

Solid Polymer Electrolytes. XI. Preparation, Characterization and Ionic Conductivity of New Plasticized Polymer Electrolytes Based on Chemical-Covalent Polyether–Siloxane Hybrids

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ABSTRACT: A new hybrid polymer electrolyte system based on chemical-covalent polyether and siloxane phases is designed and prepared via the sol–gel approach and epoxide crosslinking. FT-IR, ¹³C solid-state NMR, and thermal analysis (differential scanning calorimetry (DSC) and TGA) are used to characterize the structure of these hybrids. These hybrid films are immersed into the liquid electrolyte (1M LiClO₄/propylene carbonate) to form plasticized polymer electrolytes. The effects of hybrid composition, liquid electrolyte content, and temperature on the ionic conductivity of hybrid electrolytes are investigated and discussed. DSC traces demonstrate the presence of two second-order transitions for all the samples and show a significant change in the thermal events with the amount of absorbed LiClO₄/PC content. TGA results indicate these hybrid networks with

excellent thermal stability. The EDS-0.5 sample with a 75 wt % liquid electrolyte exhibits the ionic conductivity of $5.3 \times 10^{-3} \text{ S cm}^{-1}$ at 95°C and $1.4 \times 10^{-3} \text{ S cm}^{-1}$ at 15°C, in which the film shows homogenous and good mechanical strength as well as good chemical stability. In the plot of ionic conductivity and composition for these hybrids containing 45 wt % liquid electrolyte, the conductivity shows a maximum value corresponding to the sample with the weight ratio of GPTMS/PEGDE of 0.1. These obtained results are correlated and used to interpret the ion conduction behavior within the hybrid networks. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1000–1007, 2006

Key words: organic–inorganic hybrid; sol–gel approach; plasticized polymer electrolyte; ionic conductivity

INTRODUCTION

The composites of poly(ethylene oxide) (PEO) and lithium salts (LiX) are recommended as the solid electrolytes for lithium batteries. The basic structure of these composites involves PEO chains coiled around the Li⁺ cations, thereby separating them from the X⁻ counter anions.¹ With the recognition that the ion conduction of PEO-based electrolytes is facilitated in the amorphous phase of PEO, significant research efforts have been devoted in tailoring a host structure having a highly flexible backbone and a larger proportion of the amorphous phase.^{2–6}

To enhance the conductivity of a solid polymer electrolyte (SPE), various plasticizers, such as propylene carbonate (PC), ethylene carbonate (EC), and tetraethylene glycol (TEG), were added to swell the polymers whereby plasticized electrolytes are

formed.^{7,8} Plasticization of high-molecular-weight PEO–LiX electrolytes with PC and/or EC was found to form soft solids with poor mechanical stability, although these electrolytes exhibit conductivities up to the order of $10^{-3} \text{ S cm}^{-1}$ at room temperature.^{9,10} The poor mechanical stability was mainly due to the solubility of the PEO in the plasticizer.¹⁰ Another strategy for conductivity enhancement is to add inorganic fillers into polymer electrolytes. These fillers are able to improve the mechanical, thermal, and electrochemical stability as well as the ionic conductivity.^{11–17} To prepare an SPE for practical applications, the high conductivity and good physical properties, such as chemical stability and mechanical strength, have to be considered in the mean time regarding to its structure.

Ion-conducting materials based on organic–inorganic hybrids are prepared with the aim to modulate the physical properties of the products by coupling suitable amounts of organic and inorganic polymer moieties along the polymer chains.¹⁸ In general, polyethers are used as organic components and siloxane, polysiloxane, or polyphosphazene derivatives are used as inorganic components.^{18–20} The sol–gel approach has been demonstrated as a practical method

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for the production of an organic-inorganic hybrid.²¹ In the present work, a new hybrid polymer electrolyte system containing polysiloxane and polyether segments is designed and prepared via the sol-gel approach and epoxide crosslinking, in an attempt to obtain good processability and high ionic conductivity of polymer electrolytes with good physical properties. The structures of the prepared hybrids are characterized by FT-IR, differential scanning calorimetry (DSC), TGA, and solid-state NMR. The effects of hybrid composition, liquid electrolyte (1M LiClO₄/PC) content, and temperature on the ionic conductivity of these hybrid electrolytes are investigated and discussed.

EXPERIMENTAL

Materials

Poly(ethylene glycol) diglycidyl ether (PEGDE; Kyocera Chemical Co., Ltd.) and α,ω -diamino poly(propylene oxide) (Jeffamine D2000, Huntsman Corp.) were dehydrated at 80°C under vacuum for 24 h prior to use. 3-Glycidoxypropyltrimethoxysilane (GPTMS; Dow Corning Corp.), lithium perchlorate (LiClO₄; Aldrich), tetrahydrofuran (THF; Tedia), and PC (99.99%, Acros) were used as received. All solvents were of reagent grade or were purified by standard methods.

