

NOTES

Ionic Conductivity of Ethylene Oxide and Propylene Oxide Copolymer Complexes with Sodium Thiocyanate

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Polymer complexes formed by polyether, such as poly(ethylene oxide) and poly(propylene oxide), with alkali metal salts have been extensively studied recently, because of their potential application for high energy density batteries as solid electrolytes.^{1,2} It is considered that the interaction between the salt cations and the oxygen atoms in the polyether backbones contributes to the generation of ionic carriers. Many recent reports show that the dominant process of ionic transportation is within the amorphous region of the polymer complex, rather than in the crystalline region as proposed in the initial stage of the study.³⁻⁵ Large enhancement of polymer complex ionic conductivity in the amorphous phase over that in the crystalline material was indicated by Shriver *et al.*⁶ As the most used polyether, poly(ethylene oxide) is highly crystalline and its complexes of Na salts generally exhibit even higher crystallinity (> 70%) which is not beneficial to the transport of ions from the above point of view. For poly(propylene oxide), although it is an amorphous polymer, the side methyl groups hinder the ion dissociation and reduce the number of ionic carriers.⁷

To obtain ionic conductor with high ambient temperature conductivity, high molecular weight copolymers of ethylene oxide and propylene oxide were prepared using the catalyst system: $\text{Nd}(\text{P}_{204})_3$ *¹-Al(iso-Bu)₃-H₂O.⁸ In this study, the copolymers were used to synthesize copolyether-NaSCN complexes. It was revealed that the incorporation of an appropriate amount of propylene oxide unit into the polymer chains increased the ionic conductivity of the copolyether complex by interrupting long ethylene oxide segments.

EXPERIMENTAL

Processes of preparing ethylene oxide and propylene oxide random copolymer poly(EO-co-PO), and diblock copolymer poly(EO-*b*-PO) using $\text{Nb}(\text{P}_{204})_3$ -Al(iso-Bu)₃-H₂O catalyst system were described elsewhere.⁸ The copolymers obtained were white solids with high molecular weight ($[\eta] > 3$, CH₃Cl, 30°C). Contents of ethylene oxide and propylene oxide (molar ratio) were determined from ¹H NMR spectrum of copolymer by following equation⁹:

*¹ $\text{Nd}(\text{P}_{204})_3$: Neodymium tris(2-ethylhexylphosphonate).

$$M_{EO}/M_{po} = 3(B-A)/4A$$

in which A and B are the areas of peaks at $\delta=3-4$ ppm, and $\delta=1.1$ ppm, respectively. Differential scanning calorimeter (DSC) was measured with a CDR-1 calorimeter at a heating rate of $20^{\circ}\text{C min}^{-1}$.

NaSCN was oven dried at 573K for 4h before use and then dissolved in an acetonitrile solution of EO-PO copolymer. Complex film was formed by casting the solution onto a Teflon plate and evaporating the solvent in dry air then *in vacuo*. The concentration of NaSCN in the copolymer was represented by the molar ratio of Na^+ to oxygen (Na^+/O), which was kept at a constant value of 0.06 in this study.

The complex film so prepared, sandwiched

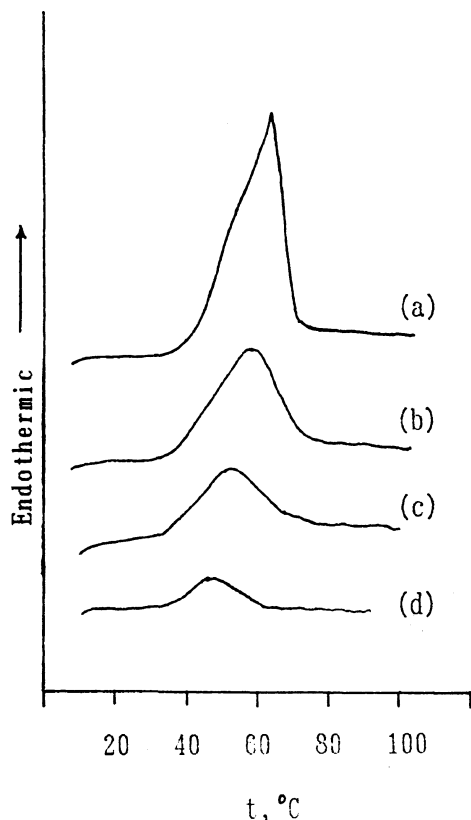


Figure 1. DSC patterns of poly(EO-co-PO) with PO (molar percent) of 0% (a), 5% (b), 27% (c), and 49% (d).

between copper electrodes of the same diameter as the sample, was packed in a sealed cell filled with dry nitrogen. Conductivity was measured using a GQ-70 High Frequency Q-meter at 60 kHz.

