

## The Effect of Aggregation States on Ionic Conductivity of Solid Polymer Electrolytes Based on Waterborne Polyurethane

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*Received August 24, 2001*

**Abstract :** Waterborne polyurethane as a new polymer electrolyte was synthesized by using relatively hydrophilic polyols. The morphology of polyurethane was changed as it was dispersed in water. In contrast to polyurethane ionomer, waterborne polyurethane did not form an ionic cluster but produced a binary system composed of hydrophilic and hydrophobic groups. In the colloidal system, the former and the latter existed at outward and inward, respectively. Waterborne polyurethane was prepared from poly(ethylene glycol) (PEG) /poly(propylene glycol) (PPG) copolymer, 4,4'-diphenylmethane diisocyanate (MDI), ethylene diamine as a chain extender, and three ionization agents, 1,3-propane sultone, sodium hydride and lithium hydroxide. PEG/PPG copolymer was used for suppressing the crystallinity of PEG and N-H bond was ionized for increasing the electrochemical stability of polyurethane. Low molecular weight poly(ethylene glycol) and poly(ethylene glycol dimethyl ether) (PEGDME) were used as plasticizers. DSC, FT-IR and <sup>1</sup>H-NMR of the waterborne polyurethane were measured. Also, the ionic conductivity of solid polymer electrolytes based on waterborne polyurethane and various concentrations of low molecular weight poly(ethylene glycol) or PEGDME were measured by AC impedance.

### Introduction

At the turn of millennium the consciousness of the need to use energy more efficiently spreads, at least in developed countries. The efficient use of energy also includes efficient storage of electricity, meaning that one need to have high energy density batteries having low energy losses during storage, electrical charging and discharging, and last, but not least, batteries with long life times and a minimum of production and disposal costs. From this point of view, solid polymer electrolyte attracted attention widely. Since Wright<sup>1</sup> and Armand<sup>2</sup> first reported for poly(ethylene oxide) (PEO) electrolytes, many researchers have studied solid polymer electrolytes (SPEs).

From the study of ionic conducting mechanism<sup>3-8</sup> for PEO-LiX electrolytes, it was found that the ionic transport took place in the amorphous region and ionic conductivity depended on the mobility

of ions, the flexibility of polymer chain and the degree of dissociation of salts. The linear PEO chain demonstrated a very high solvating power and high flexibility at high temperature.

Moreover polyether based electrolyte showed desirable features such as good adherence to the electrode and ability to dissolve many inorganic salts forming a homogeneous solution. However, at the ambient temperature, the PEO-LiX system exhibited low ionic conductivity due to its high crystallinity. As a decrease in crystallinity of PEO, the ionic conductivity of PEO-LiX system increased but mechanical strength decreased unfortunately. Blending of polymer matrix and inorganic component,<sup>9</sup> introducing liquid crystal into PEO main chain,<sup>10</sup> and solid polymer electrolyte based on various polyethylene oxides<sup>11</sup> were used to overcome this problem but they were not satisfied.

Amorphous region contributed to ionic conduction but did not give mechanical stability to the electrolyte. In this reason another researcher tried to use segmented polyurethane (SPU) for solid

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polymer electrolyte.<sup>12</sup> SPU consists of soft and hard segments. Soft segments of SPU contributed to ionic conducting and hard segments of SPU served mechanical strength but interrupted ionic conduction due to its immobility. Thus, SPU did not candidate for solid polymer electrolyte. It is reason why we considered waterborne polyurethane (WPU) as a polymer electrolyte matrix. N-H bonds in urethane and urea were ionized to disperse SPU in water. By ionizing N-H bond, hard segments in WPU can get ionic conduction and electrochemically unstable N-H bond is eliminated.<sup>13</sup>

In this study, WPU was synthesized and compared with polyurethane ionomer (PUI) to investigate the effect of ionic aggregation on ionic conductivity.

