# Sodium Ion Conduction of Perfluorosulfonate Ionomer/ Poly(oxyethylene) Composite Films

**Shinji Takeoka, Kohji Horiuchi, Shin Yamagata, and Eishun Tsuchida***

*Department of Polymer Chemistry, Waseda University, Tokyo, 169, Japan*

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ABSTRACT: A composite film of $Na^+$-form Nafion and diendoacetylated poly(oxyethylene) ($\bar{M}_w$ = 400) ($POE_{400E}$) was cast from a dimethylformamide solution at 120 °C. The ionic conductivity of this thin film was measured. The resulting film showed good flexibility, transparency, and no leakage of $POE_{400E}$ up to the POE incorporation of 55 wt %. At this composition, sodium ionic conductivity was $1.0 \times 10^{-6}$ S $cm^{-1}$, which is relatively high as a single-ion conductor because of the high dissociation of the sodium perfluorosulfonate groups. The ionic conductivity increases with POE incorporation. This can be explained from a decrease in the glass transition temperature ($T_g$) of POE regions and the connection of ion clusters swollen by POE.

## Introduction

The design of solid polymer electrolytes with high ionic conductivity has been a key to their application in many electric devices.[1] Three requirements should be met for such solid polymer electrolytes (SPE): (1) low ion-ion interaction and appropriate ion-polymer interaction, (2) low glass transition temperature, and (3) low crystallinity. Furthermore, mechanical, chemical, and electrochemical stabilities of the SPE thin film are also important. Many poly(oxyethylene) derivatives/inorganic salt hybrids have been synthesized to satisfy these requirements.[2-5]

When nonblocking electrodes such as alkali-metal electrodes are used in an ordinary SPE/alkali metal salt system, a significant decrease in ionic conductivity is observed under dc polarization because of migration of the anion. Therefore, single-ion conductors, which have only the cation as the carrier, have been proposed.[6-13] There are three approaches to the synthesis of single-ion conductors: (1) blending a polyelectrolyte with an ion-conductive polymer (or an oligomer),[6,7] (2) the copolymerization of corresponding monomers,[8-11] and (3) the polymerization of sophisticated electrolyte monomers.[12,13] In general, the ionic conductivity of a single ion conductor is about $10^{-2}$ times that of the ordinary amorphous SPE because of the low ion dissociation of carboxylate or sulfonate salts in comparison with $MClO_4$ or $CF_3SO_3M$.

We measured the ionic conductivity ($\sigma_i$) of diendoacetylated poly(oxyethylene) ($\bar{M}_w$ = 400; $POE_{400E}$) containing $CH_3COONa$, $CF_3COONa$, $CH_3SO_3Na$, or $CF_3SO_3Na$. Since the mobility of the anion and the viscosity of POE in each system is similar, the difference in ionic conductivities represents the difference in dissociation of the salts. The $\sigma_i$ of $CH_3SO_3Na$ is about 10 times that of $CH_3COONa$, and $\sigma_i$ of the $CF_3COONa$ and $CF_3SO_3Na$ systems is $10^4$ and $10^3$ times each corresponding hydrocarbon system. This order indicates the order of the degree of dissociation of the salts. Taking into consideration the highest $\sigma_i$ of the $CF_3SO_3Na$ system, a perfluorosulfonate ionomer should be a good solid polymer electrolyte with high single-ion conductivity.

On the other hand, an acid-form perfluorosulfonate ionomer ($H^+$-form Nafion) containing water is known to show high protonic conductivity as well as excellent stability and has already been used in some applications. In our laboratory, a $M^+$ form of Nafion film was first applied as a solid polymer electrolyte.[14] However, the Nafion was used as a support for the liquidlike $POE_{400E}/LiClO_4$ complex, and the microphase-separated structure produced an ion-conductive pathway. The two methods used to prepare samples were *immersion* and *casting*. The immersion method resulted in low incorporation of POE. In this case, the single-ionic conductivity of $Li^+$-form Nafion/POE was about $10^{-8}$ S $cm^{-1}$. Although the casting method performed at 70 °C gave a higher incorporation of POE, it caused extensive phase separation, leading to leakage of POE. A higher incorporation ratio of POE appears to be the key for higher ionic conductivity.

We succeeded in obtaining a Nafion/POE film with a high incorporation ratio by modifying Moore's method.[15] Casting at a high temperature of about 120 °C gave a thin transparent film with high qualities. This paper clarifies the factors that influence the single-ionic conductivity of the $Na^+$-form Nafion/POE system, such as ion dissociation, glass transition temperature, and phase state.

