Syntheses and Characterizations of Soft-Segment Ionic Polyurethanes

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ABSTRACT: Novel soft-segment ionic polyurethane (linear and crosslinking) have been prepared based up on sodium sulfonate–side chains poly(ethylene oxide) (SPEO). SPEO was synthesized by grafting the sodium sulfonate onto the chain of poly(ethylene oxide) with molecular weights of 400, 600, 800, and 1000. The SPEO and the ionic polyurethane were characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, gel permeation chromatography, and impedance analysis. The effect of plasticizer on the ionic conductivity of the polyurethane was also investigated. These solid polymer electrolytes possess a higher ionic conductivity (about 10^{-6} S/cm at room temperature) than the corresponding sulfonated hard-segment polyurethane electrolytes. The presence of the hydroxyl group in the electrolyte tends to lower the ionic conductivity. Crosslinking of polyurethane results in the enhancement of the dimensional stability, while maintaining the same level of the ionic conductivity. © 1999 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 37: 837–845, 1999
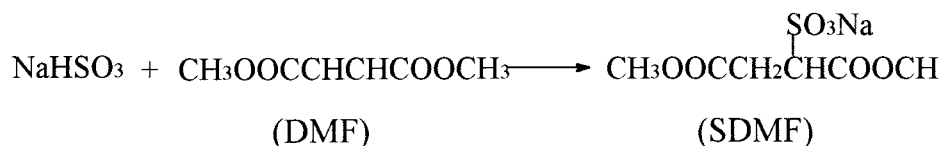**Keywords:** soft-segment ionic polyurethane; SPEO

INTRODUCTION

Solid polymer electrolytes have been extensively studied due to their potential applications in extrathin, rechargeable lithium batteries. Particularly, rechargeable lithium batteries that can supply over 3 V from a single unit cell are important for driving large-scale integration or related devices such as liquid–crystal displays and electrochromic displays. The polymer electrolytes that have attracted most interest are those comprised of poly(ethylene oxide) (PEO) or their derivatives and lithium salts.[1–5] These electrolytes display a higher ionic conductivity, about $10^{-4}10^{-5}$ S/cm at room

temperature. When used in a rechargeable battery, lithium ions and their counter anions migrate between the two electrodes during the charging and discharging processes. Such electrolytes are referred to as "bi-ionic" conductors. In such "bi-ionic" conductors, the migration of anions toward the cathode causes polarization and results in a serious decay of the DC conductivity and the time-dependent increase of the cell impedance.[6] These electrolytes are unsuitable for a rechargeable battery. Recently, single-ionic conductors have been investigated to minimize the polarization.[7–9] When anionic sites are fixed on polymer chains via a covalent bond, these anions are unable to migrate because of the entangled high molecular weight polymer chains. Therefore, cations are the only carrier ions that can transmit electrons. These electrolytes are referred to as single-ionic conductors. Various types

$$\text{NaHSO}_3 \;+\; \text{CH}_3\text{OOCCHCHCOOCH}_3 \longrightarrow \overset{\overset{\displaystyle \text{SO}_3\text{Na}}{|}}{\text{CH}_3\text{OOCCH}_2\text{CHCOOCH}}$$

$$\text{(DMF)} \qquad\qquad\qquad\qquad \text{(SDMF)}$$

Scheme 1.

of polyurethanes have been used as solid polymer electrolytes because of their good chemical stability, excellent mechanical properties, and low glass transition temperature (T_g). A poly(urethane) chain is comprised of hard segments and soft segments. A hard-segment ionic polyurethane, sodium sulfonate groups are grafted onto the nitrogen of the urethane (—NHCOO—) group, shows good dimensional stability, less polarization but a lower conductivity, about 10^{-7}–10^{-8} S/cm at room temperature.[10,11] The main reason for the lower ionic conductivity of these hard-segment ionic polyurethanes is that the ions are located in the hard segments, but the solvent (EO units) is situated in the soft segments.
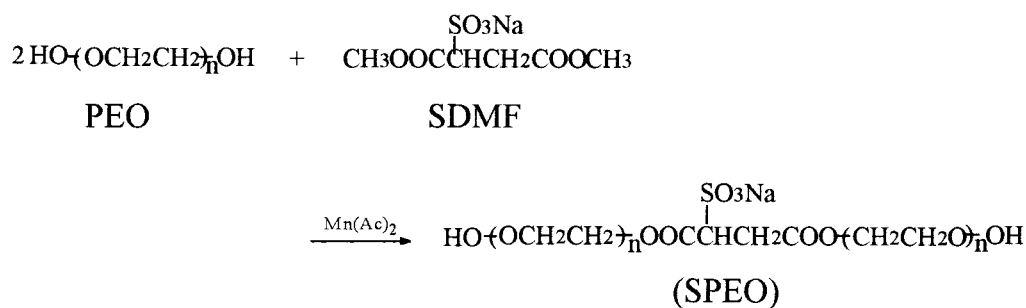
In this article, we would like to report a new type of soft-segment ionic conductor—grafted sodium sulfonate–side chain poly(ethylene oxide)