## Experimental

The raw materials employed in this study are listed in Table I. Polyol (PE-62T, Korea Polyol Co.) was dried and degassed at 80°C for 24 h under vacuum prior to use. Extra pure grade of *N,N'*-dimethyl acetamide (DMAc) was dried using 4 Å molecular sieve before use. Ethylene diamine (EDA), 4,4'-diphenylmethane diisocyanate (MDI), 1,3-propanesultone (PS), sodium hydride (NaH), and lithium hydroxide (LiOH) were used as

received. Low molecular weight polyethylene oxide (PEO) ( $M_w = 400$ ) and poly(ethylene glycol dimethyl ether) (PEGDME) ( $M_w = 350$ ) were dried 4 Å molecular sieve before use.

A 1000 mL four-necked round bottom and separable flask equipped with a mechanical stirrer, thermometer, condenser with a drying tube and N<sub>2</sub> inlet was used as reactor. Reaction was carried out in a constant water bath. Total reaction scheme is shown in Figure 1. MDI and polyol were first mixed and reacted at 60°C to obtain NCO-terminated prepolymer. And then NCO-prepolymer was cooled at 25°C, and EDA in DMAc was added and reacted for 1 h to obtain segmented polyurethane urea (SPUU). After synthesizing SPUU (hard content: 15 wt%), N-H bond was ionized with 1,3-propane sultone and NaH. SPUU-SO<sub>3</sub>Na was carefully added to an excess of dilute hydrochloric acid to convert the sodium salt into the acid.<sup>14</sup> The solution was evaporated to remove both water and HCl, and then the residue was precipitated in toluene. After filtration twice, SPUU-SO<sub>3</sub>H was obtained. SPUU-SO<sub>3</sub>H was dissolved in DMAc, and LiOH dissolved in water was added to convert SPUU-SO<sub>3</sub>H to SPUU-SO<sub>3</sub>Li (ionomer). The solution was evaporated to remove both DMAc and water, and SPUU-SO<sub>3</sub>Li was dispersed in water.

The films were obtained from the solvent evaporation method by casting on a Teflon disk, followed by drying at 60°C for 24 h. And, it was confirmed that the water content of film was around 10 ppm. Solid polymer electrolytes were prepared with WPU, LiClO<sub>4</sub>, and plasticizer (low molecular weight PEG or PEGDME).

## Results and Discussion

**FT-IR Spectroscopy.** The FT-IR spectrum of SPUU is shown in Figure 2. Four main regions were assigned as follows:

1. A broad absorption band of the N-H stretching mode in 3300-3600 cm<sup>-1</sup> was observed.
2. Aliphatic C-H stretching mode of 2800-2900 cm<sup>-1</sup> was observed.
3. The carbonyl (C=O) stretching absorption band was observed at 1600-1700 cm<sup>-1</sup>.
4. C-O-C stretching absorption band corre-

**Table I. Raw Materials**

Designation	Chemical identification	Suppliers
PE-62T	$M_w = 2440$ , PEO/PPO block copolymer, EO unit content = 29%	Korea Polyol Co.
MDI	4,4'-diphenylmethane diisocyanate	Merck Co.
EDA	Ethylene diamine	Junsei Co.
DMAc	<i>N,N'</i> -dimethyl acetamide	Junsei Co.
PS	1,3-propane sultone	Aldrich Co.
NaH	Sodium hydride	Aldrich Co.
LiOH	Lithium hydroxide	Aldrich Co.
PEG	Poly(ethylene oxide)	Shinyo Co.
PEGDME	Poly(ethylene glycol dimethyl ether)	Fluka Co.
LiClO <sub>4</sub>	Lithium perchlorate	Aldrich Co.

