Effect of Hard Segment and Concentration of NaClO$_4$ on Poly(ethylene oxide)–Urethane/NaClO$_4$ Complex

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ABSTRACT: Solid poly(ethylene oxide)–urethane electrolytes were prepared from blends of polyurethane and NaClO$_4$. The samples were characterized by FTIR, DSC, atomic force microscopy, and complex impedance analysis. The effect of the concentration of NaClO$_4$ on the poly(ethylene oxide)–urethane/NaClO$_4$ complex were studied. The results showed that the concentration of NaClO$_4$ had an important effect on the ion–polymer interaction, ion–ion interaction, glass-transition temperature, morphologic structure, and ionic conductivity of the complex. We also prepared a model compound of hard segments and found that the conductivity of the complex decreased when the model compound was blended into the complex. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2502–2510, 2001

Key words: polyurethane; ionic conductivity; solid polymer electrolyte; poly(ethylene oxide)

INTRODUCTION

As a good candidate for a solid polymer electrolyte (SPE), polyurethane (PU) and its ionomer were recently studied by several groups.[1–5] When used to prepare SPEs, the hard segment of PU acts as a physical net point that contributes good mechanical properties to the material while the soft segment is used as an oligoether or oligoester in which particles with ionic charge can transfer easily. However, a SPE based on PU is normally a complex system; many factors such as the hard segment, soft segment, concentration of salt, and so forth, have great effects on the properties of this kind of materials.[2,3,6] In order to direct the design of new good SPEs, it is important to study the factors and their effects on the ionic conductive properties of the materials.

Poly(ethylene oxide)–PU (PEO-PU) was chosen as the host polymer in this study. By blending PEO-PU with NaClO$_4$, we got a series of SPEs based on PU. We utilized FTIR, DSC, atomic force microscopy (AFM), and complex impedance analysis to study the samples. The effects of the concentration of NaClO$_4$ on the ion–polymer interaction, ion–ion interaction, glass-transition temperature, morphologic structure, and ionic conductivity of the PEO-PU/NaClO$_4$ complex were discussed in detail. We also prepared a model compound of hard segments and studied its effect on the complex system.

EXPERIMENTAL

Materials

4,4′-diphenylmethane diisocyanate (MDI) was distilled in a nitrogen atmosphere. 1,4-Butanediol (BD) and *N*,*N*′-dimethylacetamide (DMAc) were dried with CaH$_2$ and then distilled. The NaClO$_4$ was bought from Shanghai Number 4 Reagent
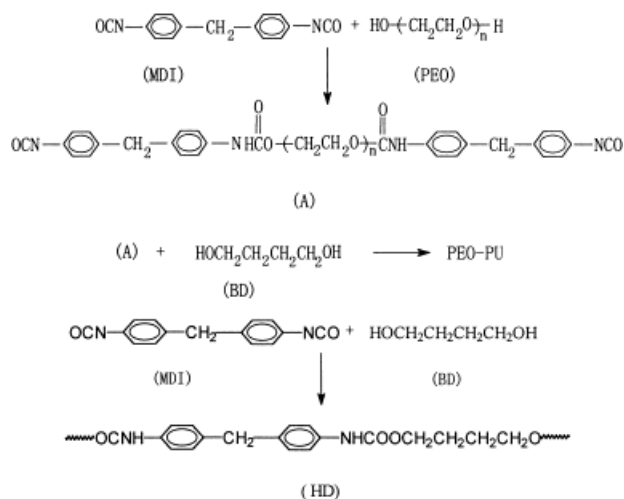
Figure 1   The route of the experiment.

Factory and was dried in a vacuum-drying oven for 72 h at 60°C. The PEO ($M_n = 1000$) was also treated in a vacuum-drying oven for 72 h at 60°C.

Synthesis of PEO-PU

The molar ratio of MDI:BD:PEO was 3:2:1, and dibutyltin dilaurate was used as the catalyst. The route of synthesis is shown in Figure 1. The solution of PEO in DMAc was gradually added into the MDI that was also solvated in DMAc while the temperature was 40°C. After stirring the mixture for 4 h at 75°C, we decreased the temperature to 40°C and added the solution of BD in DMAc into the reacting system within 0.5 h. We warmed the reaction to 75°C for 2 h, and then ended the reaction. The mixture was placed in the water, and the deposition was washed with water several times. After being immersed in alcohol for 24 h, the material obtained was dried in a vacuum-drying oven for 48 h at 60°C.