## Experimental Section

**Materials. Diendoacetylated poly(oxyethylene) ($POE_{400E}$)**: Poly(oxyethylene) with a number-average molecular weight of 400 was purchased from Kanto Chemical Co., Inc., and dried in vacuo at 70 °C for 24 h. Terminal hydroxy groups were esterified with an excess of acetyl chloride. The product was dried in vacuo at 60 °C for 24 h. The $^1H$ NMR spectrum confirmed the complete reaction of the hydroxy groups.

**Nafion**: A $H^+$-form Nafion 117 solution (5 wt % in lower aliphatic alcohols and water) was purchased from E.I. du Pont de Nemours & Co.

The first-grade sodium amalgam containing 5.0% of sodium was purchased from Wako Pure Chemical Industries, Ltd.

**Methods.** An as-received solution of $H^+$-form Nafion was neutralized with a methanol solution of sodium methoxide, and a given amount of $POE_{400E}$ was added to it. The film was cast from DMF in accordance with Moore's method.[15] Namely, after adding DMF to the mixture, alcohols and water were evaporated on a Teflon plate at 100 °C, and then DMF was evaporated at 120 °C. The resulting film was annealed in vacuo at 120 °C for 24 h. A circular film (10 mm $\phi$) was cut out and sandwiched between the same size of stainless steel electrodes. The ionic conductivity (ac 1 V) was measured at 25 °C with a Solartron 1286 electrochemical interface and a Solartron 1255-HF frequency response analyzer over a frequency range from 1 to 500 kHz. The dc (1 V) conductivity was measured at 25 °C with a Solartron 1286 electrochemical interface. Sodium amalgam or stainless steel were used as electrodes.

IR and $^1H$ NMR spectra were obtained with an IR spectrophotometer (Japan Spectroscopic Co., Ltd., Model IR 810) and with a JEOL FX-90Q NMR spectrometer at 90 MHz, respectively.

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* To whom all correspondence should be addressed.

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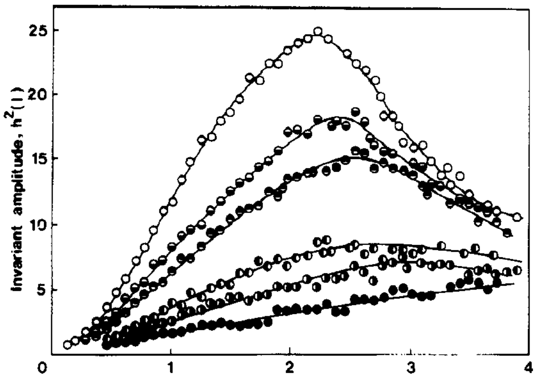

**Figure 1.** SAXS scans of $Na^+$-form Nafion/$POE_{400E}$ composite films at the Na/OE unit ratios of (○) 0.06, (◒) 0.10, (⊖) 0.15, (◐) 0.20, and (◑) 0.40. (●) no POE.

Differential scanning calorimetry (DSC) data were obtained with Seiko DSC-10 and SSC-580 with a scanning rate of 5 °C/min. The $T_g$ was determined as the temperature of the lower intersectiion point of the base line with the extrapolated slope in the thermogram.

Small-angle X-ray scattering measurements (SAXS) were taken with a NaI scintillation counter mounted on a goniometer with a step-scanning device. Cu K$\alpha$ radiation was used for the incident X-ray beam generated by a X-ray generator (Ru-200B, Rigaku-Denki). The SAXS data were plotted as the invariant amplitude ($h^2I$) versus $2\theta$, where $h = (4\pi/\lambda)\sin\theta$, $I$ is the intensity of the scattered X-rays, $\lambda$ is the X-ray wavelength (1.54 Å), and $2\theta$ is the scattering angle.

Transmission electron microscopy (JEOL-100CX) was employed to obtain micrographs of the film. The solution before casting was mixed with a small amount of uranyl acetate saturated solution as staining agent for the phase-separated POE regions, and the mixture was dropped onto a carbon-coated copper grid. A film on the grid was annealed in vacuo at 120 °C for 24 h.