Preparation of crosslinked polyether-siloxane, organic-inorganic hybrids

The different amounts of GPTMS were dissolved in appropriate amount of THF respectively, and then hydrolyzed under acidic condition, with HCl as the catalyst. The molar ratio between the reagents was H⁺/H₂O/Si = 0.04/3/1. The volume ratio GPTMS:THF = 45:55 was used. The sol-gel process was carried out at room temperature. After 3 h, the homogeneous solutions were obtained. Subsequently, a mixture of PEGDE and the stoichiometric amount of D2000 was added and mixed well. These solutions were then poured into aluminum plate, and followed by slowly removing the solvent at room temperature, cured at 100°C for 24 h and 155°C for 2 h to form an intercrosslinked hybrid material. The thickness of these specimens was controlled to be in the range of 150–200 μm . The hybrid films were dried under vacuum at 80°C for 72 h until no weight loss was observed, and then, stored in an argon-filled glove box (the moisture content is <5 ppm) (Vacuum Atmosphere, USA) for further measurements. Samples are labeled as EDS-*x*, where *x* refers to the weight ratio of GPTMS to PEGDE.

Preparation of plasticized hybrid electrolytes and swelling study

To obtain plasticized hybrid electrolytes, the resulted films were dipped in a 1M LiClO₄/PC solution for

different periods of time to obtain various contents of LiClO₄/PC. The swollen percentage (SP) of hybrid film was defined as:

$$\text{SP}(\%) = \frac{W - W_0}{W} \times 100$$

where *W* is the weight of swollen hybrid film, and *W*₀ is the original weight of dry hybrid film.

Characterizations

FT-IR spectra were measured by using a Nicolet 550 system with a wavenumber resolution of 2 cm⁻¹, and a minimum of 64 scans was signal-averaged at room temperature under dry air atmosphere. Each sample was prepared by mixing with potassium bromide (KBr) pellet, and films were vacuum-dried at 80°C for several days to remove the absorbed water in the sample.

Solid-state ¹³C cross-polarization/magic angle spinning (CP/MAS) NMR experiments were carried out on a Bruker AVANCE-400 spectrometer, equipped with a 7 mm double-resonance probe, operating at resonance frequencies of 400.13 and 100.63 MHz for ¹H and ¹³C nuclei, respectively. The Hartmann-Hahn matching conditions were determined using adamantane. A recycle delay time of 4 s and a 90° pulse width of 4.5 μs for ¹H excitation were used. ²⁹Si MAS NMR spectra were acquired at 79.46 MHz with $\pi/2$ pulse width of 4.6 μs and a recycle delay of 200 s. Both ¹³C and ²⁹Si chemical shifts were externally referenced to tetramethylsilane (TMS) at 0.0 ppm.

DSC (Du Pont TA2010) measurements were conducted over the temperature ranges of -120 to 120°C at a heating rate of 10°C/min under dry nitrogen atmosphere. The samples sealed into aluminum pans were first annealed at 120°C for 10 min to remove trace indications of their thermal history, cooled down to -120°C and then scanned. Glass-transition temperature (*T*_g) was reported as the midpoint of the transition process. All the thermograms are baseline-corrected and calibrated against indium metal. An empty aluminum pan was used as a reference.

TGA analyses were carried out using a thermogravimetric analyzer (Perkin-Elmer TGA 7) over a temperature range of 100–800°C at a heating rate of 20°C/min under nitrogen atmosphere.

Alternating current impedance measurements of the samples were performed using a CH Instrument Model 604A Electrochemical Analyzer (CH Instruments, Inc., TX) under an oscillation potential of 10 mV from 100 kHz to 10 Hz. All the thin electrolyte films were sandwiched by two polished stainless steel blocking electrodes and the cells were sealed with O-ring for conductivity tests. The presenting ionic