Synthesis of Model Compound of Hard Segment (HD)

The molar ratio of MDI and BD was 1:1, and dibutyltin dilaurate was used as the catalyst. The route of synthesis is shown in Figure 1. The solution of BD in DMAc was gradually added into the MDI that was also solvated in DMAc while the temperature was 40°C. After stirring the mixture for 4 h at 75°C, the reaction was ended. We put the mixture into the water, and the deposition was washed with water several times. After immersion in alcohol for 24 h, the material obtained

was dried in a vacuum-drying oven for 48 h at 60°C.

Preparation of Polymer Electrolyte Film

The PEO-PU, HD, and NaClO$_4$ were solvated in DMAc; then the solution was cast into a Teflon plate. A film formed in an oven at 60°C, and it was then dried in a vacuum-drying oven for 48 h at 60°C. The composition of the SPE samples are listed in Table I. In the samples with HD, the molar ratio of the PEO unit in PEO-PU and the BD unit in HD was always 5:1.

Measurements

The IR spectra were recorded on a Perkin–Elmer model 963 FTIR spectrophotometer in the range of 400–4000 cm^{-1}. The samples were transparent films. The complex impedance spectra were recorded on a Hewlett–Packard 4192A LF impedance analyzer in a frequency range of 10 Hz–10 MHz and a temperature range from room temperature to 120°C. The testing system was a cell of Cu, a SPE, and Cu. The AFM analysis was performed with a Digital Instruments Nanoscope IIIa SPM analyzer with a scanning rate of 2.001 Hz and an image height scale of 50 nm. The section of samples was detected. DSC analysis was carried out on a Perkin–Elmer Pyris-1 DSC analyzer with a temperature range of −100 to 100°C. Nitrogen was used at 20 mL min^{-1}.

RESULTS AND DISCUSSION

Analysis of FTIR Spectra of Samples

Figure 2 shows the IR spectra of the PEO-PU/NaClO$_4$ and PEO-PU/NaClO$_4$/HD complexes, and the results of the spectra are listed in Table II. From Figure 2 and Table II we found that there were strong absorption peaks of ether bonds in the 1000–1200 cm^{-1} region. The strong absorption peaks of —NH were at 3330 and 3530 cm^{-1}. We also found the absorption peaks of carbonyl at 1700–1750 cm^{-1} and those of ClO$_4^-$ at about 628 cm^{-1}. The results showed that the complexes were in fact what we wanted.

Figure 3 shows the carbonyl absorption peaks of the PEO-PU/NaClO$_4$ samples with different salt concentrations. With the increase of the salt concentration ([EO]/[Na$^+$] decreased) the absorption peak of carbonyl shifted to the region of lower wave numbers, and the shift became more obvi-

Table I   Composition of Solid Polymer Electrolyte Samples

Samples	PEO-PU/NaClO$_4$ (w/w)	[EO]/[Na$^+$]	
		Anticipated	Calculated
PEO-PU-4	2.772	4	3.999
PEO-PU-8	5.492	8	7.924
PEO-PU-12	8.093	12	11.676
PEO-PU-16	10.665	16	15.386
PEO-PU-20	14.064	20	20.290
PEO-PU-40	27.696	40	39.957
PEO-PU-60	41.620	60	60.045
PEO-PU-80	55.571	80	80.173
PEO-PU-100	65.694	100	94.778
PEO-PU-HD-4	2.965	4	3.997
PEO-PU-HD-8	5.881	8	7.932
PEO-PU-HD-12	8.833	12	11.899
PEO-PU-HD-16	11.781	16	15.878
PEO-PU-HD-20	14.804	20	19.953
PEO-PU-HD-40	29.182	40	39.330
PEO-PU-HD-60	43.086	60	58.032
PEO-PU-HD-80	60.114	80	81.021
PEO-PU-HD-100	74.975	100	101.061

[EO]/[Na$^+$], the molar ratio of the ether group and the Na$^+$ of the complex.

ous. Especially when the salt concentration was high, the shift was large. This meant that with the increase of the salt concentration the bonding degree of Na$^+$ with carbonyl increased, but it was not obvious when the salt concentration was low and only when the salt concentration was high did the bonding degree increase to a large extent.

