# A Novel Polymer Electrolyte Based on Polydioxolane Polyurethane with Na<sup>+</sup> Single-Ionic Conductivity

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**ABSTRACT:** A series of novel polyurethane ionomers with polydioxolane (PDXL) as soft segment was prepared and characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, and dynamic mechanical analysis. The ionomers obtained were Na<sup>+</sup> single-ionic conductors. Their ionic conductivity and water absorption were tested. At medium temperature (> 75°C), the conductivity of ~ 10<sup>-5</sup> s cm<sup>-1</sup> was reached. The temperature dependence of conductivity could not be well expressed by both Arrhenius and VTF equations. When ionization level was fixed, the conductivity increased as the *Mn* of PDXL decreased. We also discussed the effect of ionization level on water absorption. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1711–1719, 1999

**Key words:** single-ionic conductors; polyurethane ionomers; polydioxolane; ionic conductivity; water absorption

### **INTRODUCTION**

Due to their potential applications, such as high energy-density batteries, electrochromic devices, chemical sensors, and so on, polymer electrolytes have received a great attention in recent years. But, most of the polymer electrolytes were based on complexes of polymers with salts in which both cations and anions were found mobile. When the conductors were put in an electric field, anion gradient formed, and this led to polarization losses that were harmful to electrochemical devices. So, there are a few people who are interested in single-ionic conductors in which only cations are mobile and the direct current conductivity is almost the same<sup>1</sup> when time changes. Recent research on single-ionic polymer electrolytes was focused on blends of ionomer and polyether<sup>2</sup> or copolymers of ionomer and PEO-based macromer.<sup>3</sup> Because polyurethane (PU) has good mechanical property and it can be converted into ionomer that may be of high ionic conductivity, PU ionomer is a good candidate for single-ionic conductor that can be used in practical devices.

In this study, we synthesized a new kind of single-cation polymer electrolytes based on polydioxolane (PDXL)-PU ionomers, and we discussed the temperature dependence of conductivity, the effects of soft segments' Mn and ionization level on conductivity, and the effect of ionization level on water absorption.

#### **EXPERIMENTAL**

#### **Materials**

Dioxolane (Shanghai Solvent Factory, Shanghai, China) was treated with  $CaH_2$  for 3 h and then distilled. Diphenylmethane-4,4'-diisocyanate (MDI) was distilled in a nitrogen atmosphere. 1,4-Butane diol (BD) and *N*,*N*'-methyl acetamide (DMA) were dried and distilled. NaH (Aldrich Chemical Co., Milwaukee, WI) is a complex of 60% NaH and 40% paraffin oil.  $\gamma$ -Trimethylene sultone (TMST) was bought from Aldrich.

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# Synthesis of PDXL with Two Hydroxyls as Terminal Groups

The mixture of  $BF_3 \cdot O(C_2H_5)_2$  and BD was stirring for 0.5 h at 0°-5°C. Then dioxolane was added into the mixture gradually, kept reacting at 0-5°C for 2 h, then warmed the reaction to 30°C for 4 h. N-Butylamine was added to terminate the reaction. The mixture obtained was solvated by methanol. After cooling the solution overnight, we got a kind of white solid. Methanol was removed, and the material obtained was dried at 60°C in a vacuum-drying oven for 2 days. Two kinds of PDXLs (Mn = 600, 1200) were prepared in this way.

# Synthesis of PDXL-PU

The molar ratio of MDI, BD, and PDXL was 3:2:1, and the catalyst was dibutyltin dilaurate. PDXL was added into MDI (both were solvated in DMA) gradually while the temperature was 40°C. The mixture was stirring for 4 h at 75°C. The temperature was decreased to 40°C, and BD added (solvated in DMA) into the reacting liquid within 0.5 h. Warming the reaction to 75°C for 2 h, then ended the reaction. The liquid was put into water, and deposition was washed by water. Immerse the deposition into alcohol for 24 h. The material obtained was dried in a vacuum-drying oven for 48 h at 60°C.

# Synthesis of PU Ionomer

PDXL-PU was solvated in DMA. Temperature was kept at  $0-5^{\circ}$ C. NaH was added into the solution, kept stirring for 1 h and then TMST added into the mixture. The reaction was gradually warmed to 50°C for 2 h. Some solvent was removed through vacuum distillation. The mixture was put into toluene, and the deposition was washed with methanol. NaH and TMST were removed by immersion. The ionomer was dried at

60°C for 1 day and then dried in a vacuum-drying oven at 60°C for 2 days.