## Results and Discussion

**Film Formation by Casting.** A thin film about 30–50 μm thick was prepared by casting a DMF solution of Nafion/POE at 120 °C. The resulting film was flexible and transparent. On the other hand, the film prepared by casting an as-received Nafion solution at 80 °C did not show such good properties. This phenomenon was the same as that previously reported by Moore et al.[15] Nafion dissolved in solvents is known to take micelles having perfluorocarbon cores and ionic surfaces due to the complete incompatibility of fluoorocarbon with solvents. In order to obtain a Nafion film with good mechanical properties, the formation of continuous fluorocarbon phases by the connection of micelles is necessary for casting. This can be achieved by annealing at high temperature with high-boiling solvents, which provide a high segmental motion for the fluorocarbon chains. DMF is the best solvent because it has a good plasticization effect and a high boiling point. Therefore, Nafion/$POE_{400E}$ films cast from a DMF solution show good mechanical properties. Furthermore, the leakage of a part of $POE_{400E}$ from the membrane does not occur up to the $POE_{400E}$ incorporation of 55 wt % (a Na/OE unit ratio = 0.04).

**Phase Separation of the Nafion/$POE_{400E}$ Film.** Figure 1 shows the smeared SAXS scans of $Na^+$-form Nafion/$POE_{400E}$ films at various Na/OE unit ratios. The intensity of the peak increases with a decrease in the Na/OE unit ratio and the position of the peak shifts to lower scattering angle. This was the same as the Nafion/water systems reported by Gierke et al.,[16] indicating that ion clusters also exist in the Nafion/$POE_{400E}$ system and they are swollen by $POE_{400E}$. The increase in peak intensity with increasing $POE_{400E}$ content is attributed to an increase in the difference in electron densities between the perfluorocarbon matrices and the ion clusters. The Bragg spacing (*d*), which represents the spacing between the clusters, is calculated from Bragg's equation. The Bragg spacing of $Na^+$-form Nafion film was calculated to be 3.0 nm, while that of the $Na^+$-form Nafion/$POE_{400E}$ film at the Na/OE unit ratio of 0.06 was 4.0 nm. The cluster diameter, calculated from the mass of $POE_{400E}$ and Bragg spacings,[16] was 4.6 nm when the Na/OE unit ratio was 0.06 and 3.0 nm when the ratio was 0.4.

The swelling of the ion clusters by $POE_{400E}$ was directly observed by transmission electron micrography (TEM) as shown in Figure 2. Since the staining agent was soluble in $POE_{400E}$, ion clusters were stained positively. The sizes of ion clusters of the Nafion/$POE_{400E}$ film at the Na/OE unit ratio of 0.85 (Figure 2a) are apparently smaller than those of the film at the ratio of 0.06 (Figure 2b). The mean area of black regions at the ratio of 0.06 is 2 times that at the ratio of 0.85, which agrees with the results obtained from SAXS.

**Ion Conduction in Nafion/POE Systems.** The stability of direct current was shown in Figure 3 for a $Na^+$-form Nafion/POE film at the Na/OE unit ratio of 0.04. The applied voltage was 1.0 V. Sodium amalgam (Na-amalgam) and stainless steel (St) electrodes were used as nonblocking electrodes and blocking electrodes, respectively. The Na-amalgam was used instead of Na because the high reactivity of Na caused an increase in sample/electrode interfacial resistance. When the sample was sandwiched between St electrodes, the current decreased immediately due to the polarization of $Na^+$. For the cell configuration of Na-amalgam/sample/St, the stable current shown in Figure 3 indicates that a $Na^+$-form Nafion/POE film is a $Na^+$ conductor. This single-ion conduction is attributed to the fixed perfluorosulfonate groups on the polymer matrix.

Ionic conductivity of the Nafion/POE composite films was correctly evaluated by the ac impedance technique. Figure 4 shows the ionic conductivity ($\sigma_i$) of the films containing various amounts of POE. When the ratios were above 0.2, the $\sigma_i$ was too low to be measured correctly at room temperature, while at ratios less than 0.04, the $\sigma_i$ could not be measured because of the leakage of $POE_{400E}$ from the film. At a Na/OE unit ratio of 0.04, the ionic conductivity was $1.0 \times 10^{-6}$ S cm$^{-1}$. This high sodium ion conductivity when compared with the systems having carboxylate or the sulfonate groups is due to the high degree of dissociation of perfluorosulfonate groups. It is noted that the $\sigma_i$ decreases with an increase in the Na/OE ratio. A maximum in the ionic conductivity was not observed in this region of the Na/OE ratio. The variation of ionic conductivity with POE incorporation was analyzed in terms of the degree of ion dissociation, the mobility of ions due to the segmental motion of $POE_{400E}$, and the ratios of connected ion clusters in a Nafion film.