Figure 4 shows the ether group absorption peaks of the PEO-PU/NaClO$_4$ samples with different salt concentrations. With the increase of the salt concentration the absorption peak of the ether group shifted to the region of lower wave numbers, but the shift became less obvious. Especially when the salt concentration was high, the shift almost disappeared. This meant that with the increase of the salt concentration the bonding
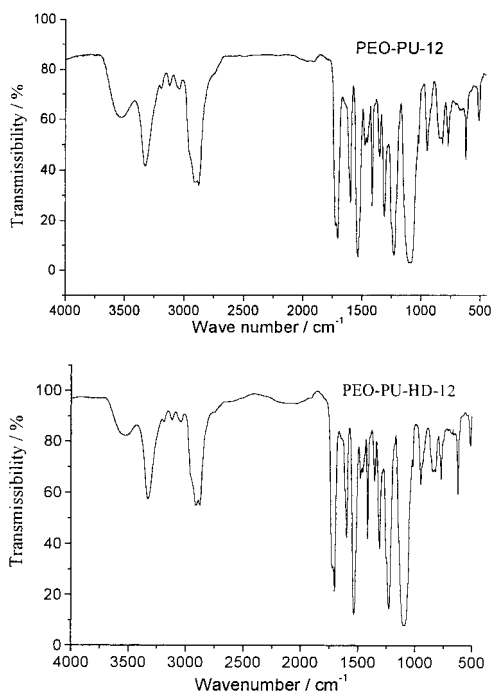

Figure 2 The FTIR spectrum of PEO-PU-12 and PEO-PU-HD-12.

Table II   FTIR Analysis of PEO-PU-12 Samples

Wave Number (cm^{-1})	Groups	Relative Intensity
3530	νNH (spectral free)	S
3330	νNH (bonded)	S
2910	νCH$_2$	vS
1730	νC=O (spectral free)	vS
1700	νC=O (bonded)	vS
1600	νC=C (benzene)	S
1530	δ(NH) + ν(CN)	vS
1320	ν(CN) + δ(NH)	S
1100	ν(CH$_2$—O—CH$_2$)	S
628	νClO$_4^-$	S

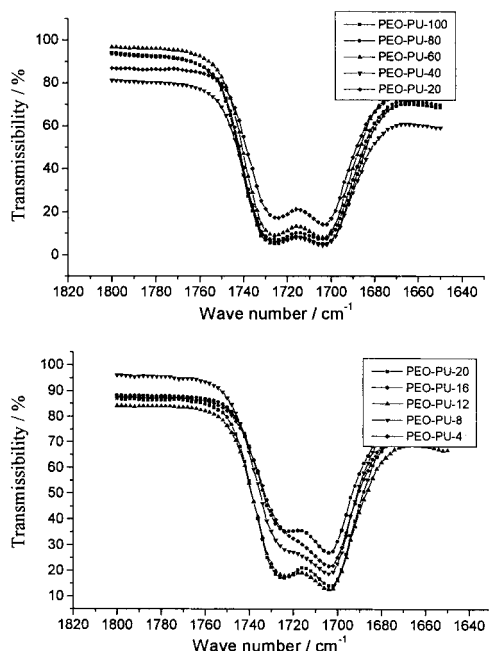**Figure 3** The FTIR spectrum of the PEO-PU series (carbonyl).

Figure 5 The FTIR spectrum of the PEO-PU-100 (ClO_4^- group).

degree of Na$^+$ with the ether group increased; however, when the salt concentration was high, the bonding degree of Na$^+$ with the ether group reached a saturated state.
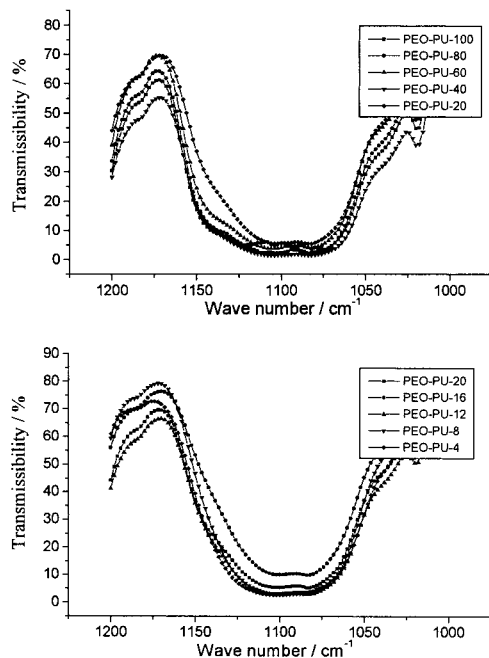
From Figures 3 and Figure 4 we could draw the following conclusions: when the salt concentration in the PEO-PU/NaClO$_4$ samples was increased, Na$^+$ preferred bonding with the ether group at first and, when the salt concentration reached a certain level, the bonding of Na$^+$ with the ether group reached a saturated state; then the Na$^+$ bonded with the carbonyl.