RESULTS AND DISCUSSION

In the ^{13}C NMR spectrum of poly(EO-co-PO) so prepared,⁸ the signal at 68.46 ppm was attributed to the methylene carbon in ethylene oxide unit linked to the propylene oxide unit ($-\text{C}-\text{c}-\text{O}-\underline{\text{C}}-\text{C}-\text{O}-$) according to Whipple.¹⁰ This indicates that the ethylene oxide segments were interrupted by propylene oxide units. Figure 1 shows DSC patterns of poly(EO-co-PO) with different propylene oxide content. For each copolymer, only one endothermic peak corresponding to the poly(ethylene oxide) crystal melting appeared in the temperature range of $40-70^{\circ}\text{C}$. Since the analysis was carried out under the same

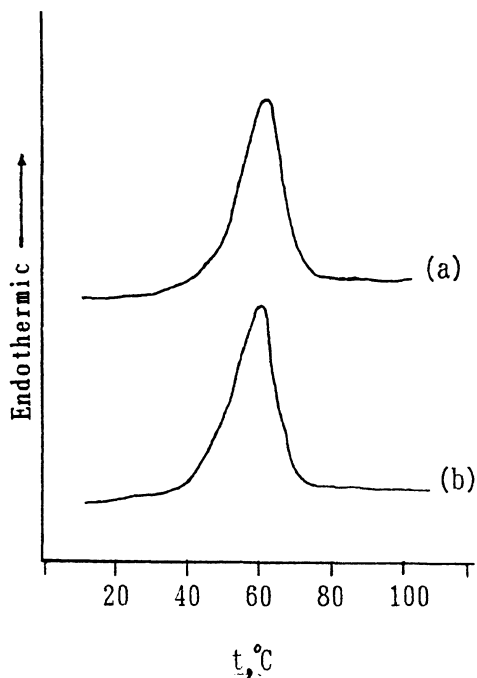


Figure 2. DSC patterns of poly(EO-b-PO) with PO content (molar percent) of 13% (a), and 27% (b).

conditions including the same amount of sample, relative crystallinity of the copolymer could be estimated from the area of the melting peak. It is clearly seen from Figure 1 that the crystallinity of poly(EO-*co*-PO) as well as the melting point decreases with increasing propylene oxide content. It was determined that the reactivity ratios of ethylene oxide and propylene oxide were 1.60 and 0.45, respectively, in this rare earth catalyst system.⁸ Thus the formation of ethylene oxide segments is much easier than that of propylene oxide, and the crystal in poly(EO-*co*-PO) should be provided by long ethylene oxide segments. Contrary to poly(EO-*co*-PO), poly(EO-*b*-PO) exhibits almost the same crystallinity independent of its propylene oxide content ranging from 13% to 27% (molar percent), as shown in Figure 2.

Table I illustrates the propylene oxide content dependent conductivity (σ) of poly(EO-*co*-PO)-NaSCN complex at different temperature. The conductivity was enhanced dramatically with the introduction of propylene oxide units into the polymer, and reached the maximum ($5 \times 10^{-5} \text{ Scm}^{-1}$, 30°C) at a propylene oxide content of about 27%, and then decreased gradually. It is well known that con-

ductivity is represented by $\sigma = \sum ne\mu$, where n is the number of carriers, e is the charge of a carrier, and μ is carrier mobility which depend on the segment mobility of polyether in the case of polymer complex.¹¹ With increasing propylene oxide content in poly(EO-*co*-PO), segmental mobility increased with the copolymer crystallinity and consequently the mobility of the carrier is thought to increase. The side methyl group in propylene oxide may hinder the generation of ionic carrier and reduce the number of carriers. Thus, increasing conductivity in the low PO content region may be attributed to increasing μ , while reduction in conductivity in high PO content region is due to decrease in n . The appearance of the maximum value resulted from the addition of both effects.