1. **Ion Dissociation.** Ion dissociation could be analyzed by IR measurements. The Nafion film shows one distinct absorption band around 1060 cm$^{-1}$, attributed to the symmetric stretching vibration of $-SO_3^-$ groups ($\nu(SO_3^-)$).[17,18] In the case of a dry $Na^+$-form Nafion film, $\nu(SO_3^-)$ was observed at 1066 cm$^{-1}$. When tetrabutylammonium ion was used instead of sodium ion, the value shifted to 1051 cm$^{-1}$. This shift is explained in terms of the changes in polarization of the S–O dipole by counterions. Namely, the polarization caused by sodium ion is strong in comparison with that caused by tetrabutylammonium ion because of the steric hindrance of tet-

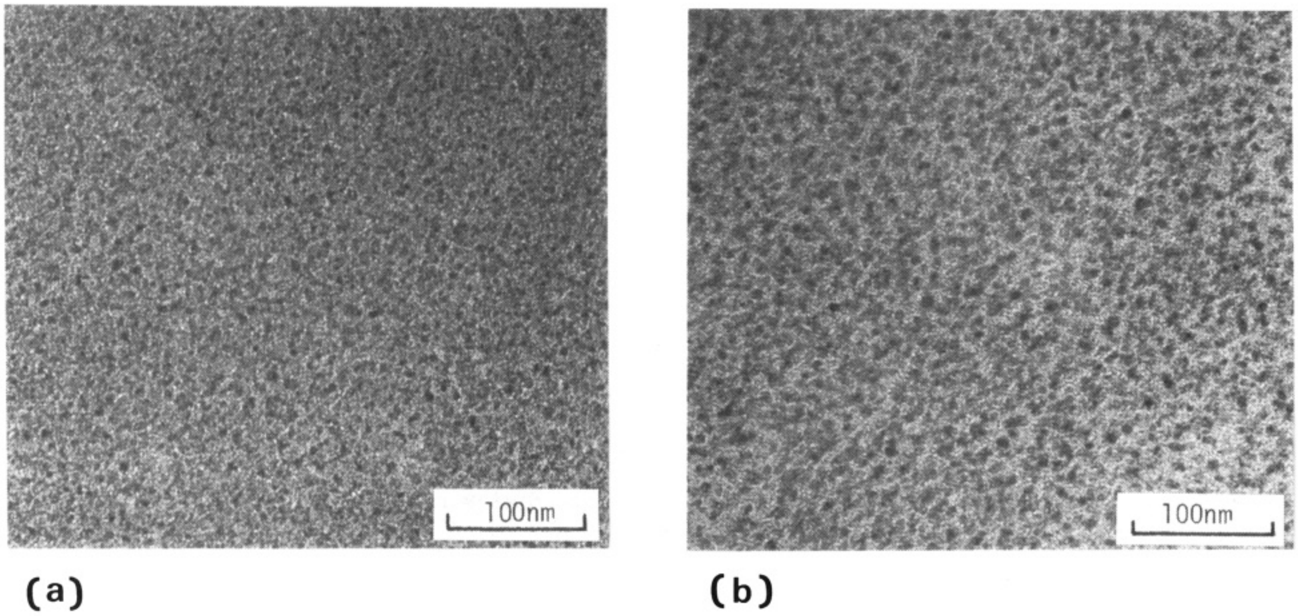

**Figure 2.** Transmission electron micrographs of Na$^+$-form Nafion/POE$_{400E}$ composite films at the Na/OE unit ratios of (a) 0.85 and (b) 0.06.

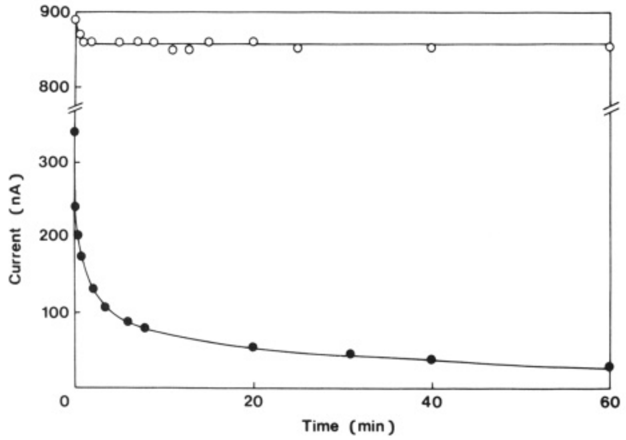

**Figure 3.** Stability of dc (1.0 V) short-circuit current of a Na$^+$-form Nafion/POE$_{400E}$ composite film (a Na/OE unit ratio = 0.04) at 25 °C: (○) Na-amalgam; (●) stainless steel electrodes.

rabutylammonium ion. Therefore, a $\nu(SO_3^-)$ of 1066 and 1051 cm$^{-1}$ would mean the formation of ion pairs between $-SO_3^-$ and Na$^+$ and the completely dissociated state, respectively.