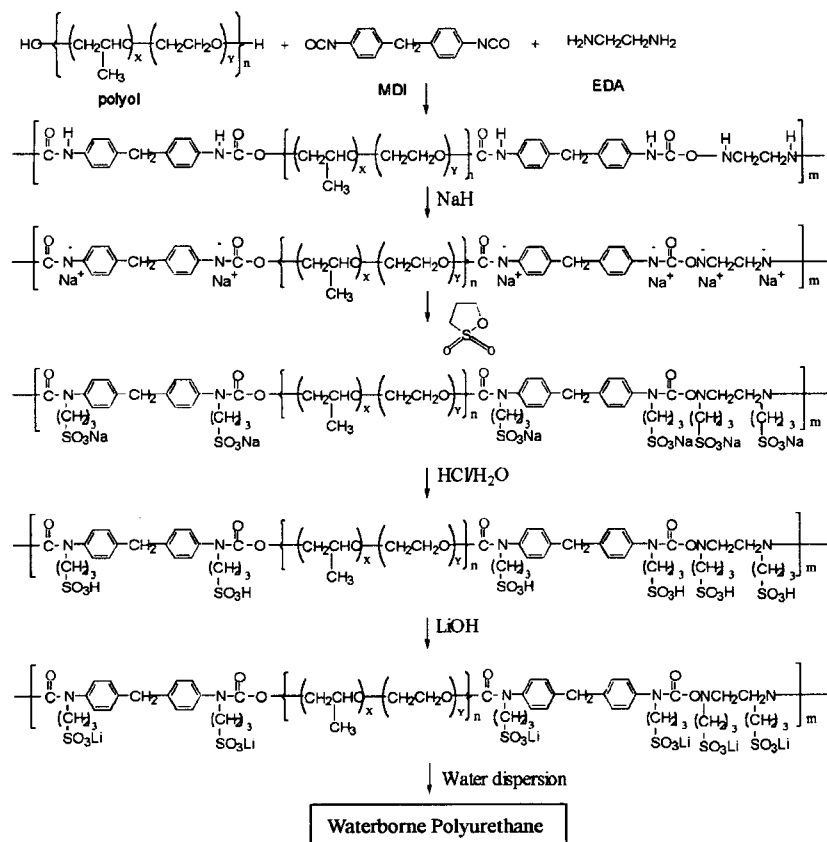


Figure 1. Synthesis of waterborne polyurethane.

sponding to the ether oxygen of soft-segment was observed at  $1000-1150\text{ cm}^{-1}$ .

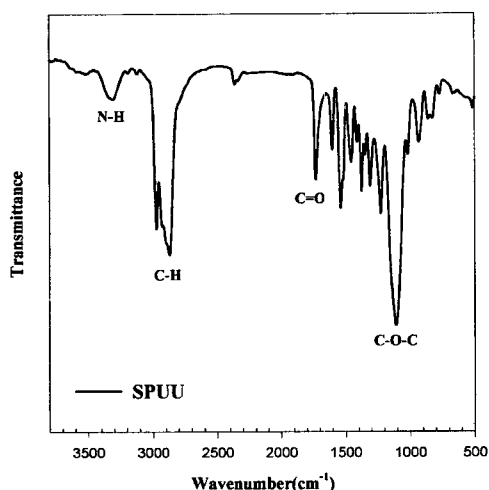


Figure 2. FT-IR spectrum of segmented polyurethane urea (SPUU).

Figure 3 shows the spectrum of WPU. Typical inorganic sulfate peaks were observed. From these data, it was confirmed that SPUU and WPU were successfully synthesized.

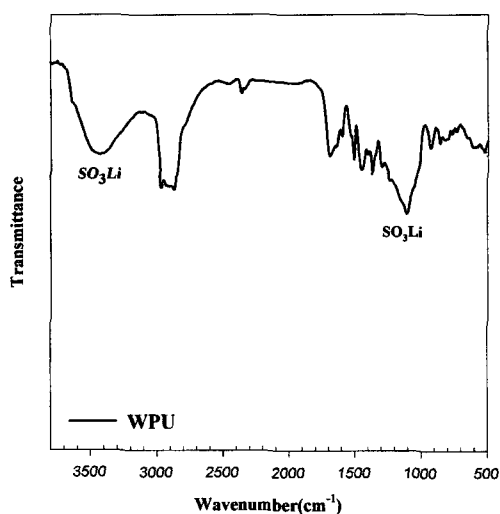
**<sup>1</sup>H-NMR Measurement.** The <sup>1</sup>H-NMR spectrum is shown in Figure 4 and Figure 5 for SPUU and WPU, respectively. The N-H peak of SPUU was observed at  $\delta = 9.6$  in Figure 4, but it was disappeared in Figure 5, indicating that N-H bond was successfully ionized.