Conductivity comparison between poly(EO-*co*-PO) and poly(EO-*b*-PO) complexes can also be seen from Table I. The block copolymer complexes have lower conductivity than those

Table I. Effect of PO content on conductivity (σ) of poly(EO-*co*-PO)-NaSCN complex

In content (mol%)	-log σ (Scm ⁻¹) at different temp/°C					
	30	40	50	60	70	80
0	5.9	5.7	5.2	4.5	3.7	3.4
10	5.2	4.8	4.4	3.7	3.5	3.3
13	4.9	4.5	4.0	3.5	3.4	3.2
		(5.8) ^a	(5.2)	(4.5)	(4.3)	(4.1)
17	4.4	3.8	3.6	3.3	3.2	3.0
27	4.2	3.7	3.4	3.2	3.0	2.8
		(4.8)	(4.5)	(4.2)	(4.0)	(3.8)
33	4.4	3.9	3.6	3.4	3.3	3.2
40	4.4	4.0	3.8	3.6	3.5	3.4
49	4.5	4.2	4.0	3.8	3.7	3.6
58	4.8	4.6	4.4	4.2	4.1	4.0

^a Parenthetical values are for the poly(EO-*b*-PO)-NaSCN complex.

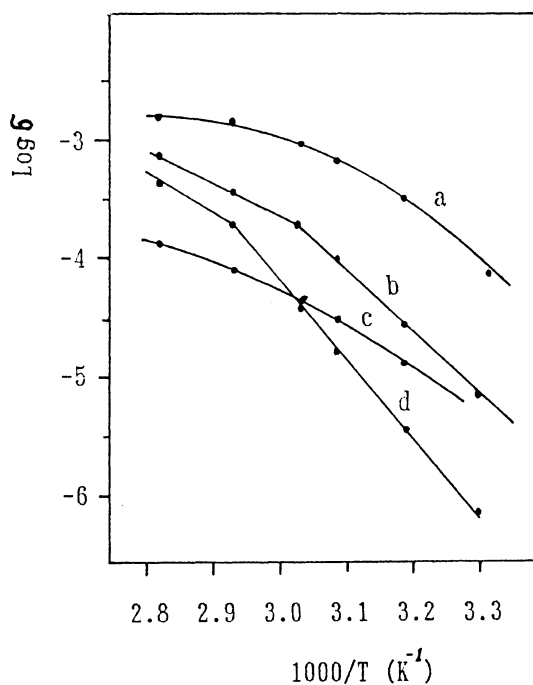


Figure 3. $\log \sigma$ vs. $1/T$ relationship of poly(EO-*b*-PO)-NaSCN complex with PO content (molar percent) of 27% (a), 10% (b), 49% (c), and 0% (d).

of random copolymer complexes. It is assumed that the poor segmental mobility of poly-(EO-*b*-PO) leading to lower μ causes lower conductivity.

Studies indicate that crystalline and non-crystalline polymer complexes have different $\log \sigma$ vs. $1/T$ behavior.¹ Poly(EO-*co*-PO)-NaSCN complexes with propylene oxide content $\geq 27\%$ displayed a curved $\log \sigma$ vs. $1/T$ relationship typical of a non-crystalline complex, as shown in Figure 3. In plots of poly-(EO-*co*-PO) complexes with low PO content, two linear segments were observed, and the break (60°C), being close to the melting point of the copolymer, may be associated with the melting of residual pure or lightly doped poly(EO-*co*-PO).

From the above results, it can be concluded that the introduction of an appropriate amount of propylene oxide units into poly-(ethylene oxide) through random copolymerization promotes the mobility of ionic carrier without decreasing their number the ionic conductivity of poly(EO-*co*-PO)-NaSCN

($\text{Na}^+/\text{O}=0.06$) complex by as much as $5 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C .

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