polyurethanes (SPU) in which the ions are situated in soft segments. This soft segment ionic poly(urethane) possesses better dimensional stability, less polarization, and a higher ionic conductivity.
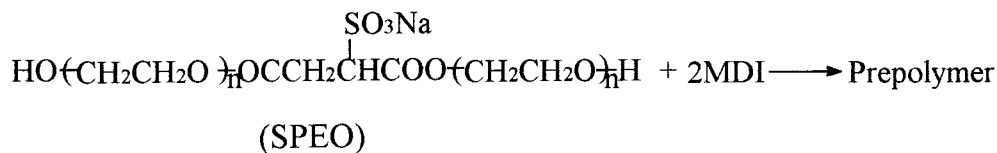
EXPERIMENTAL

Materials

Poly(ethylene oxide)s (PEO) with different molecular weights of 400, 600, 800, and 1000 from the Aldrich Chemical Co. were dried under vacuum at 60°C for 48 h before use. PEO monomethyl ether (PEOMM) and PEO dimethyl ether (PEODM) were used as plasticizers, also from Aldrich Chemical Co. The 4,4′-methylenebis(phenyl iso-

$$2\,\text{HO}(\text{OCH}_2\text{CH}_2)_n\text{OH} \;+\; \overset{\overset{\displaystyle \text{SO}_3\text{Na}}{|}}{\text{CH}_3\text{OOCCHCH}_2\text{COOCH}_3}$$

$$\text{PEO} \qquad\qquad\qquad \text{SDMF}$$

$$\xrightarrow{\text{Mn(Ac)}_2} \;\; \overset{\overset{\displaystyle \text{SO}_3\text{Na}}{|}}{\text{HO}(\text{OCH}_2\text{CH}_2)_n\text{OOCCHCH}_2\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{OH}}$$

$$\text{(SPEO)}$$

or:

$$2\,\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{CH}_3 \;+\; \overset{\overset{\displaystyle \text{SO}_3\text{Na}}{|}}{\text{CH}_3\text{OOCCHCH}_2\text{COOCH}_3}$$

$$\text{(PEOMM)} \qquad\qquad \text{(SDMF)}$$

$$\xrightarrow{\text{Mn(Ac)}_2} \;\; \overset{\overset{\displaystyle \text{SO}_3\text{Na}}{|}}{\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OOCCHCH}_2\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3}$$

$$\text{(SPEOMM)}$$

Scheme 2.

$$\underset{\text{(SPEO)}}{\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{\overline{n}}\text{OCCH}_2\overset{\overset{\textstyle\text{SO}_3\text{Na}}{|}}{\text{CHCOO}}(\text{CH}_2\text{CH}_2\text{O})_{\overline{n}}\text{H}} + 2\text{MDI} \longrightarrow \text{Prepolymer}$$

Scheme 3.

cyanate)(MDI), also from Aldrich Chemical Co., was distilled under vacuum and used immediately. *N,N*-Dimethylacetamide (DMA) and 1,4-butanediol (BDOL) from Riedel-de Haën of Germany were dried by refluxing over CaH for 4 h to exclude trace water and then distilled under vacuum. Dimethyl fumarate (DMF), sodium hydrogensulfite ($NaHSO_3$), dimethyl sulphoxide (DMSO), and calcium hydride, from the Aldrich Chemical Co., were used without further purification.

The sulfonated dimethyl fumarate (SDMF) was prepared by dissolving DMF and $NaHSO_3$ in methanol and water solution and refluxing at 80°C for 8 h. The solvent was removed under vacuum. The product was extracted by DMSO, precipitated by large amount of acetone, and dried under vacuum at 60°C for 24 h. The degree of conversion of the reaction as shown in Scheme 1 was at the order of 90%.