Figure 5 shows the absorption peaks of ClO_4^-. There were two kinds of peaks: the one at 624 cm^{-1} belonged to spectral free ClO_4^-, while the other one at 638 cm^{-1} belonged to the bonded group of ClO_4^-.
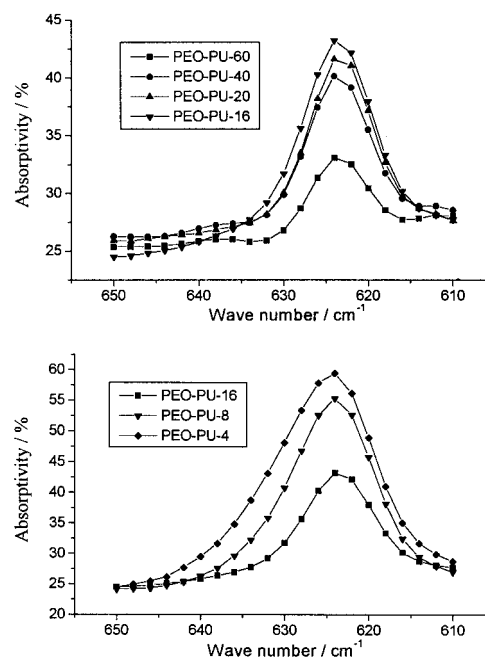

Figure 4 The FTIR spectrum of the PEO-PU series (ether group).

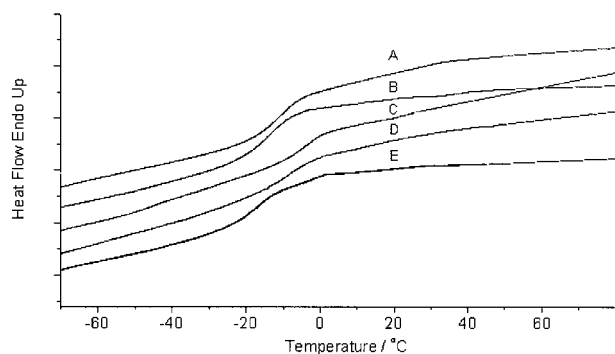**Figure 6** The FTIR spectrum of the PEO-PU series (ClO_4^- group).

Figure 7   DSC curves of the PEG-PU/NaClO$_4$ series.

The effects of the salt concentration on the absorption peaks of ClO$_4^-$ are shown in Figure 6. With the increase of the salt concentration, compared with the peak of spectral free ClO$_4^-$, that of bonded ClO$_4^-$ increased gradually, which resulted in the shift of ClO$_4^-$ peaks to a higher wave number region; and the shift became large when the salt concentration was high. This meant that the increase of the salt concentration caused more ions to bond, especially when the salt concentration reached a certain level.

We also studied the IR spectra of the PEO-PU/NaClO$_4$/HD complex, and the results were similar to those of the PEO-PU/NaClO$_4$ complex.

DSC Analysis of Samples

It is well known that ion transference in SPEs greatly depends on the mobility of the polymer chain,[7-11] which can be characterized by the glass-transition temperature (T_g). In general, the polymer chain mobility was higher for the materials of lower T_g.

The DSC curves for the poly(ethylene glycol) (PEG)-PU/NaClO$_4$ series are shown in Figure 7, and DSC data are listed in Table III. It was shown that the T_g of the samples was increased with the