**Ionic Conductivity.**

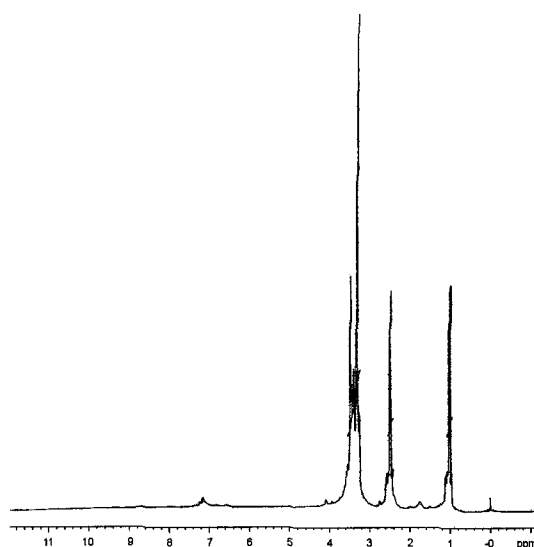
**Effect of Hard Content:** Polyurethane had various properties according to the hard content, which was calculated as follows.

$$\text{Hard content of PU(\%)} = \frac{(\text{chain extender} + \text{diisocyanate})(g)}{(\text{polyol} + \text{chain extender} + \text{diisocyanate})(g)} \times 100$$

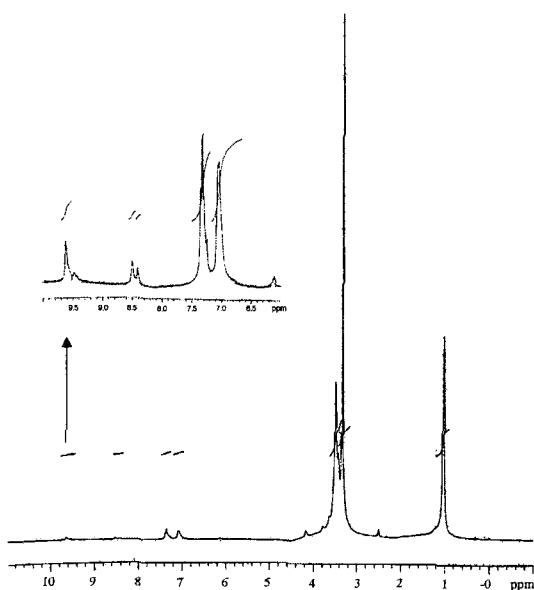
In general, polyurethane showed elastomeric properties in the case that the hard content was