The sodium sulfonate–side chain-grafted poly(ethylene oxide) (SPEO) was prepared by mixing SDMF, PEO, and catalyst under nitrogen atmosphere at 175°C for 5 h. SPEO was solubilized in the acetone, and the precipitate was subsequently filtered. SPEO was dried under vacuum at 60°C for 24 h after the acetone was removed by distillation. The reaction is shown in Scheme 2.
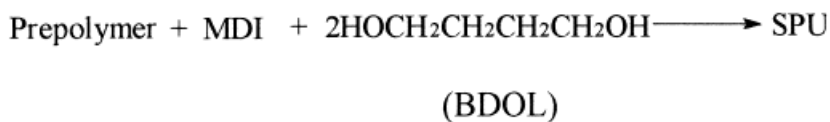
In preparing the soft-segment ionic polyurethanes (SPU), the DMA solution containing SPEO was added dropwise to the DMA solution containing MDI under nitrogen atmosphere at 40°C for 3 h. Subsequently, the DMA solution containing BDOL was added dropwise over a period of 30 min, and continually reacted for 1.5 h. The polymer formed was precipitated and recovered in a large amount of acetone and then immersed in ethanol for 24 h. The polymer was filtered and dried under vacuum at 60°C for 24 h. These reactions are shown in Schemes 3 and 4:
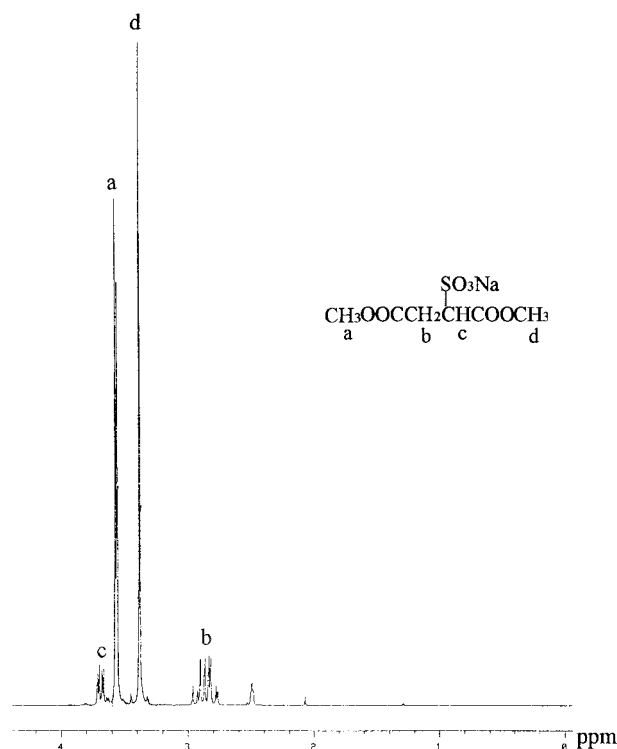
The typical procedure for preparing the new solid polymer electrolyte (SPE) was carried out by dissolving the appropriate amount of the ionic polyurethane and the plasticizer in DMA solvent. The resultant solution was then poured into a teflon dish to allow the DMA to be evaporated at 60°C in an oven. A free-standing electrolyte film with diameter 10 mm and thickness 0.2–0.3 mm was formed, and then dried under vacuum at 60°C for an additional 24 h. This electrolyte film was then sandwiched between two stainless steel electrodes and used for ac conductivity measurements.

Characterizations

Sodium sulfonate dimethyl fumarate, sodium sulfonate grafted poly(ethylene oxide), and the ionic polyurethane were characterized by elemental analysis (Heraeus CHN-OS Rapid), ^{1}H-NMR, and ^{13}C-NMR spectroscopy (AVANCE DRX 300). The average molecular weights of sodium sulfonate–side chain-grafted poly(ethylene oxide) and ionic polyurethane were measured by gel permeation chromatography (GPC, Waters 486). The ionic conductivities of these polymers were measured using an impedance analyzer (Schlumberger SI 1286, Electrochemical Interface SI 1260). The frequency was varied from 0.1 Hz to 10 MHz. The bulk electrolyte resistance was determined from the width of the high-frequency semicircle in the Cole–Cole plots.[12] The measured temperature range was set from 298 to 353 K. Differential scanning calorimetry (DSC, Thermal Analyst 2100) was used to measure the glass transition temperature (T_g) of the samples. The tempera-

$$\underset{\text{(BDOL)}}{\text{Prepolymer} + \text{MDI} + 2\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}} \longrightarrow \text{SPU}$$

Scheme 4.

Figure 1. ^{1}H-NMR spectra of SDMF in DMSO-d_6 at 25°C.

ture range was set from 173 to 473 K, and the thermal response was analyzed employing a scanning rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

Characterization of Structure

The structure of SDMF was characterized by ^{1}H-NMR spectra. Figure 1 shows chemical shifts of four kinds of protons at 2.86, 3.38, 3.56, and 3.68 ppm, respectively. The ratios are approximately 3 : 2 : 1 : 3, which are consistent with the expected SDMF structure. Figure 2 shows the ^{13}C-NMR spectra of the SPEO and the corresponding ^{13}C-NMR chemical shifts are at 33.0, 60.3, 167.7, and 170.3 ppm, respectively. This result indicates that the expected transesterification reaction between SDMF and PEO has indeed taken place. The element analyses of SDMF, SPEO, and SPU are summarized in Table I, indicating high purity in general of these prepared samples.