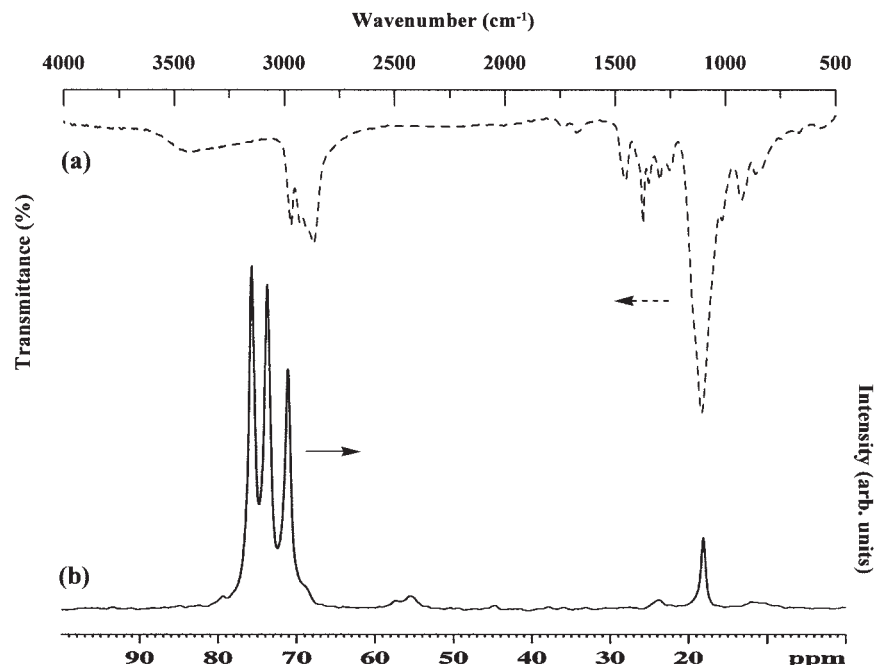


Figure 1 (a) FTIR and (b) Solid-state ¹³C CP/MAS NMR spectra recorded for the EDS-0.5 hybrid network.

conductivity values (σ) are obtained from the relationship, $\sigma = t / (R_b \times A)$, where R_b is the bulk electrolyte resistance, t is the thickness, and A is the area of the sample.

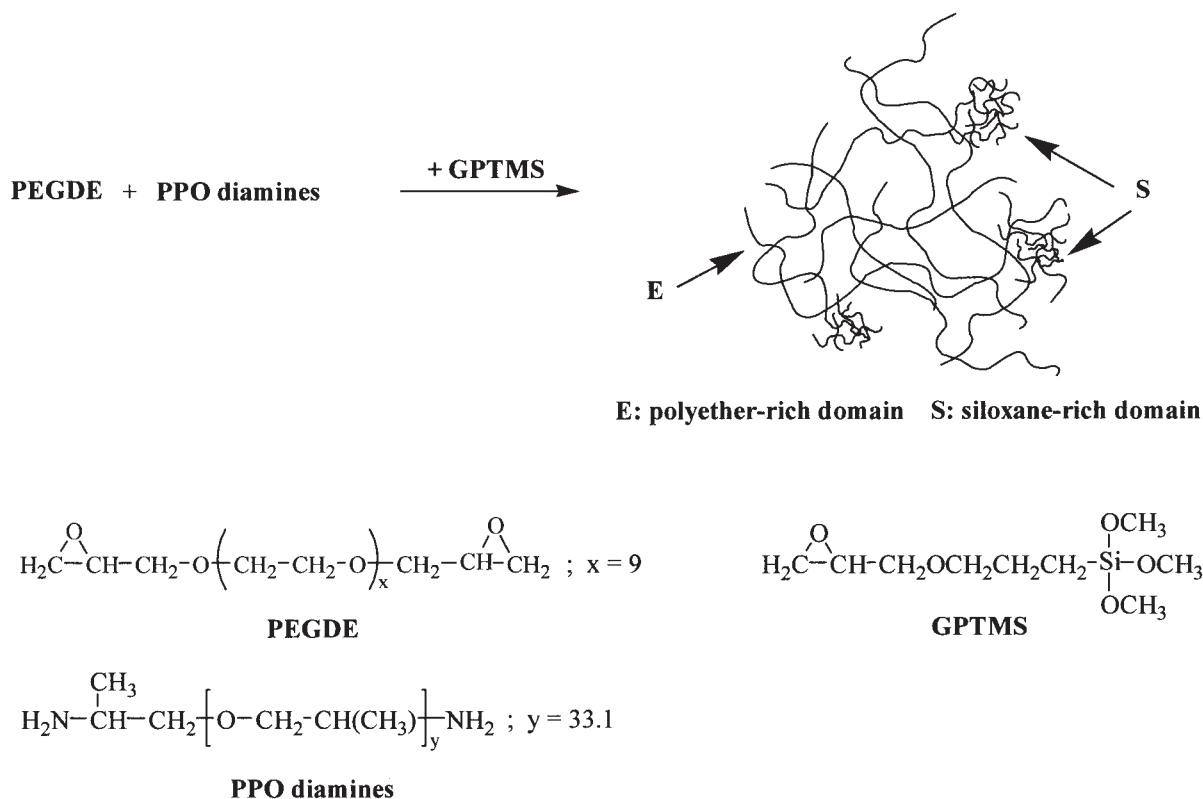
RESULTS AND DISCUSSION

Synthesis and characterization

In an attempt to obtain a polymer electrolyte with high segmental mobility of the polymer chains and high fraction of the amorphous domains as well as with good mechanical strength, in this study, a series of dual-crosslinked polyether-siloxane hybrid networks were prepared on the basis of PEGDE blended with 3-GPTMS in various ratios, using α,ω -diamino poly(propylene oxide) (Jeffamine D2000) as the curing agent. The synthetic route was designed to produce the inorganic SiO₂ network covalently linked to organic phase. The first step of the synthesis was to hydrolyze the alkoxy silanes in GPTMS. A clear and homogenous solution was formed without any observable phase segregation, when the hydrolyzed silica precursor was blended with the mixture of PEGDE and D2000 at room temperature. The apparent mechanical strength of the obtained hybrid films depends upon the weight ratio of GPTMS/PEGDE used. Flexible, transparent and brownish films are obtained for the existence of higher amounts of GPTMS incorporated into hybrid matrix, whereas slightly gummy resins are obtained for smaller quantity of GPTMS added.

