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Ionic conductivity and morphology of complexes formed by polyurethanes and lithium perchlorate

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Summary

Segmented polyether urethane (SEU) and urethaneurea (SEUU) were synthesized using ABA type triblock copolymer as a prepolymer, where A stands for poly(oxyethylene) and B stands for poly(oxytetramethylene). Lithium perchlorate was dissolved in SEU or SEUU to prepare $LiClO_4$ complexes (SEU / $LiClO_4$ and SEUU / $LiClO_4$) in film form. The highest conductivities observed here were 5.13×10^{-6} S cm^{-1} at 30°C and 3.34×10^{-5} S cm^{-1} at 50°C for $LiClO_4$ / SEUU (oxyethylene-units content, 31 mol%). The ionic conductivity of these complexes was found to show the Arrhenius type temperature dependency. The effect of lithium perchlorate dissolution on the morphology of SEU and SEUU were also discussed.

Introduction

Polymeric solid electrolytes (PSE) (1,2) have been paid much attention due to their importance for electronic devices, especially chemical batteries. PSE is expected to be indispensable to prepare solid electrolytes that are light weight and are easily formed into thin films. It will become possible to fabricate thin and light weight batteries of high performances, once we get an excellent PSE having high conductivity and good durabilities as well as feasibility to an industrial process for production. Among various polymers, elastomer is superior to the other polymers, because its flexibility and processability are very useful for thin and flexible paper-like batteries and electrochromic displays (3). In addition, elasticity affords an excellent contact between an electrolyte layer and an electrode in chemical batteries where interface resistance is one of the very important factors to determine the performance of battery.

In this communication segmented polyurethane (SEU) (4) and polyurethaneurea (SEUU) (5,6) are chosen as matrixes for ionic conductors. Polyurethanes are known to be one of the best elastomers due to their superior mechanical properties (7,8). We succeeded in preparing new polyurethanes that had hydrophilic poly(oxyethylene) units (5), and showed that they had a very good biocompatibility as well as an excellent mechanical properties (4,6). Because of their hydrophilicity and flexibility, we assume

that they can be an excellent matrix for ionic conduction to prepare flexible PSEs with a high conductivity.

Additionally, biocompatible ionic conductors are needed in some applications, for example, electrodes of medical diagnostic instruments which are applied on human skin. In ordinary circumstances, surface of human body has a conductivity about the order of 10^{-5} through 10^{-4}. Comparable conductivity is necessary for the above mentioned applications at room temperature.

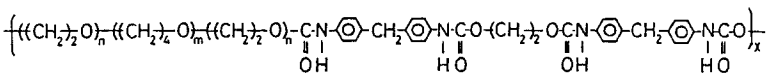
Experimental

The chemical structures of SEU and SEUU are shown in Fig. 1. The prepolymers were synthesized from hydroxyl terminated poly-(oxytetramethylene) with molecular weight of 1830 followed by anionic polymerization of ethylene oxide to result in the formation of ABA type triblock copolymer (5). The contents of A blocks i.e. poly(oxyethylene)(PEO) segments, were 0, 31, and 62 mol%. The complex with lithium perchlorate was prepared mainly by casting N,N'-dimethylacetamide solution of the polymer and $LiClO_4$ (method A) and some samples by soaking polymer film in methanol solution of $LiClO_4$ (method B). IR spectra and DSC were measured on a Hitachi IR spectrophotometer 215 and Seiko DSC 20, respectively.