Effect of PEO Molecular Weight on T_g and Ionic Conductivity of SPU

It is well known that PEO with molecular weight greater than 1000 tends to crystallize, and results

in substantially lower segment mobility and lower ionic conductivity at room temperature[13,14] In this study, molecular weights of PEO used in preparing SPU are 400, 600, 800, and 1000, respectively.

The ionic conductivity of a polymer electrolyte depends on the effective number of carrier ions and the ion mobility. The effective number of carrier ions is related to the concentration of the dissolved ions. The ion mobility in a polymer electrolyte formed by the dissolution of ions in poly-(ethylene oxide) is facilitated by the segment mobility of the poly(ethylene oxide) chains. In an ionic conducting polymer, the ionic conductivity (σ) is generally expressed by the Vogel–Tamman–Fulcher (VTF) equation:[15]

The preexponential factor is related to the number of charge carriers and the exponent to the mobility of the charge carriers. E_a is the activation energy, and T_0 a temperature related to the glass transition temperature. This equation suggests that the polymer will exhibit higher ionic conductivity (σ) with the decrease of its T_g. Figures 3 and 4 reveal the effect of PEO molecular weight or the mole ratio of EO units vS. concentration of sodium ions ([EO]/[Na$^+$]) on the T_g and
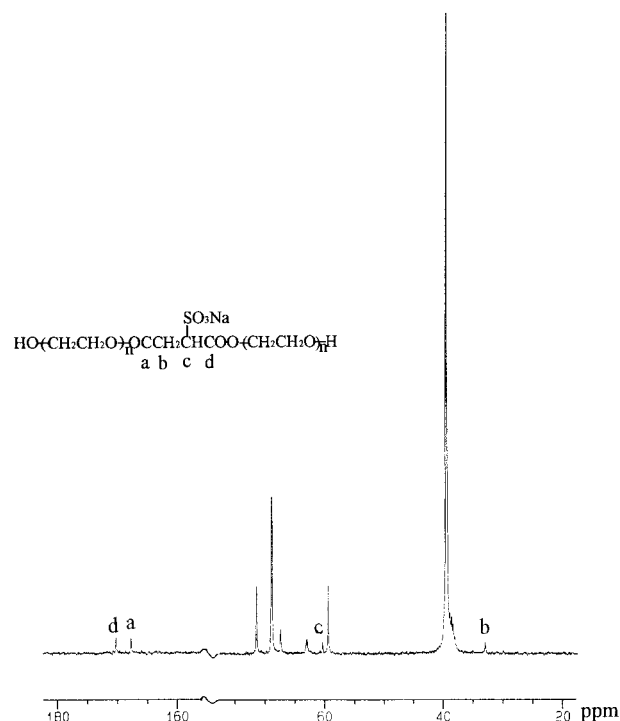
Figure 2. ^{13}C-NMR spectra of SPEO in DMSO at 25°C.

Table I. Element Analysis Results of SDMF, SPEO, and SPU

	C%		H%		S%	
Sample	Calculated	Measured	Calculated	Measured	Calculated	Measured
SDMF	29.04	28.64	3.69	3.54	12.90	13.25
SPEO400[a]	46.96	46.23	7.52	7.31	3.36	3.46
SPU400	57.57	55.96	6.41	6.19	1.67	1.76
SPU1000	56.41	54.92	7.43	7.25	1.03	1.30

[a] SPEO400 indicates PEO molecular weight 400.

on the ionic conductivity under different temperatures of SPU. The mole ratio of [EO]/[Na$^+$] has a strong influence on the T_g and, therefore, the ionic conductivity of the polymer electrolyte. The flexibility and mobility of the polymer chain is increased with the increase of the [EO]/[Na$^+$] value in the SPU and results in a lower T_g and a higher ionic conductivity. SPU with higher [EO]/[Na$^+$] value signifies a higher density of the polar group and thus favors the dissociation of the ions and produces a more effective num-

ber of carrier ions, even though it has a lower concentration of ions. The SPU1000 with a higher [EO]/[Na$^+$] value is more active in solvation. Therefore, the ionic conductivity of SPU1000 is higher, at 1.1×10^{-6} S/cm at room temperature. The relationship between the ionic conductivity and the T_g of the SPU are in agreement with the VTF equation.