Figure 5 shows the $\nu(SO_3^-)$ of the Nafion/POE system. The shift of $\nu(SO_3^-)$ from 1066 to 1057 cm$^{-1}$ by the incorporation of POE up to the Na/OE unit ratio of 0.2 means that the dissociation of sodium ion surely occurs by POE. A further shift to 1053 cm$^{-1}$ occurred by further incorporation of POE up to 0.06. This indicates that the degree of dissociation increases with the incorporation of POE. However, the difference in dissociation ratios cannot explain the observed large differences in ionic conductivities ($10^3$) between the films whose Na/OE unit ratios are 0.04 and 0.2, because the degree of dissociation should be accompanied by a proportional shift of $\nu(SO_3^-)$.

**2. Segmental Motion.** The segmental motion of oxyethylene units greatly influences the ionic mobility. Therefore, a low glass transition temperature is important for a solid polymer electrolyte with high ionic conductivity. As shown in Figure 6, the glass transition temperatures ($T_g$) of POE$_{400E}$ relate to the Na/OE unit ratios of the Nafion/POE films. Namely, $T_g$ increases with an increase in the Na/OE unit ratio because of the interaction between

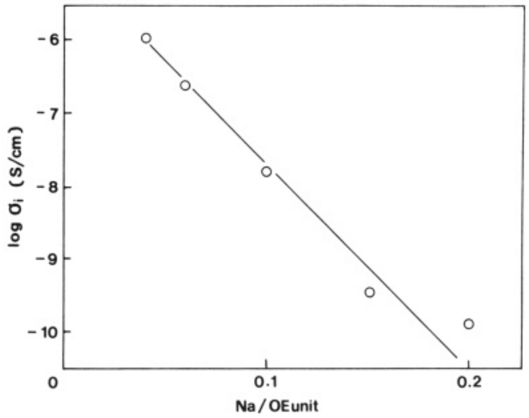

**Figure 4.** Dependence of ionic conductivity of Na$^+$-form Nafion/POE$_{400E}$ composite films on the Na/OE unit ratio at 25 °C.

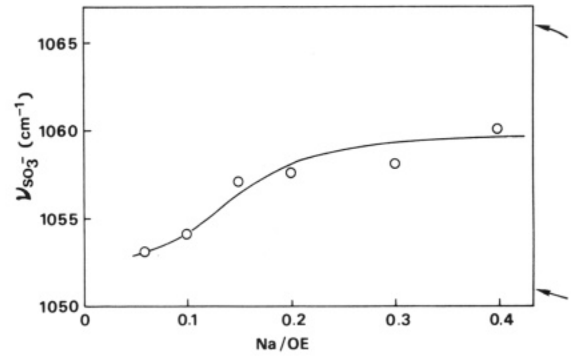

**Figure 5.** Ion dissociation of Na$^+$-form Nafion/POE$_{400E}$ composite films at various Na/OE unit ratios analyzed from the value of the symmetric stretching vibration of groups. The upper arrow represents the value of $\nu(SO_3^-)$ where no ion dissociation occurs. The lower one represents the value where complete ion dissociation is considered to occur.

sodium ions and ether oxygens. The $T_g$ of POE at the ratio of 0.4 is 50 °C higher than that of pure POE (−67 °C). On the other hand, the $T_g$ of POE at the ratio of 0.04 is about the same as that of pure POE. Therefore, the decrease in $T_g$ by POE incorporation should be a large factor in explaining the increase in ionic conductivity. At

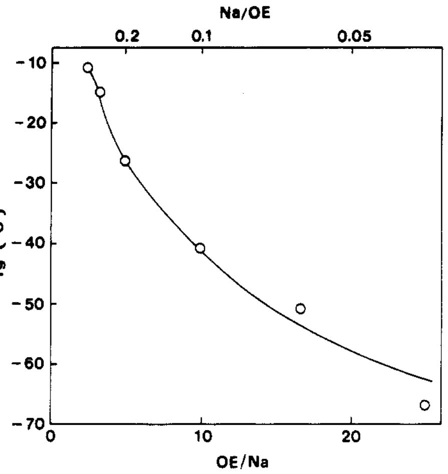

**Figure 6.** Glass transition temperatures of a Na$^+$-form Nafion/POE$_{400E}$ composite film at various Na/OE unit ratios.