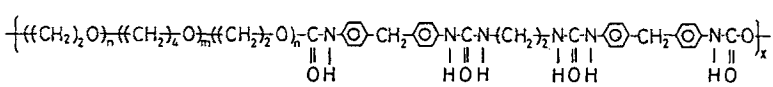
Polymer film doped with lithium perchlorate was treated in a dry box under a pure nitrogen stream to make up a conductivity cell using platinum electrodes. In order to evaluate ionic conduction, electrical ac conductivity was measured by the complex impedance method (9) using Yokogawa-Hewlett Packered LF Impedance Analyzer 4192A (Frequency range, 5 Hz - 1 MHz). The equivalent electrical circuit is shown in Fig. 2, where Cg is geometrical capacitance, Rb is bulk resistance of soft segment matrix, and Ri and Ci are resistance and capacitance, respectively, at the interface of hard segment domain and the matrix. The complex impedance associated with this circuit is expressed as

$$Z = \frac{Rb\ (1 + i\omega\ Ci\ Ri)}{(1 - \omega^2\ Cg\ Ci\ Rb\ Ri) + i\ \omega(Ci\ Ri + Ci\ Rb + Cg\ Rb)} \qquad [1]$$

where ω is an angular frequency.



S E U



S E U U

Fig. 1 Structures of SEU and SEUU.

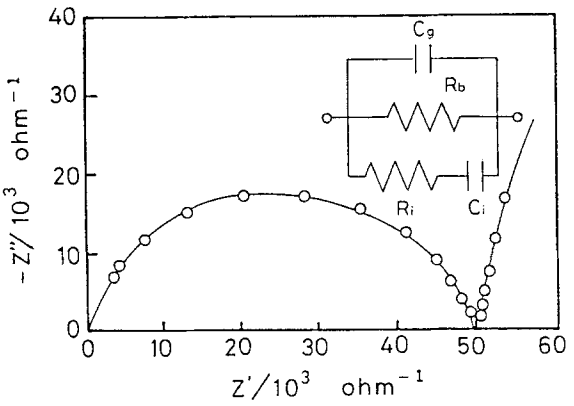


Fig. 2 The Cole-Cole plot for SEU / $LiClO_4$(EO content, 62 mol%) at 40 °C: Z' and Z" are real and imaginary components of the complex impedance, respectively.

Table 1 Effect of lithium perchlorate concentration on ionic conductivity at 50°C.

$LiClO_4$	Ionic conductivity (σ) x 10^6 (S cm^{-1})	
(wt %)	SEU / $LiClO_4$ (EO, 62 mol%)	SEUU / $LiClO_4$ (EO, 31 mol%)
5	4.72	0.178
9	9.98	33.4
17	5.67	0.095

Results and Discussion

Ionic conductivity of polyurethane/$LiClO_4$ complexes

In Fig. 2 is shown an example of the Cole-Cole plot for polyurethane / $LiClO_4$ complex by complex impedance measurements. Usual arc was observed, and after the arc experimental points tended to diverge because blocking electrodes (Pt) were used. According to eq. [1] we obtain Rb from the the value where the arc hit the axis of real part of complex impedance (Z').

Table 1 shows the effect of dopant concentration on conductivity (σ). There seems to be an optimal value to give the highest conductivity. Conductivity is expressed by

$$\sigma = \sum_i ni \times \mu i \times e \qquad [2]$$

where ni is number of i-th carrier, μi mobility, and e the elementary electronic charge. As the dopant concentration increased, the carrier number n increased. However, this increase induced the more crystallization of soft segments which depressed

the mobility of ions resulting in the decrease of conductivity. As a conpromise of the two effect optimal dopant concentrations were observed.

Fig. 3 shows effect of oxyethylene-unit contents in SEUU on σ in the form of the Arrhenius plot. In the temperature range examined, SEUU having oxyethylene-unit content of 31 mol% relative to total ether units in the prepolymer displayed higher σ's than the other two. Temperature dependence of σ shows an excellent linearity. Watanabe et al. reported convex curves for temperature dependency of σ's of poly(oxypropylene) based