Table III   DSC Data of PEG-PU/NaClO$_4$ Series

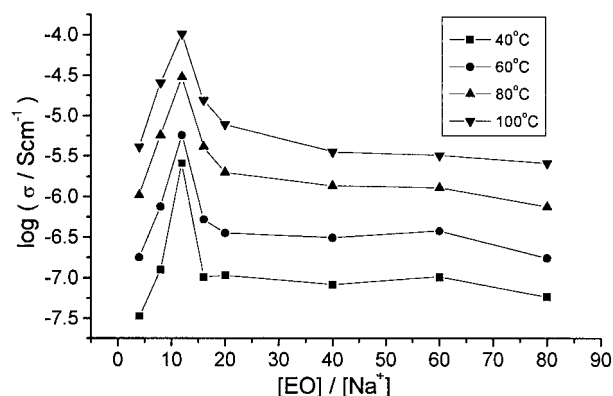| [EO]/[Na$^+$]	Onset (°C)	Midpoint (°C)	ΔC_p (kJ/mol)
8	254.362	260.849	0.542
12	254.188	260.348	0.474
16	264.556	270.318	0.421
20	258.35	265.754	0.436
40	252.771	257.345	0.26

Figure 8   The effect of the salt concentration on the ionic conductivity of the PEO-PU series: [EO]/[Na$^+$] = 8 (curve A), 12 (curve B), 16 (curve C), 20 (curve D), and 40 (curve E).

increase of the salt concentration, while the T_g of the samples was decreased with the increase of the salt concentration when the salt concentration reached a certain level.

For the samples studied in this article, the DSC curves showed no endothermic peaks in the temperature range of 40–80°C, which was attributed to the ordered structure of the soft segment. Thus, the conglomeration of the hard segment was the main conglomeration of the PU chain. The results of the IR analysis showed that the
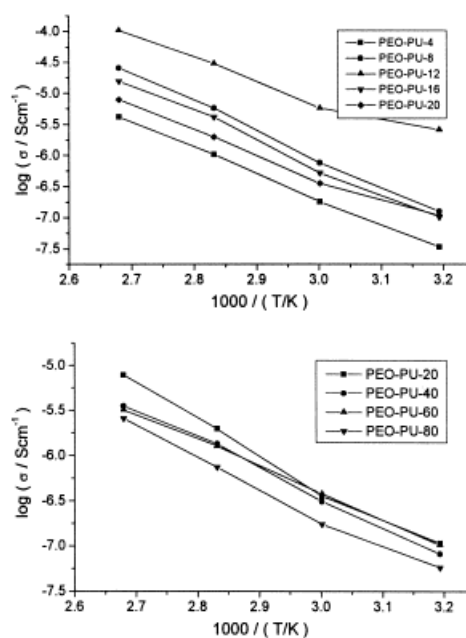

Figure 9   The effect of temperature on the ionic conductivity of the PEO-PU series.

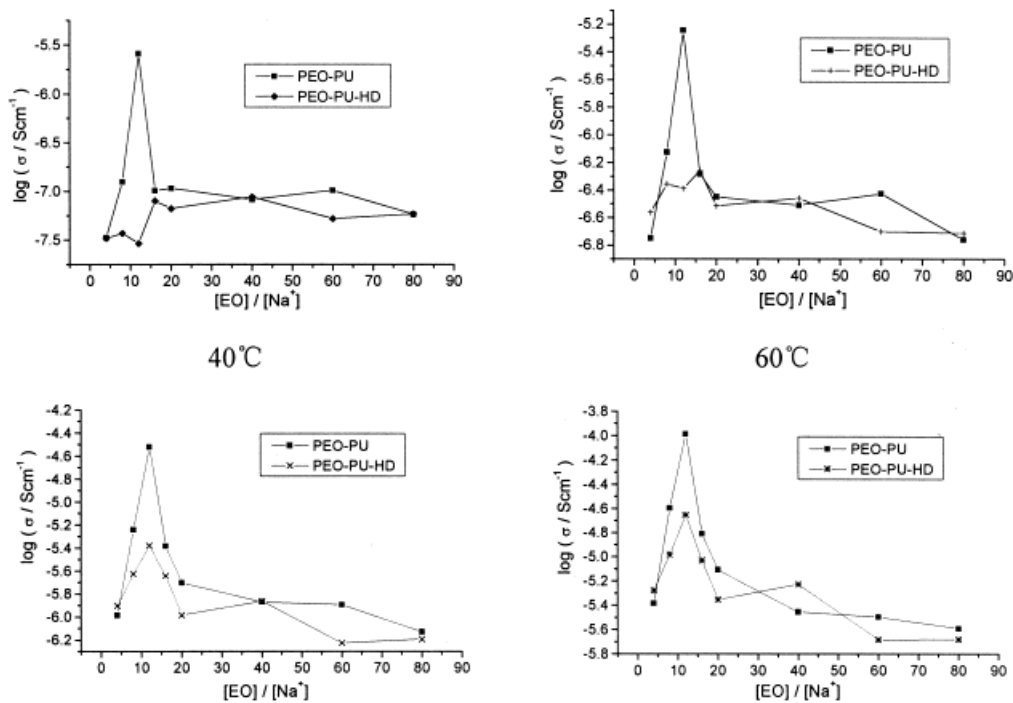40°C   60°C

Figure 10 A comparison of the ionic conductivity and salt concentration curves for the PEO-PU-HD and PEO-PU series.

hard segment and soft segment of PU could have both interacted with the sodium cations and salt could have been dissolved in the domains of the hard and soft segments.