Effect of Plasticizer on Ionic Conductivity of SPU

Generally, a plasticizer hinders the degree of crystallization of the polyurethane, and thus,
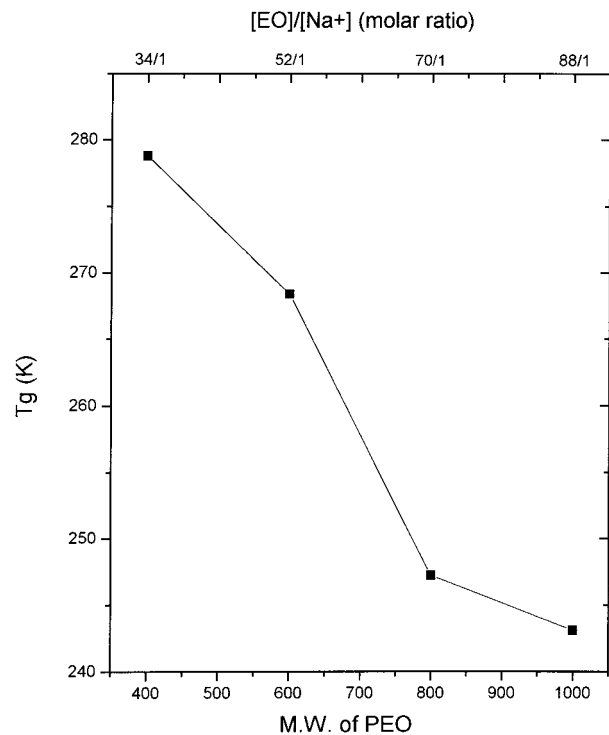
Figure 3. Effect of PEO molecular weight on T_g of SPU.
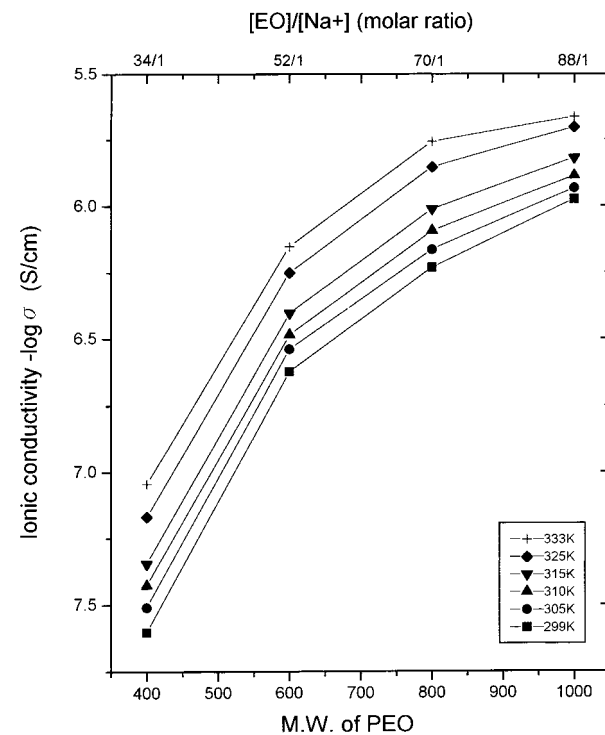
Figure 4. Effect of PEO molecular weight on ionic conductivity under different temperatures of SPU.

Table II. Effect of Plasticizer on T_g of Polymer Electrolyte

| Sample	T_g (K)	ΔT_g^* (K)
SPU400/PEODM	254.6	24.2
SPU600/PEODM	231.1	34.8
SPU1000/PEODM	236.2	6.9
SPU400/PEOMM	243.0	35.8
SPU400/PEO1000	241.1	37.7
SPU400/SPEO600	247.5	31.3

SPU/plasticizer: 3/1, wt ratio.
[a] The ΔT_g refers to the difference in the value of T_g between the SPU and SPU/plasticizer.

reduces the energy barrier for transportation of carrier ions and enhances the corresponding ionic conductivity. The data presented in Table II show that the T_g of SPU is substantially reduced with the addition of the plasticizer, except in the case of SPU1000. This result indicates that the segment mobility is significantly increased with the addition of PEODM as a plasticizer in SPU.