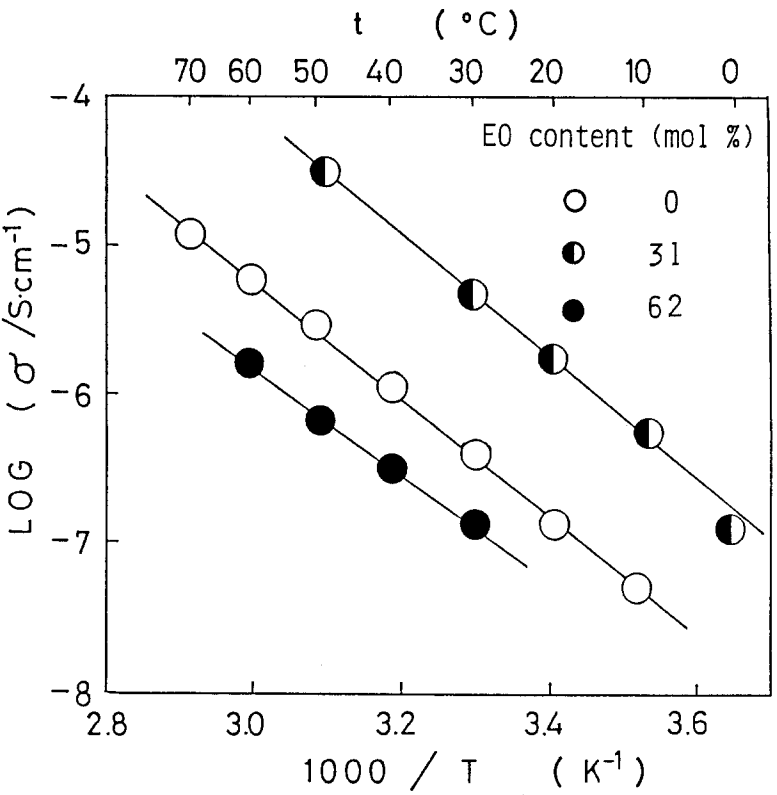


Fig. 3 Temperature dependency of ionic conductivity of SEUU/ lithium perchlorate prepared by method A. The concentration of lithium perchlorate was 9 wt %.

polyurethanes doped with inorganic salts (9). They explained the results by the William-Landel-Ferry (WLF)-type dependency, i.e., in terms of free volume theory. The difference between theirs and ours is probably due to the different temperature ranges, i.e., their results were obtained around (Tg + 50) K, while ours around (Tg + 100) K due to lower Tg,s of our samples than that of theirs. It is well known that the WLF equation, eq. [3], holds well just above Tg through (Tg + 100) K (10).

$$\log \frac{\sigma\ (T)}{\sigma\ (Tg)} = \frac{C_1\ (T - Tg)}{C_2 + (T - Tg)} \qquad [3]$$

Since the conduction matrix is heterogeneous, it is very probable that how the dopant is dissolved into the matrix affects the conductivity. In fact, Fig. 4 depicts the effect of difference in the preparation method of the complex. Method B (immersing) gave much better conductivity than method A (dissolving). In method B SEUU was simply soaked in the methanol solution of lithium perchlorate, hence it is estimated that Li salt was present mainly in soft segment matrix because the soft-segment matrix swelled in methanol but the hard segment domains did not. The ions dissolved in the soft segments are ready to migrate.