When the salt concentration was low in the samples, with an increase of the salt concentration the ordered structure of the hard segment was destroyed because of the bonds of the cations with the carbonyl groups located in the hard segment. Then some chains of the hard segment structure entered into the domain of the soft segment, which worked against the mobility of the chains in the soft segment and led to an increase of the T_g. When the salt concentration was higher than a certain level, the results of the IR analysis showed that an interaction between the cations and carbonyl groups located in the hard segment obviously increased. Then the chain of the hard segment structure formed an ordered structure in a new style. (An interaction between the carbonyl and cations led to a physical net point.) In addition, the number of chains of the hard segment structure that entered the domain of the soft segment decreased, which was in favor of the mobility of the chains in the soft segment and led to a decrease of the T_g.

Ionic Conducting Property of PEO-PU/NaClO$_4$ Complex

As shown in Figure 8, the salt concentration had important effects on the ionic conducting property of the PEO-PU/NaClO$_4$ complex. At a certain temperature the ionic conductivity of the complex increased with the increase of the salt concentration, and it reached a maximum when the [EO]/[Na$^+$] was about 12. With the further increase of
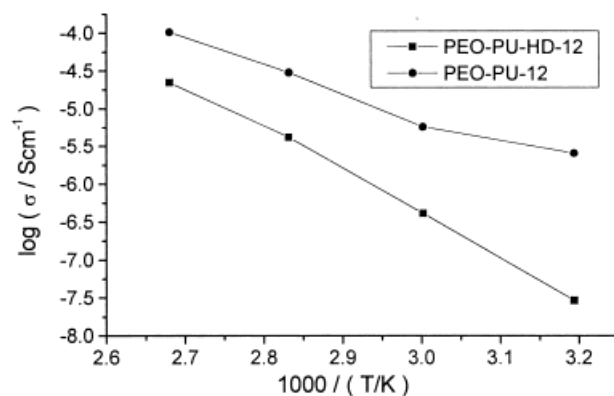

Figure 11 A comparison of the ionic conductivity and temperature curves for the PEO-PU-HD-12 and PEO-PU-12 series.
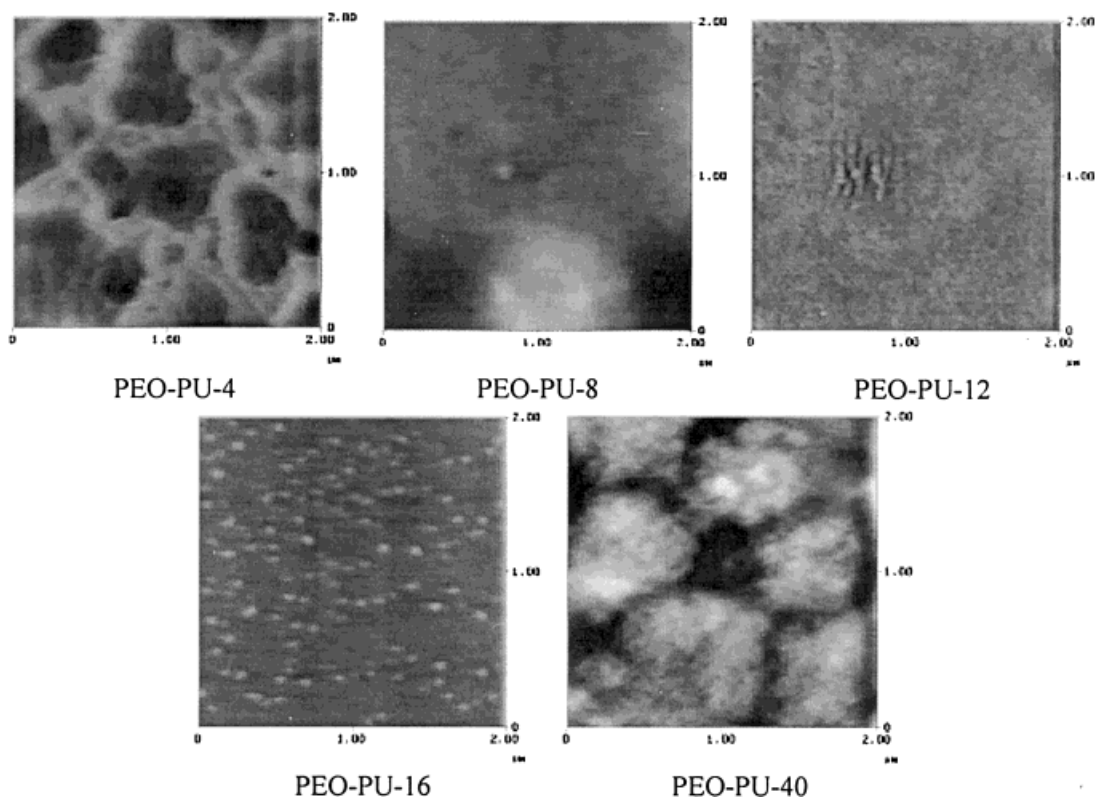
Figure 12   AFM pictures of the PEO-PU/NaClO$_4$ system.