Figure 5 shows that the plasticizer PEODM is able to enhance the ionic conductivity of SPU400 substantially. Table III indicates the plasticizer PEODM is able to lower the activity energy of SPU400 from 1.724 to 1.145. The ionic conductivity of SPU400/PEODM is 3.3×10^{-6} S/cm, which is significantly higher than that of the unplasticized SPU400 (2.2×10^{-8} S/cm) at room temperature. For the SPU1000 system, however, the difference of ionic conductivity between SPU1000 and SPU1000/PEODM is insignificant (1.1×10^{-6} vs. 3.4×10^{-6}) because the SPU1000 is inherently more flexible. Table III shows that the activity energy of the SPU1000/PEODM is close to that of the SPU1000 (1.065 vs. 0.914). Effect of PEODM on segment mobility of the SPU600 is great but is still less than that of the SPU400. The activity energy of SPU600/PEODM is higher than that of SPU400/PEODM (1.251 vs. 1.145). The ionic conductivity of SPU600 is increased from 2.2×10^{-7} to 1.2×10^{-6} S/cm at room temperature by the addition of PEODM. The ionic conductivity difference between SPU400/PEODM and SPU1000/PEODM is insignificant because the sodium ion concentration in the SPU400/PEODM is much higher than that in the SPU1000/PEODM.

Figure 6 shows that the ionic conductivity of a polymer electrolyte decreases drastically with in-

creasing of the terminal hydroxyl content of the added plasticizer. The terminal hydroxyl group of a plasticizer is able to interact with other terminal hydroxyl of PEO, urethane of SPU, and ether oxygen to form hydrogen bonds and thus reduces the crystallinity and T_g of the polymer electrolyte as shown in Table II. However, the terminal hydroxyl tends to reduce the ion mobility and result in lower ionic conductivity. Table III shows the activity energy of polymer electrolytes with hydroxyl group is higher than that without containing hydroxyl group. In the SPU system, the concentration of carrier ions is reduced when a plasticizer is added to the polymer electrolyte. To counteract the negative effect due to the decrease of the carrier ion concentration, SPEO600 is used as a plasticizer. The SPU400/SPEO600 has higher ionic conductivity than that of SPU400/PEO1000 (Fig. 6) because the segment mobility is improved while the carrier ion concentration does not decrease. However, the ionic conductivity of SPU400/SPEO600 is still lower than that of the SPU400/PEODM because of the negative effect of the SPEO600 terminal hydroxyl group. These results indicate that the effect of the increase in segment mobility of the SPU400 is more than to offset the decrease of the ion concentration (from
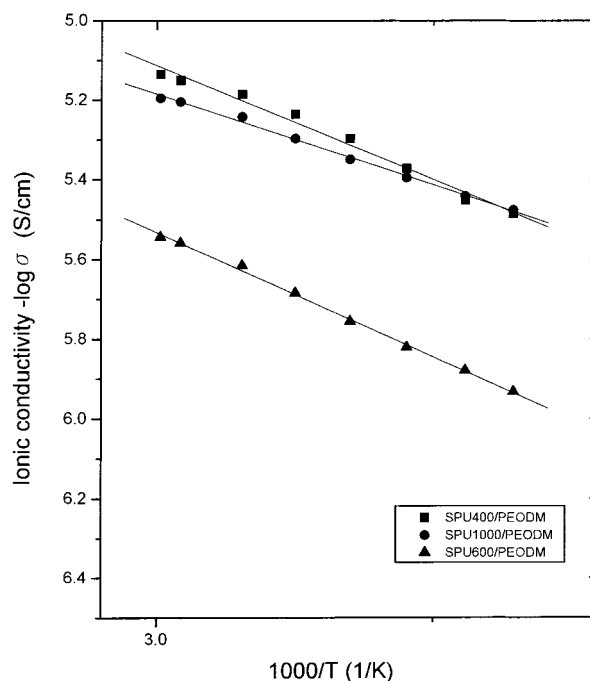
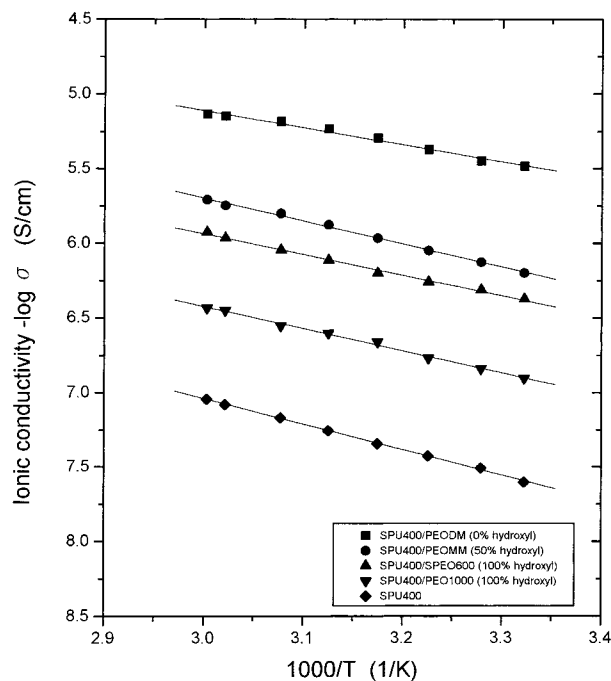**Figure 5.** Effect of PEODM on ionic conductivity of SPU.