Infrared spectroscopy is a convenient method to have an insight into the development of an organic-inorganic network. A typical FT-IR spectrum of the hybrid network with the weight ratio of GPTMS/PEGDE of 0.5 (EDS-0.5) is shown in Figure 1(a). It is clearly shown that the characteristic absorption bands for the —OH and —C—O— stretching vibrations at 3600 to 3150 and 1200 to 1050 cm⁻¹ respectively, and the absorption peak of epoxide at 912 cm⁻¹ disappeared indicating the complete reaction of epoxide on PEGDE and GPTMS. In addition, the absorption band at ~1034 cm⁻¹ is the asymmetric stretching of Si—O—Si. The absorption at 960 to 950 cm⁻¹ is the band of Si—OH. The bands located around 800 cm⁻¹ are attributed to the vibrations of the silica network.²²

Figure 1(b) gives the representative ¹³C CP/MAS NMR spectrum for EDS-0.5. As evidenced in this figure, there are three major peaks at ~70 ppm, which are associated with the polyether backbone moieties. Two peaks at 76 and 74 ppm are attributed to the PPO segments of D2000, whereas the peak at 71 ppm is assigned to the ether carbons in PEGDE.²³ The peak at 18 ppm is due to the methyl groups on the PPO backbone. Two peaks at 10 and 24 ppm are assigned to the methylene carbons in α and β position to the silicon atom, respectively. No peaks at 44 and 51 ppm for the carbons in the oxirane ring are observed, suggesting the completeness of curing reaction. Furthermore, the peak at 57 ppm corresponding to those carbons adjacent to nitrogen atom is observed.



Scheme 1. Schematic structure for polyether-siloxane, organic-inorganic hybrids.

Solid-state ^{29}Si NMR measurements were also performed to gain further information regarding the structure of the inorganic component inside the hybrids. The acquired spectra have a feature that the peak at ~ 65 ppm is observed, showing the homocondensed siloxane fragments in T^m arrangements. However, the identification of the different types of silicate substructures present is not allowed to accomplish because of low peak intensity. The schematic structure of these hybrid networks is illustrated in Scheme 1.

Thermal analysis

DSC and TGA were utilized to examine the thermal properties of these crosslinked polyether-siloxane hybrids, and the obtained results are summarized in Table I. As seen in Table I, two second-order transitions for all the samples are observed. These two transitions could be associated with the biphasic character of the polyether chains inside the hybrid networks. The polymer far away from silica networks behaves as unrestricted polyether chains, possessing glass-transition temperature, T_{g1} , at around -60°C . On the contrary, the polymer near the silica nodes is more rigid due to covalent bond with silica, showing the slight inflection in the range of $45\text{--}80^\circ\text{C}$, T_{g2} . Additionally, the T_{g1} value almost remains invariant with the further increase in GPTMS uptake, possibly because of

the relatively small content within the network. No melting transition is observed in the range of analyzed temperatures in the thermograms, indicating that all the hybrids are in the amorphous state.

Table I also lists the results from TGA curves, in terms of the initial 10% weight-loss temperature ($T_d^{0.1}$) and the residual weight at 800°C (R_{800}). The $T_d^{0.1}$ for all the samples occurs around 330°C , indicating that these hybrid networks show excellent thermal stability. An increase in R_{800} is observed with increasing the GPTMS content in the hybrids.

Figure 2 shows the DSC thermograms for EDS-0.5 immersed in $1\text{M LiClO}_4/\text{PC}$ to have the increased

TABLE I
Thermal Data of the Crosslinked Polyether-Siloxane Hybrids with Various Weight Ratios of GPTMS/PEGDE

GPTMS/ PEGDE	DSC		TGA	
	T_{g1} ($^\circ\text{C}$)	T_{g2} ($^\circ\text{C}$)	$T_d^{0.1}$ ^a ($^\circ\text{C}$)	R_{800} ^b (wt %)
2	-60	46	327	0.0
10	-59	63	336	0.2
30	-60	80	337	0.7
50	-60	62	351	1.9
70	-59	55	339	2.2
100	-59	53	346	3.2

^a The 10% weight loss temperature.

^b The residual weight at 800°C .