**Figure 3.** FT-IR spectrum of waterborne polyurethane (WPU).

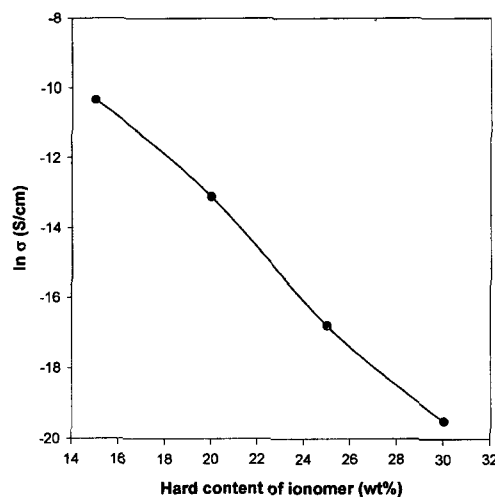


**Figure 5.** <sup>1</sup>H-NMR spectrum of WPU.



**Figure 4.** <sup>1</sup>H-NMR spectrum of SPUU.

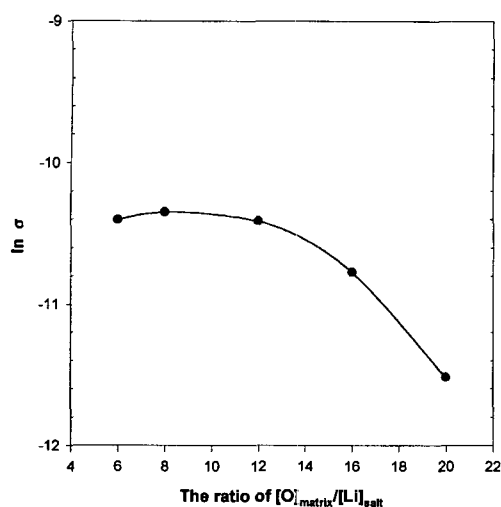
20~50%. Figure 6 shows the ionic conductivity of polyurethane ionomer (PUI) with various hard contents. In this case, ionization concentration was fixed at  $[O]_{\text{matrix}}/[Li]_{\text{LiOH}} = 20$  to obtain the highest ionic conductivity.<sup>15</sup> As the hard content increased, ionic conductivity decreased. On the other hand, if the hard content was smaller than 15%, PUI could not sustain its mechanical proper-



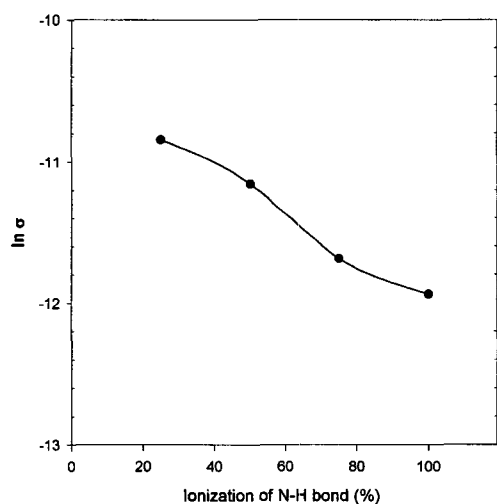
**Figure 6.** Ionic conductivity of PUI with various hard contents.

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**Effect of Lithium Salt Content:** Ionic conductivities of PUI with various lithium salt concentrations are shown in Figure 7. The maximum ionic conductivity was  $3.25 \times 10^{-5}$  S/cm at  $[O]_{\text{matrix}}/[Li]_{\text{salt}} = 8$ . Ionic conductivity is determined by two major factors. One is the chain mobility that can do ion hopping for ionic conduction. The other is the ion transfer number that increases with adding a lithium salt. As lithium salt concen-



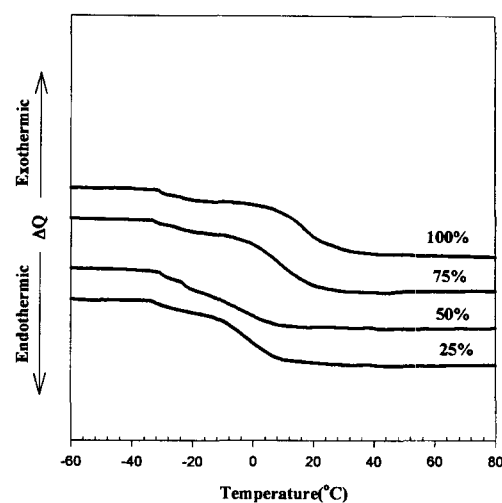
**Figure 7.** Ionic conductivity of PUI at various lithium salt concentrations.



**Figure 8.** Ionic conductivity of WPU at various ionized concentrations.

tration increased, lithium salt formed a complex with polyol, and then chain mobility of polyol decreased. Therefore, ionic conductivity had optimum point with lithium salt concentration.

**Effect of Ionized Concentration:** Figure 8 shows the ionic conductivity of WPU with different ionized concentration. In this case, the hard content of polyurethane was fixed at 20% and ionization was carried out after synthesizing polyurethane. As ionized concentration increased,



**Figure 9.** DSC thermograms of WPU with various ionized concentrations.

ionic conductivities of WPU decreased. But, it is desirable to ionize all N-H groups, because N-H bond is electrochemically unstable group.