# **Preparation of Polymer Electrolyte Film**

The ionomer was solvated in DMA, and the concentration was  $\sim 10$  wt %. The solution was cast into a Teflon plate. The film formed in an oven at 60°C and was then dried in a vacuum-drying oven at 70°C for 48 h.

### **Measurements**

Infrared spectra were recorded on a Perkin-Elmer model 963 FT-IR spectrophotometer in the range of 400-4000 cm<sup>-1</sup>. A Perkin-Elmer differential scanning calorimeter-2C was used to do the thermal analysis in a temperature range of -120-250°C, and at a rate of 20°C min<sup>-1</sup>. DMA was carried out on a Rleovibron DDV II-C dynamic viscoelastometer in a temperature range of  $-150^{\circ}$ -200°C, the frequency used was 110 Hz, and the rate was 2°C min<sup>-1</sup>. The frequency of sample collection was <sup>1</sup>/<sub>2</sub>°C. Film samples were sandwiched between silver electrodes. Conductivity measurements were conducted on a 378 Electrochemical Impedance System produced by EG & G Princeton Applied Research in a frequency range of 10 Hz–10 MHz and a temperature range from room temperature to 120°C. Water absorption was tested at 15°C, with a relative humidity of 65%.

# **RESULTS AND DISCUSSION**

# **Composition of PU Ionomers**

When preparing ionomers, we controlled the ionization level of ionomers by controlling the ratio of reactants. The so-called ionization level was, in fact, the molar fraction of —NH groups whose hydrogen atoms were substituted by TMST. The predicted value of ionization level was determined by the de-

Table I	Composition	of PU	Ionomers
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Sample Design	g NaH/g PU	Ionization Level (%)	[EO]/[Na <sup>+</sup> ]	Wt % of ${\rm (CH_2)_3SO_3^-}$
PDXL-PU-1200-8-Na $^+$	0.0438	67.57	8	18.38
PDXL-PU-1200-12-Na <sup>+</sup>	0.0292	45.04	12	13.55
$PDXL-PU-1200-16-Na^+$	0.0219	33.78	16	9.19
$PDXL-PU-1200-20-Na^+$	0.0175	27.03	20	8.74
PDXL-PU-600-12-Na $^+$	0.0203	22.52	12	10.27

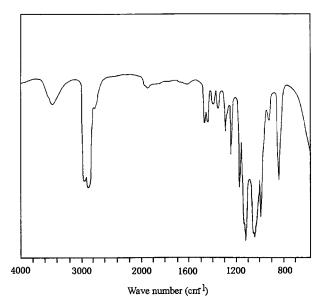


Figure 1 Infrared spectra of PDXL.

signed value of [EO]/[Na<sup>+</sup>]. The composition of PU ionomers prepared were listed in Table I. For PDXL-PU-1200-8-Na<sup>+</sup>, PDXL is the soft segment, PU is polyurethane, 1200 is PDXL's Mn, 8 is the designed value of [EO]/[Na<sup>+</sup>], and Na<sup>+</sup> is the cation in ionomer. So are the other samples.

### Structure of PDXL and PDXL-PU

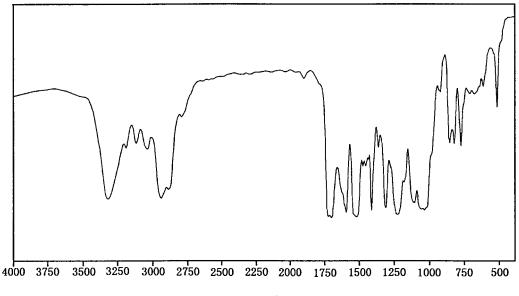
In the infrared spectra of PDXL (Fig. 1), there were strong absorption peaks of ether bond in the

 $1020-1200 \text{ cm}^{-1}$  region. The strong absorption peak of hydroxyl was at 3503 cm<sup>-1</sup>. In the infrared spectra of PDXL-PU (Fig. 2), a strong absorption peak of free carbonyl at 1729 cm<sup>-1</sup> was found. Hydrogen-bonded carbonyl had a strong absorption peak at ~1704 cm<sup>-1</sup>. The strong absorption peaks of ether bond were in the 1020– 1200 cm<sup>-1</sup> region. The peak of hydroxyl at 3505 cm<sup>-1</sup> disappeared.