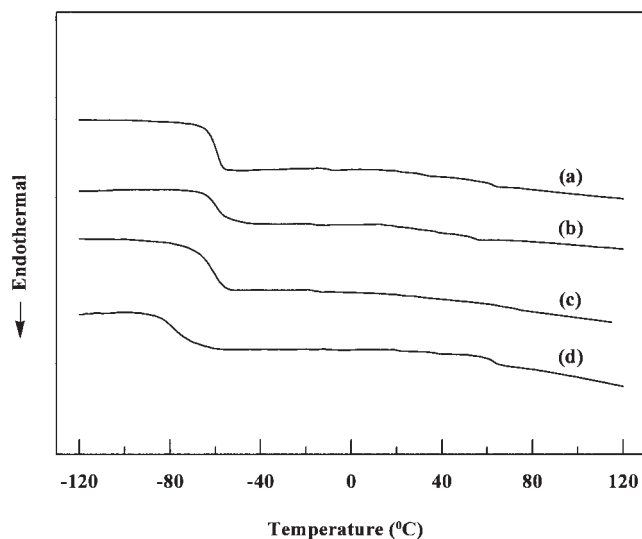


Figure 2 DSC thermograms for the EDS-0.5 hybrid network immersed in 1M LiClO₄/PC with the increased weights: (a) 0 wt %; (b) 15 wt %; (c) 45 wt %; and (d) 75 wt %.

weight of 15%, 45% and 75%. As evidenced in Figure 2, with the introduction of liquid electrolyte, a significant change in the thermal event of T_{g1} with the amount of absorbed LiClO₄/PC content is observed. Table II summarizes the variation in T_{g1} with LiClO₄/PC content for EDS-0.5 sample. At lower LiClO₄/PC content level (SP < 75%), T_{g1} value is fairly constant at -60°C ; nevertheless, the value of glass-transition zone of T_{g1} (ΔT_{g1}) increases with the LiClO₄/PC uptake. This observation is the reflection of two opposite effects, namely the increase in the number of charge carriers and the enhanced mobility of polymer chains induced by PC solvent. The increase in charge carrier density results in the decrease in segmental mobility due to the interaction of Li⁺ with ether oxygens. ΔT_{g1} is defined as the difference between the onset and endset temperatures of the thermal transition process and reflects the number of relaxation processes associated with the transition. Complexed polyether units may be located randomly along the polyether segments. The mutual influences on the behaviors of free and complexed polyether units probably undergo relaxation processes with different relaxation times, resulting in the broadening of the glass transition. At the highest LiClO₄/PC content, the T_{g1} value is obviously decreased to -77°C , suggesting that the increase in free volume as a result of the addition of PC becomes more pronounced than the increase in number of charge carriers. However, this behavior is less accentuated for T_{g2} .

Swelling behavior

The prepared hybrid films with $\sim 150\text{--}200\ \mu\text{m}$ thickness were immersed in 1M LiClO₄/PC solution, and

the SP by weight was measured after immersing with different time intervals. Figure 3 shows the SP as a function of immersion time for the hybrid films, and the total amount of LiClO₄ and the PC content at various SPs within these hybrid films are listed in Table III. The swollen rate and the saturated SP can be obtained from the slope and the plateau of the curves, respectively. It is obvious that the swollen rate in the initial stage and the saturated SP of these hybrids are in the order EDS-0.02 > EDS-0.1 > EDS-0.3 > EDS-0.5 > EDS-0.7 > EDS-1.0, and increase with the decrease in GPTMS/PEGDE ratio. These results indicate that the liquid electrolyte is more preferably absorbed in the polyether domains. In addition, as seen in Figure 3(b), no decreasing tendency in SP is observed after 7100 min. As compared with our previous studies of plasticized polymer electrolytes based on segmented polyurethanes with PEO/polydimethylsiloxane²⁴ and with PEO/perfluoropolyether²⁵ blocks, respectively, as well as crosslinked polydimethylsiloxane/polyether networks,²³ these results have revealed that the crosslinked polyether-siloxane hybrid system, in this study, possesses good chemical stability in LiClO₄/PC solution.

Ionic conductivity measurements

Figure 4 shows the Nyquist plot of the EDS-0.5 hybrid with the LiClO₄/PC content of 15 wt % attached on stainless steel cells as a function of temperature. It is observed that the resistance (R_b) of the hybrid electrolyte obtained from the intercept on the real axis decreases with raising temperature, resulting in the increase of ionic conductivity of hybrid electrolyte due to the enhancement of ionic mobility. Generally, the Z'' versus Z' plots present a semicircle in the region of higher frequency and an inclined straight line at lower frequency for polymer electrolytes. The migration of ions may occur through the free volume of polymer matrix, which acts as a resistor. The immobile polymer chains become polarized in the alternating field to act as a capacitor. Since ion migration and bulk polarization are physically in parallel, the semicircle at high frequency can be observed. As seen in Figure 4, it is evident that only the tail of semicircle at high fre-

TABLE II
DSC Results of the EDS-0.5 Hybrid Network Immersed in 1M LiClO₄/PC with Various Increased Weights

Swollen percentage (wt %)	T_{g1} ($^{\circ}\text{C}$)	ΔT_{g1} ($^{\circ}\text{C}$)	T_{g2} ($^{\circ}\text{C}$)
0	-60	7	62
15	-59	10	52
45	-62	12	72
75	-77	16	62