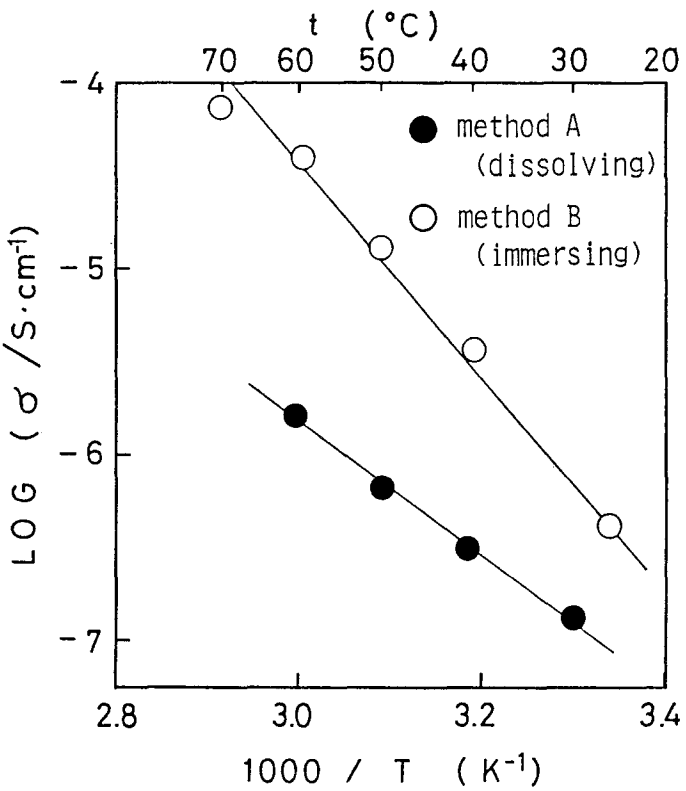


Fig. 4 Temperature dependency of ionic conductivity of SEUU / lithium perchlorate prepared by method A (dissolving) and method B (immersing). The concentration of lithium perchlorate was 9 wt %.

On the other hand, both lithium salt and SEUU were dissolved in the solvent followed by the casting of the solution to form solid films in method A. Therefore, the ions were supposed to be dissolved both in soft segment matrix and in hard segment domains. The salts in hard segment domains were confined, and had to diffuse into soft segment matrix in order to act as a carrier of electric current.

Morphology of SEU/$LiClO_4$ and SEUU/$LiClO_4$

The DSC results are listed in Table 2. In all SEUUs and SEUs, glass-transition temperature of soft segment matrix (Tg,s), melting point of soft segment matrix (Tm,s), and that of hard segment domain (Tm,h) were observed by DSC measurements. In other words, microphase separation is recognized in all polyurethanes and polyurethaneureas including those doped with lithium perchlorate.

Here, effect of dopant will be discussed. Both Tg,s and Tm,s were affected by the doping, but Tm,s seems to be more sensitive to the presence of lithium perchlorate than Tg,s. It seems that the interaction of Li cation with ether oxygen in polyether units in soft segments and/or the complex formation of the cation with oxyethylene units that has a higher melting point to result in the increase of Tm,s. It is well known that Li cation easily forms complex with poly(oxyethylene). On the other hand, dissolution of the salt in the amorphous region of soft segment matrix decreased Tg,s, which might be due to the plasticizing effect of the dopant. However, the increase of Tg,s of SEU/$LiClO_4$ by doping was an exception, the reason of which is not clear yet. It was shown that the microphase separation was not so clear in SEU as in SEUU (4), which may be a factor to be considered to explain this anomaly.

Table 2 DSC results of SEU / $LiClO_4$ and SEUU / $LiClO_4$.

Sample	EO content in prepolymer (mol%)	Soft-segment content (wt%)	Doped $LiClO_4$ (wt%)	Phase transition (°C) Tg,s	Tm,s	Tm,h
SEUU/$LiClO_4$	0	76.0	0	-74.4	-2.1	268
			5	-75.3	-2.1	264
			9	-75.4	9.4	238
	31	81.1	0	-76.3	1.9	279
			5	-78.7	2.5	271
			9	-80.3	4.0	256
	62	87.5	0	-78.4	5.4	278
			5	-80.5	8.7	271
			9	-81.6	0.4	247
SEU/$LiClO_4$	31	81.1	0	-73.8	-0.9	261
			5	-71.3	1.4	254
			9	-70.3	3.3	250

The Tm,h always went down by doping lithium perchlorate. This is a direct evidence of dissolution of the dopant into hard segment domains. From this result it does not seem to be a favorable condition for polyurethanes to have micro-heterogeneous structures when to use as an ion-conduction matrix, although the microphase separation affords excellent mechanical properties to segmented polyurethanes (4,7,8).