the salt concentration the ionic conductivity of the complex decreased. In fact, in this complex the effect of the salt concentration on the ionic conductivity of the complex has two important aspects. The number of ionic particles increased with the increase of the salt concentration, which was good for the increase of the ionic conductivity. On the other hand, as shown before, when the salt concentration increased, the interaction between ion–ion and ion–polymer became great, which went against the increase of the ionic conductivity. When the salt concentration was low, the former aspect was preponderant; when the salt concentration reached a certain level, the later dominated. Thus, there was a certain [EO]/[Na$^+$] at which the complex had the highest ionic conductivity.

Figure 9 shows the effect of temperature on th eionic conductivity of the complex. We found that the ionic conductivity also increased with the increase of the temperature, but the curve of log σ ~1/T did not follow the Arrhenius equation.

Effect of HD on Ionic Conductivity of Complex

We compared the relationship between the salt concentration and ionic conductivity of the PEO-

PU-HD complex with that of the PEO-PU complex (Fig. 10). Figure 11 shows the relationship between the temperature and ionic conductivity of PEO-PU-HD-12 and PEO-PU-12. We found that the ionic conductivity of the complex with HD was lower than that without HD. This meant that the hard segment in the SPE based on PU acted as a negative factor to the ionic conducting property.

AFM Analysis

Figure 12 illustrates the AFM pictures of the PEO-PU/NaClO$_4$ system. It was amazing to find that there was a phase transition point with an [EO]/[Na$^+$] of 12. In the picture of the sample in which the [EO]/[Na$^+$] was 12, there was little evident conglomeration. However, in the pictures of the samples in which the [EO]/[Na$^+$] was 4, 8, 16, and 40, conglomeration could be found. By relating the morphologic structure to the ionic conductive property, we could achieve more useful results. The sample with an [EO]/[Na$^+$] of 12 had an ionic conductivity 100 times those of the other samples at low temperature (Fig. 10, 40°C), and its AFM picture shows no evident conglomeration. So this kind of morphologic structure
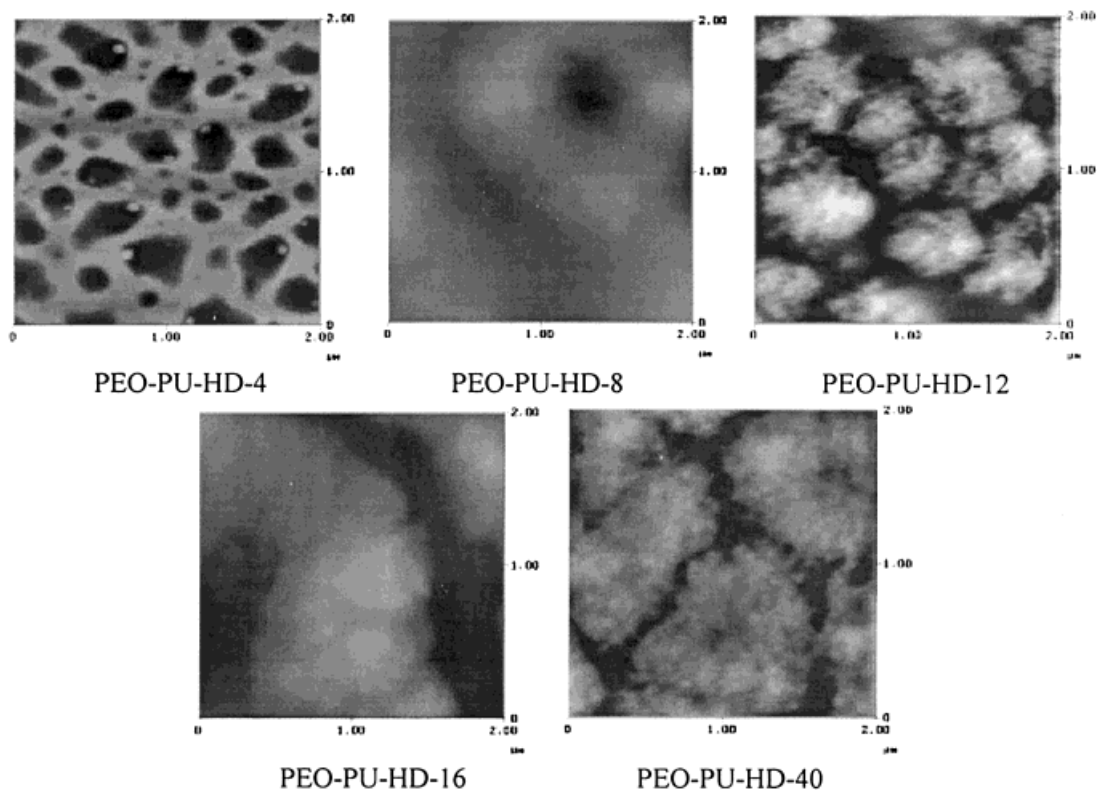
Figure 13 AFM pictures of the PEO-PU-HD/NaClO$_4$ system.

should be more propitious to ion transport. The samples with an [EO]/[Na$^+$] of 4, 8, 16, and 40 had evident conglomerations, and their ionic conductive properties were poorer. This suggested that conglomeration might work against ionic conductive properties.

