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Polyether/salt hybrid: 5. Phase and bulk electrochemical response of viologens having poly(ethylene oxide) chain*

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Poly(ethylene oxide)/viologen hybrid was prepared, and its electrochemical redox response was analysed in the bulk or in poly(ethylene oxide) (PEO) with a molecular weight of 200 (PEO_{200}). We analysed the effect of molecular weight (M_w) of the PEO part in the hybrid on the mechanical property and redox response in the bulk. Totally amorphous viologen hybrid showed a redox response in the bulk over a wide temperature range. Since the viologen hybrid with a M_w of the PEO part higher than 2000 showed a freezing point (T_f) the electrochemical response was not observed in the bulk below T_f because of low diffusion coefficient. By adding $LiClO_4$ to the polymerized hybrid, the solidifying transition enthalpy decreased and vanished, reflecting the totally amorphous matrix. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene oxide); viologen; electrochemical response)

INTRODUCTION

Ion-conductive polymers containing poly(ethylene oxide) (PEO) structure have been studied well[2–4]. Since PEO solubilizes a large amount of salt[5,6] in bulk and supports high ion mobility, PEO oligomer and its derivatives have frequently been used for the design of ion-conductive polymer matrix. The ionic conductivity in these systems is governed by both the number of dissociated ions and their mobility. It was believed to be necessary to dissolve a large amount of salt in order to increase the number of carrier ions, however the glass transition temperature (T_g) of the matrix is raised considerably so that its mobility was restrained at the same time. Therefore, the T_g was not improved with a large amount of salt in PEO derivatives. The hybridization of the salt structure and PEO oligomer is one solution to overcome this problem. We have already prepared several kinds of such hybrids, PEO oligomers having different charged groups, such as carboxylate[7,8], benzene-sulfonate[1], sulfonate, and sulfonamide groups[9], to improve their ionic conductivity in the bulk. The ionic conductivity of these PEO oligomers is closely related to the dissociation constant of the terminal groups and the ion mobility in the bulk. Totally amorphous matrix was obtained when the optimum molecular weight (M_w) of the PEO part was used for individual charged group. The high ionic conductivity was obtained in the amorphous matrix with low T_g because of the high mobility of the matrix and high dissociation constant of the terminal group.

A series of the *N*,*N*′-dialkyl-bipyridinium salt, alkylviologen, has been widely studied as an electron mediator[10–19]. Most of these studies were carried out in water or water/organic solvent in two-phase systems. A considerable decrease of hydrophilicity of viologens after reduction was used as a phase transfer electron mediator. The introduction of the PEO unit onto viologen was expected to improve the solubility of viologen in organic solvents. Endo *et al.* synthesized several kinds of polyether/viologen hybrids as electron-transfer catalysts. These PEO/viologen hybrids were reduced by $Na_2S_2O_4$ in organic solvent[20]. A similar PEO/viologen hybrid structure was also prepared by Liu *et al.*[21] and quite recently Murray *et al.* analysed the bulk electron transfer process of a viologen containing polyether structure with a molecular weight of about 150[22]. The combination of the PEO part and salt was revealed to provide an amorphous phase. PEO is now expected to make many organic salts amorphous. The totally amorphous environment of viologen should show both high redox activity and ionic conductivity, and to act as a redox active matrix without any other solvents or electrolytes. Thus, we prepared viologen with two kinds of structure with different M_w PEO from 350 to 6000 to analyse the effect on the matrix phase and its redox activity in bulk.

EXPERIMENTAL

Materials

Poly(ethylene oxide) oligomers (PEO) with molecular weight (M_w) 200–4000 were purchased from NOF Co. Ltd. Poly(ethylene oxide) monomethyl ethers (PEOM) with M_w 350–5000 were purchased from Aldrich. Thionyl bromide ($SOBr_2$) was also purchased from Aldrich. Reagent grade triethylamine and 4,4′-bipyridine (4,4′-bpy) were purchased from Kanto Chem. Co. Ltd and Tokyo Kasei Co. Ltd, respectively. All these materials were used without further purification.

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Precursors, α,ω-dibromo- and α-bromo-ω-methoxy-PEO oligomers, were obtained by the reaction of $SOBr_2$ with PEO and PEOM, respectively. The toluene solution of $SOBr_2$ was added gently to PEO derivatives in the presence of triethylamine (TEA). After the addition of $SOBr_2$, the reacted solution was heated and held at 60°C for 6–8 h. After the reaction, triethylammonium bromide (TEABr) was removed as precipitate by filtration. The supernatant solution was then cooled and held at 4°C for 1 day and filtered several times. ^1H n.m.r. spectrometry suggested that removal of byproducts was, however, insufficient after these treatments.

When the M_w of the starting PEO derivatives was equal to or less than 1000, the solution obtained was purified in benzene/H_2O. TEABr was slightly soluble in benzene, but terminal brominated PEO oligomers were readily soluble in the organic phase. The obtained solution was evaporated and pure water added to the residue. After stirring the solution for 8 h, an excess amount of benzene was added, and the solution was stirred vigorously for a further 8 h. Only the benzene phase was separated and evaporated. The residue was a brown viscous liquid and the structure were confirmed by ^1H n.m.r. spectrometry.