Figure 3 showed the DSC thermograms of the PDXL-PU series, and Table II showed the DSC data. PDXL (Mn = 1200)-PU had an exothermic peak in the  $-29^{\circ}$ C- $5^{\circ}$ C region, and an endothermic peak in the  $5^{\circ}$ C- $28^{\circ}$ C region. This showed that, in the  $-29^{\circ}$ C- $5^{\circ}$ C region, the soft segments crystallized; but, in the  $5^{\circ}$ C- $28^{\circ}$ C region, crystalline was destroyed. For PDXL (Mn = 600)-PU, no endothermic peak was found. It was because the fraction of hard segment increased with the decrease of the chain length of soft segment. So, the mobility of soft segment was prevented. In addition, the ordered structure of hard segment was found destroyed at a higher temperature.

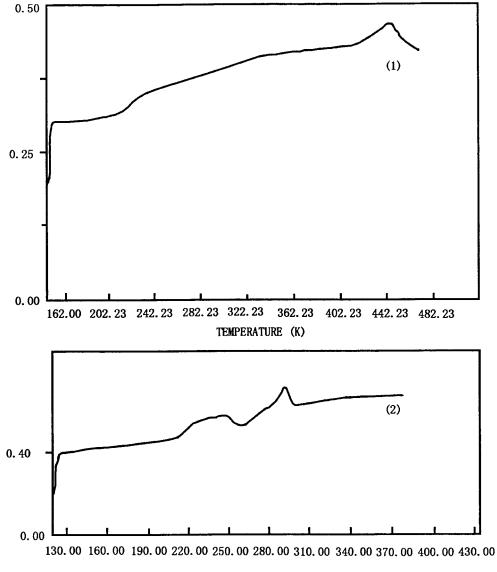
#### **Structure of PU Ionomers**

As shown in the infrared spectrum (Fig. 4), the absorption of -NH in the 3320-3330 cm<sup>-1</sup> region decreased with the increase of ionization level. We also found that as the ionization level increased, the absorption of free carbonyl at 1730



Wavenumber (cm<sup>-1</sup>)

Figure 2 Infrared spectra of PDXL-PU.



TEMPERATURE (K)

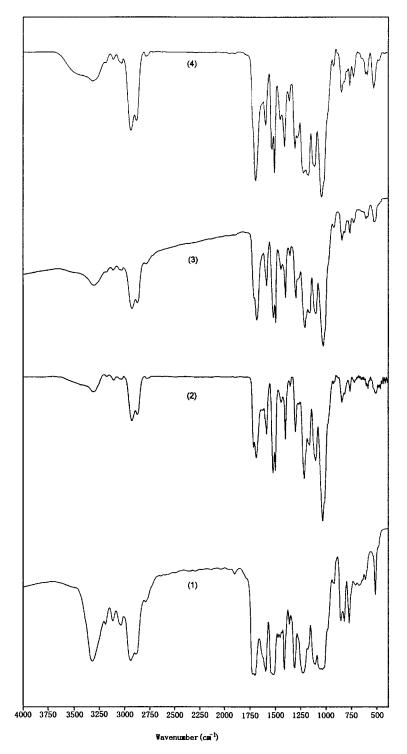
**Figure 3** DSC map of polyether PUs: (1) PDXL(Mn = 600)-PU; (2) PDXL(Mn = 1200)-PU.

 $\rm cm^{-1}$  decreased, and the absorption of hydrogenbonded carbonyl at  $\sim 1701~\rm cm^{-1}$  increased. That means the separation of microphases increased as the ionization level increased.

The DMA spectrum of PDXL (Mn = 1200)-PU in Figure 5 showed a typical character of two phases, because there were microphases of both soft segments and hard segments in the bulk. There was a

Samples	Onset	$T_{g}$ (K) Midpoint	$\Delta T(\mathrm{K})$	$\Delta Cp~({\rm cal~g^{-1}~deg^{-1}})$
PDXL ( $Mn = 1200$ )-PU PDXL ( $Mn = 600$ )-PU	$\begin{array}{c} 213.7\\ 213.7\end{array}$	$\begin{array}{c} 218.8\\ 221.4\end{array}$	$\begin{array}{c} 28.6 \\ 71.1 \end{array}$	0.118 0.092