Figure 12 shows that the when salt concentration was low, with the increase of the salt concentration the conglomeration degree of the samples decreased; when the salt concentration reached a certain level, the conglomeration degree of the samples increased with the increase of the salt concentration. It was also found that conglomerations for the samples of high salt concentration were obviously different from those for the samples of low salt concentration. By relating this phenomenon to the DSC results, we found that the explanations of the DSC results were reasonable.

The AFM pictures of the PEO-PU-HD/NaClO$_4$ system are illustrated in Figure 13. There were evident conglomerations in all the samples with an [EO]/[Na$^+$] of 4, 8, 12, 16, and 40; and the conglomeration of the sample with an [EO]/[Na$^+$] of 4 was different than those of the samples with

an [EO]/[Na$^+$] of 12, 16, and 40. The conglomeration of the sample with an [EO]/[Na$^+$] of 12 was greater than those of the other samples. It was also found that this sample had the poorest ionic conductive property at low temperature (Fig. 10, 40°C). Thus, the conclusion that conglomeration worked against ionic conductive properties was reasonable.

In comparing the AFM pictures of PEO-PU/ NaClO$_4$ with those of PEO-PU-HD/NaClO$_4$, we also found that the model compound of the hard segment had a great effect on the morphologic structure of the samples; consequently, it had a great effect on the ionic conductive property.

CONCLUSIONS

In this study it was found that, with an increase of the salt concentration, the sodium cation would prefer to coordinate with the ether group of PEO-PU/NaClO$_4$ systems. When the salt concentration reached a certain level, the coordination between the sodium cation and ether group reached saturation; the sodium cation then co-

ordinated with mostly carbonyl. The salt concentration and the model compound of the hard segment had great effects on the morphologic structure of the samples. Our study also showed that the curve of the log $\sigma \sim 1/T$ of our complex did not follow the Arrhenius equation, and the hard segment was a negative factor to the ionic conducting property. By relating the morphologic structure with the ionic conductive properties, we drew more useful conclusions that there was a direct relationship between the morphologic structure and ionic conductive property and conglomeration worked against the ionic conductive property. Thus, in a further study it would be reasonable to increase the ionic conductive property of a sample by adjusting its morphologic structure.

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