Figure 9 shows DSC thermograms of WPU at various ionized concentrations. It showed double  $T_g$ s. The lower  $T_g$  and the higher  $T_g$  were resulted from the molecular motion of polyol and the complex between lithium salt and polyol, respectively. As ionized concentration increased, the higher  $T_g$  was shifted to the higher temperature. It means that chain mobility was restricted with ionized concentration, and ionic conductivity decreased.

**Effect of Ionic Aggregation:** In contrast to polyurethane ionomer, waterborne polyurethane did not have an ionic cluster but made a binary system composed of hydrophilic and hydrophobic groups. In the colloidal system, the former and the latter existed at outward and inward, respectively.

WPU formed a profitable morphology for ionic conduction by the elimination of ionic cluster that restricted the chain mobility of polyol. Cole-Cole plots of WPU and PUI are shown in Figure 10, and it became clear that the ionic conductivity of WPU was higher than that of PUI.

**Effect of Plasticizer Molecular Weight:** In order to improve the chain mobility of WPU, plasticizer was added. In this study, low molecular

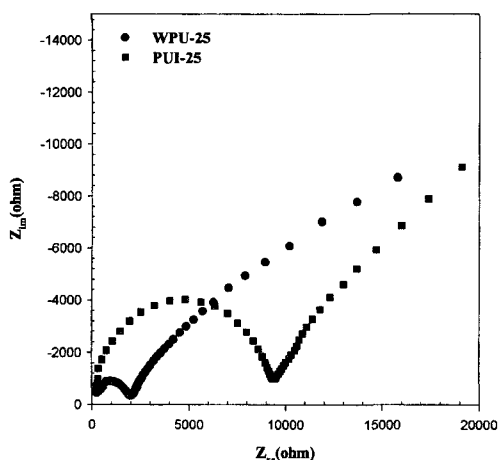


Figure 10. Cole-Cole plots of WPU and PUI.

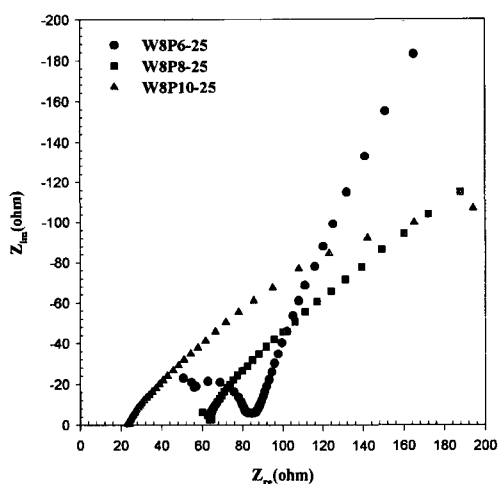


Figure 11. Cole-Cole plots of WPU containing plasticizer with different molecular weight.

weight PEGs were used as plasticizers. Figure 11 shows Cole-Cole plots of SPEs containing PEGs with various molecular weights, and their ionic conductivities are listed in Table II. From these results, it was revealed that the ionic conductivity of SPE increased with the molecular weight of plasticizer, which arose from an increase in the chain mobility of WPU according to the increase of plasticizer molecular weight.

**Effect of Plasticizer Type:** In order to investigate the effect of chemical structure of plasticizer on ionic conductivity, low molecular weight PEG ( $M_w = 400$ ) and PEGDME ( $M_w = 350$ ) were used

Table II. Ionic Conductivity of WPU Containing Plasticizer with Different Molecular Weight

Sample	PEG ( $M_w$ )	Ionic Conductivity (25 °C)
W8P6	600	$1.19 \times 10^{-4}$ S/cm
W8P8	800	$1.56 \times 10^{-4}$ S/cm
W8P10	1000	$4.17 \times 10^{-4}$ S/cm

Table III. Ionic Conductivity of WPU with Different Type of Plasticizer

Sample	Plasticizer	Ionic Conductivity (25 °C)
W10P6	PEG	$2.33 \times 10^{-4}$ S/cm
W10D6	PEGDME	$2.38 \times 10^{-4}$ S/cm