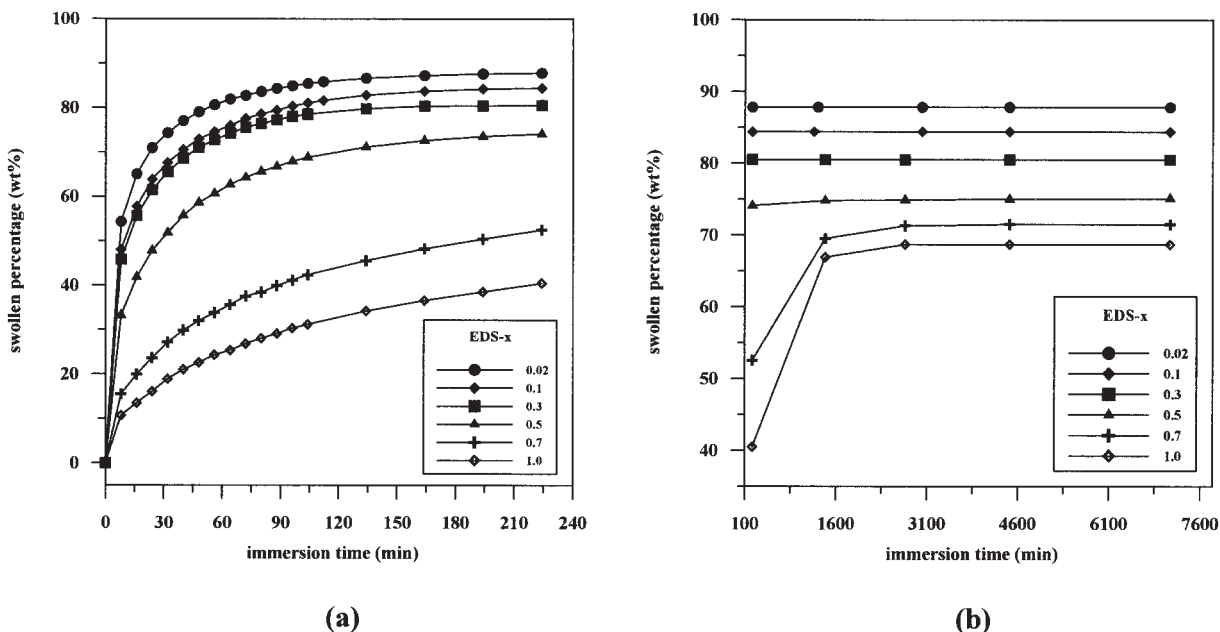


Figure 3 The swollen percentage for the prepared hybrid films with various weight ratios of GPTMS/PEGDE in 1M LiClO_4/PC as a function of immersion time.

quency is noticed, as raising the temperature, suggesting that the resistive component of hybrid electrolyte should be mainly considered.

Figure 5 illustrates the temperature dependence of ionic conductivity for EDS-0.5 with different LiClO_4/PC contents. As seen in Figure 5(a), there exists a common trend that the lower LiClO_4/PC content results in a greater slope than the higher LiClO_4/PC content. This is related to conducting pathway in the polymer electrolytes. At a higher content of PC plasticizer, plasticizer can form a local solvent channel for ion conduction, which is the major medium governing the ionic conductivity.²⁶ With a 75 wt % liquid electrolyte solution, the EDS-0.5-plasticized hybrid electrolyte exhibits the ionic conductivity of $5.3 \times 10^{-3} \text{ S cm}^{-1}$ at 95°C and $1.4 \times 10^{-3} \text{ S cm}^{-1}$ at 15°C , respectively. The Arrhenius plots of ionic conductivity for EDS-0.5 with various contents of liquid electrolyte solution are shown in Figure 5(b). As expected, ionic

conductivity progressively increases with increasing concentration of the liquid electrolyte solution. The temperature dependence is gradually changed from a Vogel–Tamman–Fulcher (VTF)-like relationship to a more Arrhenius-like relationship, as the LiClO_4/PC content exceeds 60 wt %. This observation can be rationalized by the fact that the ion transport becomes less coupled with the segmental motions of polymer chains, and becomes more related with the dynamics

TABLE III
Total Amount of LiClO_4 and the PC Content at Various Swollen Percentages within Hybrid Electrolytes

Swollen percentage (wt %)	LiClO_4 (wt %)	PC content (wt %)	O/Li ⁺ ^a
15	1.2	13.8	116
30	2.4	27.6	48
45	3.6	41.4	25
60	4.8	55.2	14
75	6.0	69.0	7

^a The molar ratio of ether oxygen to LiClO_4 .