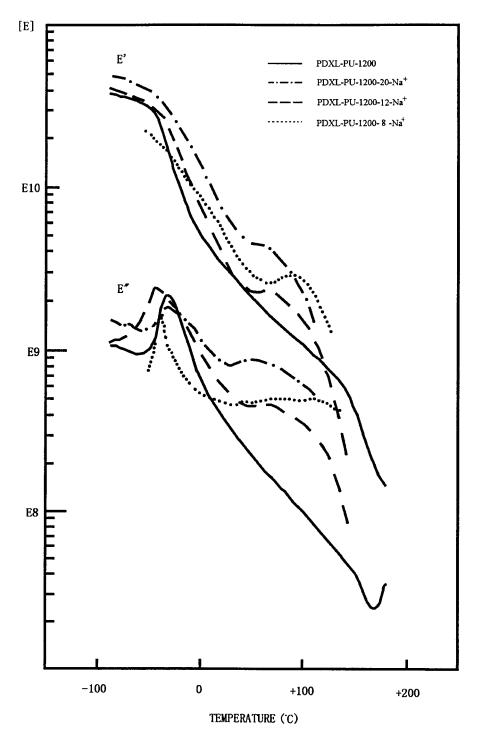
Table II DSC Data of the PDXL-PU Series



**Figure 4** Infrared spectra of PDXL (Mn = 1200)-PU and its ionomers: (1) PDXL (Mn = 1200)-PU; (2) PDXL-PU-1200-16-Na<sup>+</sup>; (3) PDXL-PU-1200-12-Na<sup>+</sup>; and (4) PDXL-PU-1200-8-Na<sup>+</sup>.

peak at  $-43.2^{\circ}$ C in the E'' - T curve, which was attributed to the glass transition of the soft-segment phase, and an abrupt decrease was found in the E' - T curve correspondingly.

Compared with unionized PU, all the samples of PU ionomers had rubbery plateau zones in the E' - T curves (Fig. 5). As the ionization level increased, the position of plateau zone shifted to



**Figure 5** DMA spectra of PDXL (Mn = 1200)-PU and its ionomers.

higher temperature, along with widening of the plateau zone. It showed that the hard segments of ionomer samples aggregated to form microzones that were physical supporting points in the bulk. With the increase of ionization level, the aggregation degree of hard segments increased. It was attributed to shifting and widening of the plateau zone.

As showed in Table III, the glass transition temperatures of ionomers were all lower than the unionized one, which was attributed to the decrease of the glass transition temperature of soft

Samples	PDXL ( $Mn = 1200$ )-PU	PDXL-PU-1200-8-Na <sup>+</sup>	PDXL-PU-1200-12-Na $^+$	PDXL-PU-1200-20-Na <sup>+</sup>
$T_g$ (°C)	-43.2	-51.2	-56.8	-46.2

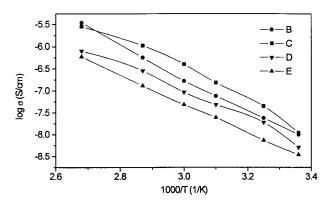
Table III DMA Data of PDXL (Mn = 1200)-PU and Its Ionomers

segment caused by the increase of microphase separation. The sample whose [EO]/[Na<sup>+</sup>] was 20 had a higher  $T_g$  than the ones of higher ionization level. It showed that the separation of microphases in this bulk increased with the ionization level. As showed in Table III, the sample whose [EO]/[Na<sup>+</sup>] was 12 had the lowest  $T_g$ ; so, separation of microphases was the greatest. We also found that  $T_g$  increased again with further increase of the ionization level.

#### Effect of Ionization Level on Conductivity

The temperature dependence of ionic conductivity of PDXL-PU-1200 series with a different ionization level was shown in Figure 6. The ionization level dependence of cationic conductivity of the PDXL-PU-1200 series at 75°C was shown in Figure 7.

As showed in the figures, maximum conductivity was reached when  $[\rm EO]/[\rm Na^+]$  was 12. In the ionomers, with the increase of  $\rm Na^+$  concentration, although the number of carriers increased, ion pairs and/or ion aggregations also formed and the  $T_g$  of soft segment increased. The former was attributed to the increase of conductivity, but the latter was attributed to the decrease of conductivity. The former effect was dominant and in-



**Figure 6** Temperature dependence of ionic conductivity of the PDXL-PU-1200 series with a different ionization level: (B) PDXL-PU-1200-8-Na<sup>+</sup>; (C) PDXL-PU-1200-12-Na<sup>+</sup>; (D) PDXL-PU-1200-16-Na<sup>+</sup>; and (E) PDXL-PU-1200-20-Na<sup>+</sup>.

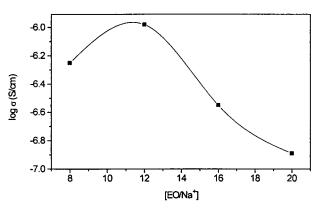
creased the conductivity of sample in a lower ionization level, whereas the latter effect dominated and decreased the conductivity in a higher ionization level. So, in the whole range of ionization level, there was a conductivity maximum.