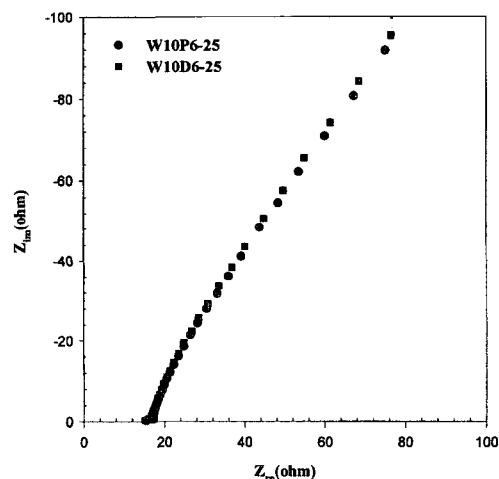
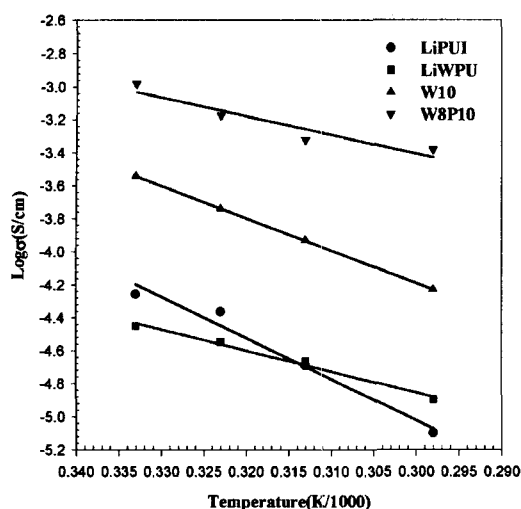


Figure 12. Cole-Cole Plots of WPU with different type of plasticizer.

as a plasticizer. They have analogous structure except end groups of main chains. The end group of PEG is -OH which can make hydrogen bonding with N-H group of polyurethane, but that of PEGDME is a methoxy group that can not make hydrogen bonding. In polyurethane systems, hydrogen bonding ability of plasticizer significantly affects on ionic conductivity due to a decrease in chain mobility. However, WPU did not have an N-H group, then there was little difference between PEG and PEGDME for ionic conductivity of WPU as shown in Figure 12 and Table III.

**Temperature Dependence of Ionic Conductivity:** Figure 13 shows the Arrhenius plots of



**Figure 13.** Ionic conductivities of WPU and PUI at various temperatures.

ionic conductivity for WPU and PUI. It was obvious from Figure 13 that all of four different SPEs obeyed the Arrhenius law, but the slope of PUI was different from that of WPU system. This might result from the difference of higher order structure between WPU and PUI.

## Conclusions

In this study, solid polymer electrolyte based on waterborne polyurethane (WPU) consisting of poly(ethylene glycol)/poly(propylene glycol) (PEG/PPG) copolymer, 4,4'-diphenylmethane diisocyanate (MDI), ethylene diamine, and three ionization agents (1,2-propane sultone, sodium hydride, and lithium hydroxide) was prepared. WPU had a good elimination effect of an ionic cluster that restricted the chain mobility of polyol. Then, it led to the enhancement of ionic conductivity about  $10^{-3.3}$  S/cm at room temperature and the relationship between ionic conductivity and temperature conformed to the Arrhenius type. Also, it became obvious that waterborne polyurethane with the higher polyol content had the higher ionic conductivity but the lower mechanical

stability. And the ionic conductivity had maximum value with lithium salt concentration, which resulted from the balance of the chain mobility of polyol and ion transfer number. Also, it was revealed that the ionic conductivity was improved by the addition of plasticizer, and the hydrogen bonding ability of plasticizer little affected on the ionic conductivity because of the absence of N-H group in waterborne polyurethane.

**Acknowledgement.** This work was supported by the Ministry of Education (Brain Korea 21 Program).

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