Infrared spectra gave informations on the microphase separation of polyurethanes (11). In the spectrum of SEUU, peaks due to hydrogen bonded structures appeared, i.e., N-H stretching at 3300 cm^{-1}, C=O stretching in urethane bonding at 1710 cm^{-1}, and C=O stretching in urea bonding at 1640 cm^{-1}. Also, non-hydrogen-bonded C=O in urethane bonding appeared at 1730 cm^{-1} which was present in soft segment matrix. In SEUU / $LiClO_4$ complex, a peak due to non-hydrogen bonded group was clearly recognized at 3440 cm^{-1} (N-H stretching), in addition to two peaks at 1100 and 610 cm^{-1} assignable to lithium perchlorate. The peak at 3300 cm^{-1} due to hydrogen bonded N-H decreased considerably compared to that of SEUU. Almost the same results were obtained on SEU and SEU / $LiClO_4$. These results suggest that lithium perchlorate was dissolved in hard segment domains, hence preventing hydrogen bonding between polyurethane molecules.

On the other hand, when films were prepared by method B (immersing), the peaks assignable to hydrogen bonded groups were clearly observed. Accordingly lithium perchlorate existed mainly in soft segment matrix in the film prepared by the immersing. This estimation is reasonable, because by immersing in methanol, only soft segment matrix was swelled to allow the penetration of lithium perchlorate. The better conductivity of the film prepared by method B is also explained by that estimation; ions in the soft segment matrix can diffuse faster than those included in hard segment domains. The ions in hard segment domains have to migrate to the soft matrix before they can give way to conductivity.

Microphase separation in matrix was not found to be favorable for ionic conductions. However, it is very important for excellent mechanical properties (4,7,12) and biocompatibility (4-6, 12,13) of polyurethanes. Therefore, some conpromises are needed for the development of ion-conducting polyurethanes for the usages in biomedical applications.

References

1) J.R.MacCallum, C.A.Vincent, "Polymer Electrolyte Reviews", 1, Elsevier Applied Science, 1987.
2) P.M.Blonsky, S.Clancy, L.C.Hardy, C.S.Harris, R.Spindler, J. S.Tonge, D.F.Shriver, Chemtech, 17, 758 (1987).
3) S.Kohjiya, Nippon Gomu Kyokaishi, 59, 320 (1986) (J. Soc. Rubber Ind. Japan, in Japanese) ; S.Kohjiya, T.Kawabata, K.Maeda, S.Yamashita, Y.Shibata, Paper presented at Second International Symposium on Polymer Electrolytes, Siena, Italy, June 14-16 (1989).
4) Y.Ikeda, S.Kohjiya, S.Yamashita, Paper no. 21 presented at ACS Rubber Division 134th Meeting, Cincinnati, OH, October

18-21 (1988): Rubber World, 200, no. 6, 21 (1989).
5) Y.Ikeda, S.Kohjiya, S.Yamashita, Nippon Kagaku Kaishi, 1986, 699 (J. Chem. Soc. Japan, in Japanese).
6) S.Kohjiya, Y.Ikeda, S.Yamashita, "Polyurethanes in Biomedical Engineering II", edited by H.Plank et al., Elsevier B. V., Amsterdam, 1987, pp. 183-195.
7) W.Meckel, W.Goyert, W.Wieder, "Thermoplastic Elastomers", edited by N.R.Legge et al., Hanser, Munich, 1987, chapter 2.
8) A.Awater et al, "Polyurethane Handbook", edited by G.Oertel, Hanser, Munich, 1985, chapter 8.
9) M.Watanabe, S.Oohashi, K.Sanui, N.Ogata, T.Kobayashi, Z. Ohtaki, Macromolecules, 18, 1945 (1985).
10) F.Bueche, "Physical Properties of Polymers", John Wiley & Sons, New York, 1970, chapter 4.
11) C.S.P.Sung, T.W.Smith, N.H.Sung, Macromolecules, 13, 117 (1980).
12) Y.Ikeda, S.Kohjiya, S.Yamashita, H.Hayashi, T.Okuno, Nihon Reoroji Gakkaishi, in press (J. Soc. Rheology, Japan, in Japanese).
13) J.B.Park, "Biomaterials Science and Engineering", Plenum Press, New York, 1984.

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