Table III. Summary of Results According to Arrhenius Equation and Parameters of Various Polymer Electrolytes in Figure 5, Figure 6, and Figure 8

Source	Sample	A[a]	E_a/k[b]	Na%	[EO]/[Na]
Figure 5	SPU400/PEODM	1.679	1.145	0.878	~46/1
	SPU600/PEODM	1.780	1.251	0.623	~64/1
	SPU1000/PEODM	2.445	0.914	0.550	~46/1
Figure 6	SPU400/PEODM	1.679	1.145	0.878	~46/1
	SPU400/PEOMM	1.101	1.533	0.878	~46/1
	SPU400/SPEO600	1.776	1.387	1.293	~32/1
	SPU400/PEO1000	1.991	1.478	0.878	~46/1
	SPU400	1.869	1.724	1.17	~34/1
Figure 8	CSPU1000/SPEOMM	2.440	0.914	0.992	~72/1
	CSPU1000/PEODM	2.620	0.914	0.550	~100/1
	CSPU1000	2.393	1.063	0.730	~88/1
	SPU1000	2.441	1.065	0.730	~88/1

[a] A is related to the pre-exponential factor of Arrhenius equation.
[b] Ea/k is related to the activity energy.

1.17 to 0.878%, wt %) caused by a plasticizer on the ionic conductivity. Therefore, the ionic conductivity is significantly increased with the presence of a plasticizer.

Figure 6. Arrhenius plots of SPU400 and SPU400/plasticizer.

Effect of Crosslinking on Ionic Conductivity of Polyurethane

Crosslinking of the polymer electrolyte is expected to result in better mechanical stability, lower degree of crystallinity, and lower glass transition temperature, and thus higher ionic conductivity.[14] However, the crosslinking of the polymer is also found to affect the ionic conductivity by restricting the segment mobility of the polymer and results in lower ionic conductivity.[16] Table III shows that the difference in activity energies of various polymer electrolytes shown in Figure 8 is insignificant. Crosslinked sodium sulfonate–side chain polyurethane (CSPU) was synthesized according to Schemes 1–4, except that a portion of 1,4-butanediol was replaced by glycerol in Scheme 4. The CSPU shows better film stability than the corresponding SPU. Table IV shows the T_g of the CSPU is lower than that of the corresponding linear SPU, except in the case of CSPU1000. Figure 7 shows that the ionic conductivity of the CSPU is nearly identical to that of the corresponding SPU. Figure 8 shows that the ionic conductivity of CSPU1000 is only slightly higher than that of the SPU1000. The crosslinking of CSPU1000 has little effect on the degree of crystallinity and segment mobility because the SPEO1000 is inherently flexible. As a plasticizer, SPEOMM is able to increase the ionic conductivity of CSPU1000 but not that of PEODM because the former does not reduce the carrier ion concentration.
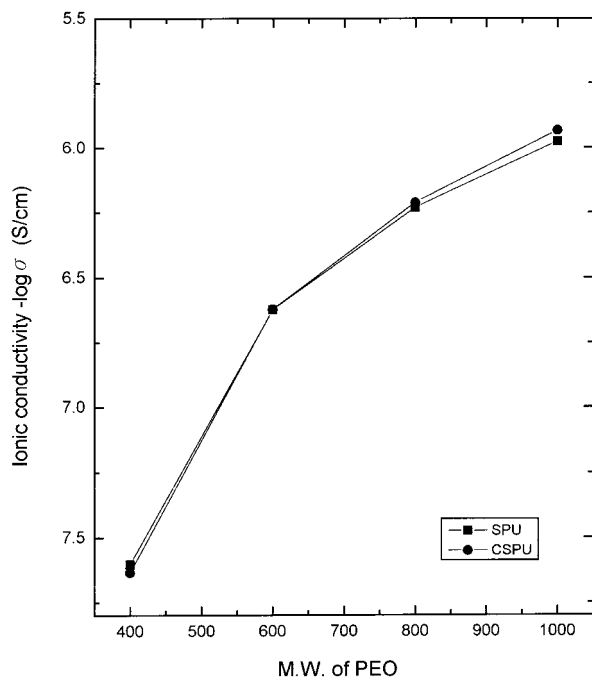
Table IV. Effect of Crosslinking of SPU on T_g

Sample	T_g (K)	ΔT_g^* (K)
CSPU400	266.1	12.7
CSPU600	259.1	9.3
CSPU800	242.7	4.5
CSPU1000	244.4	−0.7
CSPU1000/PEODM	236.3	/
CSPU1000/SPEOMM	253.3	/

[a] The ΔT_g refers to the difference in the value of T_g between SPU and CSPU.

