higher PC content in these polymer electrolytes resulted in higher ionic conductivity. A gelled polymer electrolyte network composed of PEGDE–D400–10 wt % DGEBA · LiClO$_4$ complexes at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 and at the PC concentration of 46 wt % exhibited conductivities of approximately 5 $\times$ 10^{-4} S cm^{-1} at 25°C and approximately 10^{-3} S cm^{-1} at 85°C, and the films showed good mechanical properties. This indicates that these gelled crosslinked polymer electrolyte networks have potential for prac-
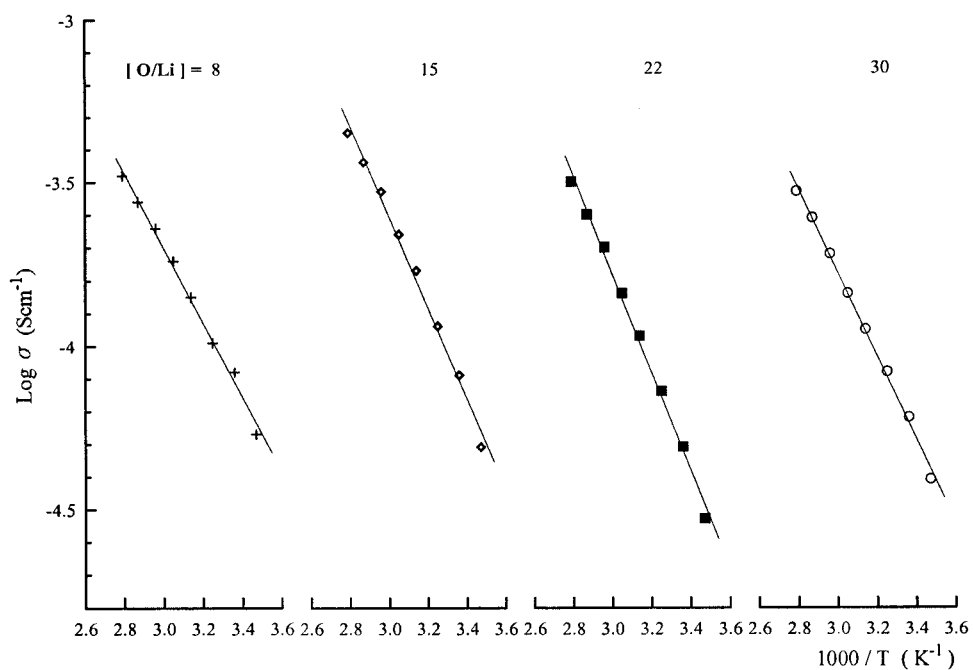
(a)

(b)

Figure 5 Temperature dependence of the ionic conductivity (σ) for PEGDE–D400–10 wt % DGEBA doped with various concentrations of LiClO$_4$ at the PC concentration of 38 wt %.
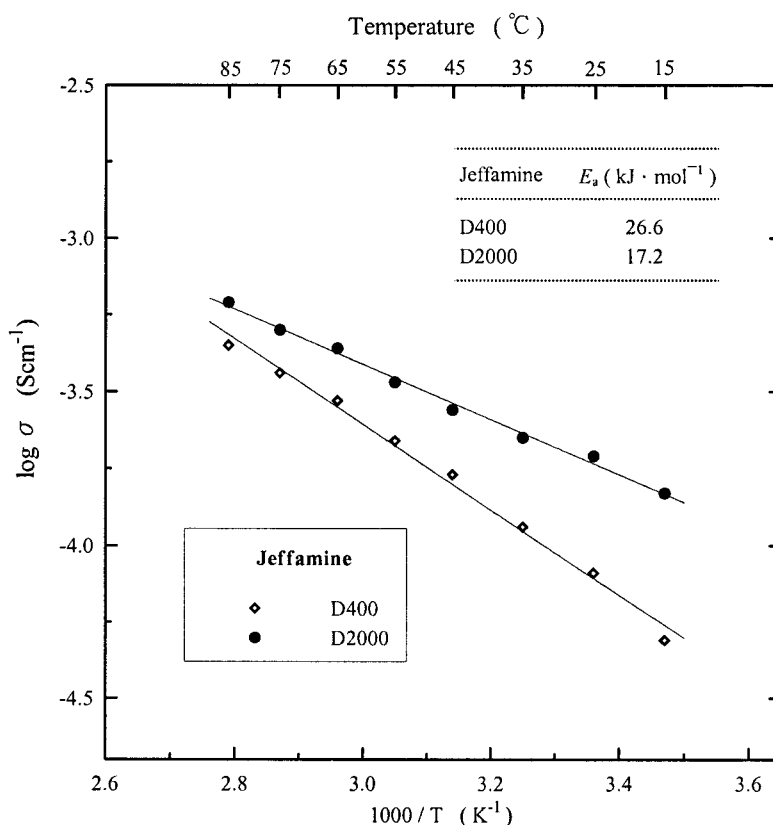
Figure 6 Temperature dependence of the ionic conductivity (σ) for PEGDE–D400–10 wt % DGEBA · LiClO$_4$ and PEGDE–D2000–10 wt % DGEBA · LiClO$_4$ complexes at the LiClO$_4$ concentration of [O]/[Li$^+$] = 15 and at the PC concentration of 38 wt %.

tical applications in high-energy-density rechargeable lithium batteries.

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