#### **Temperature Dependence of Conductivity**

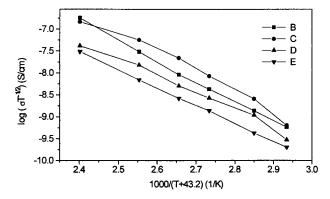
The logarithmic conductivity was plotted against 1/T, and we got Figure 6. But, in Figure 6, there was no straight line, and this showed that the temperature dependence of conductivity did not follow the Arrhenius equation. In the whole temperature range, as the temperature increased, the conductivity increased, but the rate of the increase of conductivity decreased. It had been shown that ion transport occurred in an amorphous region of the polymers<sup>4</sup> and was related to the movement of chains. So, there was no difficulty to understand the strong temperature dependence of conductivity. As the temperature increased, the mobility of chains and the free volume increased, so the ionic mobility increased. As a result, the conductivity increased.

We also plotted  $\log(\sigma T^{-0.5})$  against  $1/(T_g)$  and got Figure 8.

The curves in Figure 8 were not straight lines, and this showed that the temperature dependence of conductivity did not follow the VTF equation either.



**Figure 7** Ionization level dependence of cationic conductivity of the PDXL-PU-1200 series at 75°C.



**Figure 8** Temperature dependence of ionic conductivity of the PDXL-PU-1200 series with a different ionization level: (B) PDXL-PU-1200-8-Na<sup>+</sup>; (C) PDXL-PU-1200-12-Na<sup>+</sup>; (D) PDXL-PU-1200-16-Na<sup>+</sup>; (E) PDXL-PU-1200-20-Na<sup>+</sup>.

# Effect of PDXLs Mn on Conductivity

As showed in Figure 9, when  $[EO]/[Na^+]$  was fixed, the ionomer whose Mn of soft segment (PDXL) was 600 had a higher conductivity than the one whose Mn of PDXL was 1200. This could be explained as follows: when the Mn of PDXL increased, the interaction between chains increased, the crystalline even formed, and the conductivity decreased.

#### Water Absorption

It was shown that the water in polymer electrolytes led to a great increase in conductivity.

From Figure 10, we found that the water absorption of samples increased gradually with the increase of ionization level. At the beginning, the rates of water absorption were all fast, and the rate

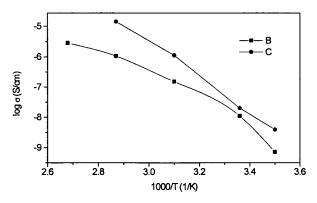
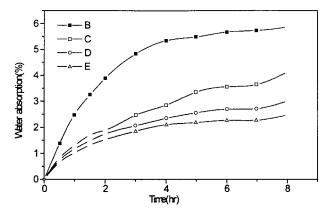


Figure 9 Temperature dependence of ionic conductivity of: (B) PDXL-PU-1200-12-Na $^+$  and (C) PDXL-PU-600-12-Na $^+$ .

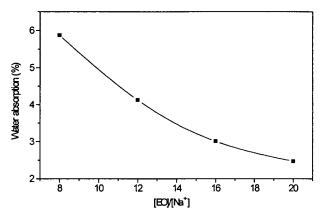


**Figure 10** Exposure time dependence of water absorption of the PDXL-PU-1200 series with a different ionization level: (B) PDXL-PU-1200-8-Na<sup>+</sup>; (C) PDXL-PU-1200-12-Na<sup>+</sup>; (D) PDXL-PU-1200-16-Na<sup>+</sup>; and (E) PDXL-PU-1200-20-Na<sup>+</sup>.

became faster with the higher ionization level. After a times, the rates all obviously decreased. We found that the water absorption gradually came close to a fixed value, and we called the fixed value saturated water absorption. Saturated water absorption also increased with ionization level (Fig. 11). This was attributed to the gradual increase of the polarity of the polymer with the increase of ionization level.

# **CONCLUSIONS**

PU ionomers prepared in this work were Na<sup>+</sup> single-ionic conductors with high conductivity. The conductivity of  $10^{-5}$  s cm<sup>-1</sup> was reached at a medium temperature (> 75°C). For all samples,



**Figure 11** Ionization dependence level of saturated water absorption of ionomers of the PDXL-PU-1200 series.

the temperature dependence of conductivity did not follow Arrhenius or VTF equations. As for the PDXL-PU-1200 system, when  $[EO]/[Na^+]$  was 12, there was a conductivity maximum. When ionization level was fixed, the decrease of the Mn of the soft segment led to an increase of conductivity. With a higher ionization level, the rate of water absorption was faster, the time used to reach the saturated value was shorter, and the saturated value of water absorption was greater.

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