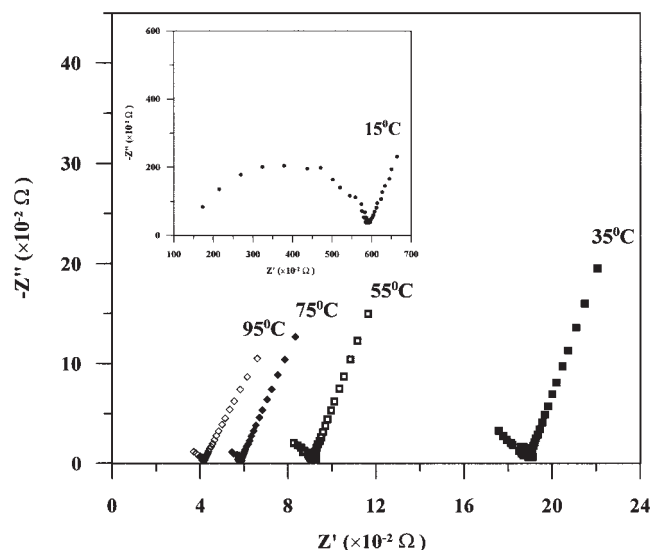
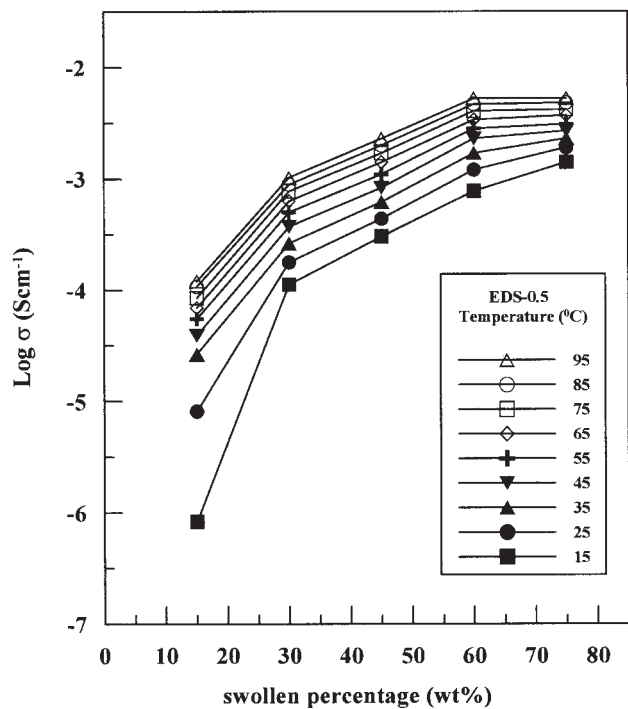
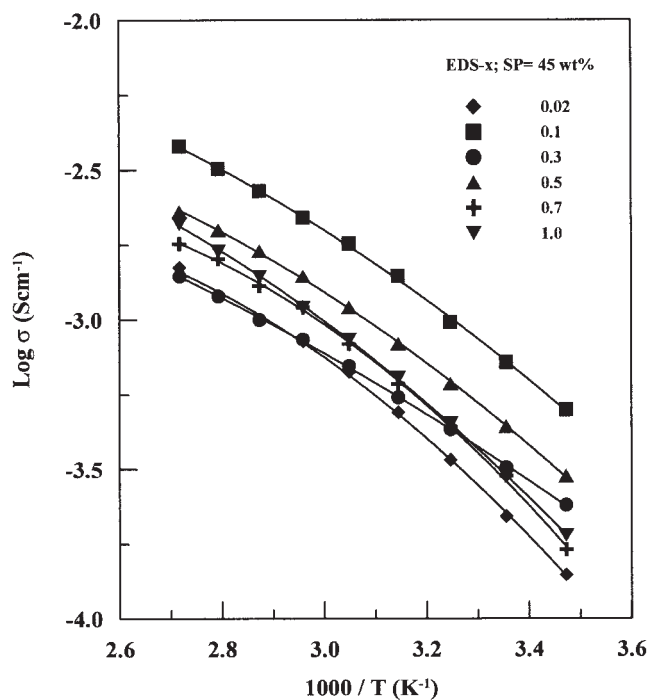


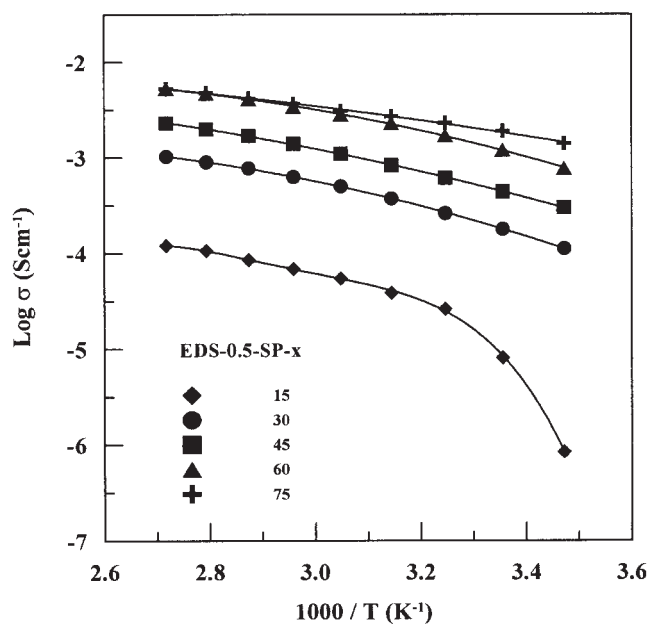
Figure 4 Nyquist plots of the EDS-0.5 film immersed in 1M LiClO_4/PC with the increased weight of 15 wt % attached on stainless-steel cells at temperatures ranging from 15 to 95°C .