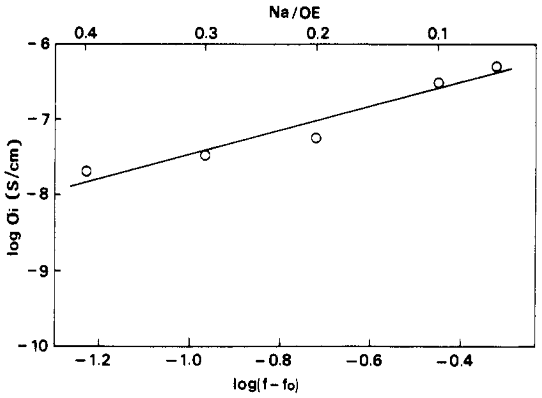

**Figure 7.** Relationship between ionic conductivity of a Na$^+$-form Nafion/POE$_{400E}$ composite film and the Na/OE unit ratio at temperatures 80 °C higher than $T_g$. The relationship between conductivity and the excess volume fraction of POE ($f - f_0$) is also shown in this figure.

a constant temperature deviation from $T_g$ ($T - T_g = 80$ °C), the segmental motion of POE$_{400E}$ incorporated into Nafion films with various ratios is considered to be the same.[12,19] The ionic conductivities at $T - T_g = 80$ °C were plotted against various Na/OE unit ratios in Figure 7. The increase in ionic conductivity with a decrease in the Na/OE unit ratio under the constant segmental motion suggests the existence of other possibilities besides the segmental motion and the dissociation ratio.

**3. Phase Separation.** Taking the phase separation of POE and Nafion analyzed by SAXS into consideration, the dependence of ionic conductivity on the incorporation ratio of POE would be explained in terms of percolation theory. Since ion clusters swollen by POE are isolated at low POE incorporation, long-range ion migration is difficult. The swelling and the association of the ion clusters occurs with an increase in POE incorporation ratio. This makes the whole system conductive at a threshold volume fraction ($f_0$) of POE. When a volume fraction is $f$ (above $f_0$), the conductivity represents the following equation in accordance with the percolation theory[20]

$$\sigma_i = \sigma_0(f - f_0)^t \tag{1}$$

where $t$ is a universal constant that normally depends only on the spatial dimension and is typically 1.5–1.7 in three dimensions and $f_0$ is ideally 0.15 for a 3D continuous random mixture. Wódzki et al. calculated $t$ and $f_0$ for Nafion-120 equilibrated with NaCl solutions[21] and found them to be 1.6 and 0.10, respectively. Figure 7 shows the log–log plots of $\sigma_i$ versus the excess volume fractions of POE$_{400E}$; $f - f_0$ at $T - T_g = 80$ °C. Since $T_g$ of POE in the films at the Na/OE unit ratios of more than 0.4 could not be measured, $f_0$ was not to be obtained from $\sigma_i$ at $T - T_g = 80$ °C. Therefore, if $t$ was estimated to be 1.6, $f_0$ was calculated to be 0.13 from the data in Figure 7. The calculated relation is shown in Figure 7 as a solid line. The small deviations in the plots may be due to the difference in the degree of dissociation. The $f_0$ value is between the theoretical and the calculated values for Nafion/NaCl aqueous solution systems.[21] This suggests a structural difference between the Nafion/POE system and the Nafion/aqueous solution system. Therefore, under the conditions of similar segmental motion, the ionic conductivity depends on the percolation theory, i.e., the degree of association of ion clusters. This is a typical feature of the solid polymer electrolytes that have phase-separated ion-conducting regions.

## Conclusions

Stable Nafion films containing a large amount of POE in phase-separated ion clusters were prepared by casting from DMF solution at 120 °C. The high ionic conductivity of a Na$^+$-form Nafion/POE film (Na/OE = 0.04) is attributed to the high dissociation ratio of the Na$^+$-form perfluorosulfonate groups. Ionic conductivity increases with POE incorporation. This is due to the increase in the degree of ion dissociation, the increase in the segmental motion of POE by lowering the $T_g$, and the formation of the long-range ion-conducting pathways by the connection of ion clusters.

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**Registry No.** POE$_{400E}$, 27252-83-1; Na, 7440-23-5; Nafion 117, 66796-30-3.