CONCLUSIONS

New soft-segment ionic polyurethanes (SPU and CSPU) have been synthesized based on sodium sulfonate–side chain-grafted poly(ethylene oxide). The ionic conductivity of these polymer electrolytes is in the range of 10^{-6} to 10^{-7} S/cm at room temperature. The addition of the plasticizer results in an enhancement of the ionic conductivity of SPU or CSPU. The ionic conductivity of a polymer electrolyte is substantially reduced with an increase in the terminal hydroxyl group content in the plasticizer. Crosslinking of the SPU

Figure 7. Effect of crosslinking on ionic conductivity of SPU.
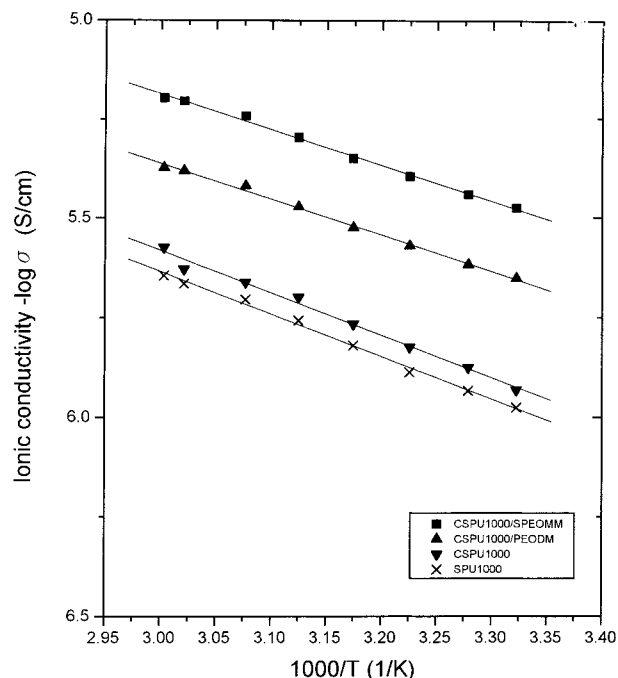
Figure 8. Arrhenius plots of CSPU1000 and CSPU1000/plasticizer.

enables improvement of the film stability and slightly enhances the ionic conductivity.

REFERENCES AND NOTES

1. Huang, F.; Wang, X.; Li, S. J Macromol Sci Chem 1991, A28, 175.
2. Manoresi, P.; Bignozzi, M. C.; Pilati, F. Polymer 1993, 34, 2422.
3. Kim, D. W.; Park, J. K.; Gong, M. S.; Song, H. Y. Polym Eng Sci 1994, 34, 1305.
4. Abraham, K. M.; Jiang, Z.; Carroll, B. Chem Mater 1997, 9, 1978.
5. Takahashi, K.; Akashi, H.; Noda, K.; Tanaka, K. U.S. Pat. 5,643,490 (1997).
6. Onishi, K.; Matsumoto, M.; Nakacho, Y. Chem Mater 1996, 8, 469.
7. Hardy, L. C.; Shriver, D. F. J Am Chem Soc 1985, 107, 3823.
8. Benrabah, D.; Sylla, S.; Alloin, F. Electrochim Acta 1995, 40, 2259.

9. Fujinami, T.; Tokimune, A.; Anne Metta, M. Chem Mater 1997, 9, 2236.

10. Ding, Y.; Register, R.; Yang, C.; Cooper, S. Polymer 1989, 30, 1213.

11. Robila, G.; Ivanoin, M.; Buruiana, E. C. J Appl Polym Sci 1993, 49, 2025.

12. Hagenmuller, P., Ed. Solid Electrolytes: General Principles, Characterizations, Materials, Applications; Academic Press: New York, 1978.

13. Kim, D. W.; Song, J. S.; Park, J. K. Electrochim Acta 1995, 40,1697.

14. Herranen, J.; Kinnuen, J.; Mattsson, B. Solid State Ionics 1995, 80, 201.

15. Torell, L. M.; Schantz, S. In Polymer Electrolyte Reviews (2); MacCallum, J. R.; Vincent, C. A., Eds.; Elsevier Applied Science Publishers: London, 1989.

16. West, K.; Christiansen, B. Z.; Jacobsen, T. Br Polym J 1988, 20, 243.