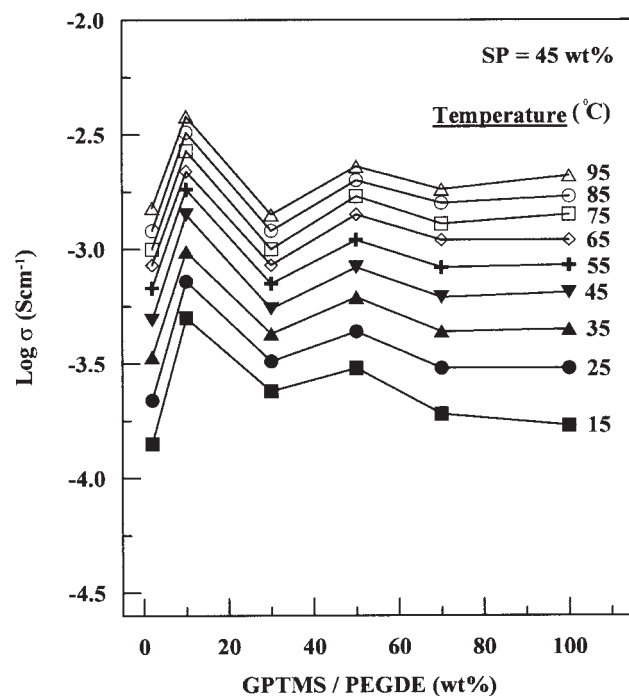
(a)



(a)



(b)



(b)

Figure 5 Ionic conductivity of the EDS-0.5 hybrid electrolyte as functions of liquid electrolyte content and temperature.

of the solvent, as the content of electrolyte solution is increased.

Figure 6 displays the temperature dependence of ionic conductivity of the crosslinked polyether-silox-

Figure 6 (a) Temperature dependence of ionic conductivity for the prepared hybrid films with various weight ratios of GPTMS/PEGDE immersed in 1M LiClO₄/PC with the increased weight of 45 wt %; (b) Effect of GPTMS/PEGDE ratio on the ionic conductivity at temperatures ranging from 15 to 95°C.

ane hybrids with various weight ratios of GPTMS/PEGDE containing 45 wt % liquid electrolyte. As evidenced in this figure, the ionic conductivity increases with increasing temperature, and moreover, variation of conductivity with temperature follows the VTF-like relationship for these hybrid electrolytes [Fig. 6(a)]. The effect of GPTMS/PEGDE ratio on ionic conductivity of these hybrid electrolytes as a function of temperature is demonstrated in Figure 6(b). As seen in Figure 6(b), the introduction of GPTMS results in an increase in ionic conductivity, and moreover, the highest one is observed at the weight ratio of GPTMS/PEGDE of 0.1. Following the maximum, the conductivity decreases with increasing GPTMS content in the hybrids. These obtained results are similar to those of earlier studies on composite electrolytes.^{27–29} The increase in conductivity is generally connected with the grain boundary effects.^{30,31} The existence of the maximum suggests that two counteracting factors, one causing an increase in conductivity and the other resulting in a decrease in conductivity, are competitive. Croce et al.³² have reported that the conductivity in composite polymer electrolytes is not a linear function of the filler concentration. At lower content level, the dilution effect is contrasted by the specific interactions of the filler surface, which promotes fast ion transport, and the overall effect is progressive enhancement of the conductivity. On the other side, in the higher content region of the filler, the dilution effect predominates and the conductivity decreases.

CONCLUSIONS

New polyether-siloxane, organic-inorganic hybrids with covalent bonds between the organic polymer chains and the siloxane phase have been prepared and characterized. The apparent mechanical strength of these obtained hybrid films depends upon the weight ratio of GPTMS/PEGDE used. It is observed that the thermal transition of the polymer chain far away from silica nodes varies obviously with the amount of absorbed LiClO₄/PC content. All of the prepared hybrids have good chemical stability in the liquid electrolyte (1M LiClO₄/PC). With a 75 wt % liquid electrolyte solution, the plasticized EDS-0.5 hybrid electrolyte exhibits an ionic conductivity of 5.3×10^{-3} S cm⁻¹ at 95°C and 1.4×10^{-3} S cm⁻¹ at 15°C, and the film possesses good apparent mechanical strength. This indicates that this hybrid is a promising candidate for practical application in lithium polymer batteries.

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