The recrystallization in ethanol was effective when the M_w of the PEO was more than 1000. After removal of toluene from the reacted solution, the residue was dissolved in ethanol at 40–50°C, and gradually cooled down to 4°C. The terminal-brominated PEO oligomers were obtained in the yellowish powder. All the structure and purity of these bromo-PEO oligomers were confirmed by the ^1H n.m.r.

The obtained α,ω-bromo-PEO oligomers were reacted with 4,4′-bpy in DMF to prepare the viologen though the Menschutkin reaction. In the case of the reaction with α-bromo-ω-methoxy-PEO oligomers, the viologen having two PEO chains on both sides was obtained as shown in *Scheme 1*. This type of PEO-viologen is abbreviated as $(PEO_m)_2$-V (m is the M_w of the PEO part) here. On the other hand, the reaction of 4,4′-bpy with α,ω-dibromo-PEO oligomers gave a polymer with a repeating unit of PEO and viologen, which is abbreviated as P(PEO_m-V). The mixed solution of these PEO derivatives and 4,4′-bpy was stirred at 80°C for 3–7 days. After the removal of DMF, the residue was dissolved in $CHCl_3$/diethylether mixed solution. $(PEO_m)_2$-V and P(PEO_m-V) were precipitated in the solution as a yellow powder when $m < 400$ or as a yellowish brown sticky liquid when $m = 600$ or 1000. $(PEO_m)_2$-V and P(PEO_m-V) with $m > 2000$ was recrystallized as a yellow crystal from that mixed solution. The obtained compounds were washed with diethylether several times, and used in the experiments after recrystallization in $CHCl_3$/diethylether. The viologens with a PEO molecular weight of less than 600 were deliquescent. The structure of all these compounds was analysed by ^1H n.m.r. spectrometry. For example, ^1H n.m.r. of $(PEO_{750}\text{-}V)_2$ in $CDCl_3$: δ 9.5 (*d*, 4H), 9.2 (*d*, 4H), 5.12 (*m*, 4H), 4.06 (*m*, 4H), 3.6 (*m*, 120H), 3.3 (*s*, 6H). In the case of P(PEO_m-V), the number of repeating units (n in *Scheme 1*) was estimated by the ratio of integration of the proton peaks for the quaternary pridinium ion (δ 9.24 and 9.54) and that of unreacted pyridine (δ 7.90 and 8.44). For example, n of P(PEO_{400}-V) was calculated to be about 3.6.

Methods

The sample-cell preparation and all the measurements were carried out under dry nitrogen gas in order to avoid contamination by water molecules. Cyclic voltammogram (CV) was measured with a NPGFZ-251-B (Nikko Keisoku Co.) potentiogalvanostat with a sweep rate of $10\,mV\,s^{-1}$. A 0.5 mmϕ plastic formed carbon electrode (Mitsubishi Pencil Co. Ltd), and 0.5 mmϕ platinum (Tokuriki Honten) wire were used as a working electrode and a counter electrode, respectively. The custom-designed Ag/Ag^+ system was used as a reference electrode. The solution for the reference electrode was constructed with $AgNO_3$ (0.5 M), $LiClO_4$ (0.5 M), and PEO_{200}. The preparation and evaluation of this reference electrode was reported previously[23]. The set of electrodes was inserted in the sample and held in a cell holder with the temperature controlled with the water circulating. The CV measurement was carried out after holding the sample with the electrodes at each temperature for at least 1 h under the dry nitrogen atmosphere.

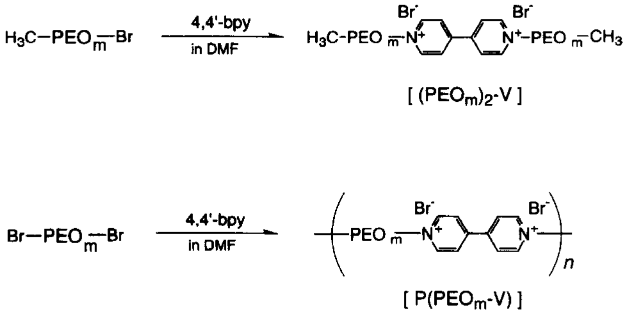
Ionic conductivity was analysed by the complex impedance method with a Schlumberger Solartron 1260 impedance analyzer. The temperature dependence of the ionic conductivity was carried out in the temperature range from 60 to 10°C during cooling. The detailed conditions of the measurement and cell design were described in our previous paper[24].

Differential scanning calorimetry (d.s.c.) measurement was done with a DSC-120 (Seiko Instruments Inc.) under a N_2 atmosphere. The heating rate was fixed at +10°C min^{-1}, and thermal analysis was carried out from −150°C to +200°C in the heating process.

RESULTS AND DISCUSSION

Electrochemical redox reaction of PEO/viologen hybrids [$(PEO_m)_2$-V]

The cyclic voltammogram for $(PEO_{350})_2$-V in PEO_{200} is shown in *Figure 1*. A two-step redox reaction of



Scheme 1 Preparation of PEO/viologen hybrids, $(PEO_m)_2$-V and P(PEO_m-V) (m is the average molecular weight of PEO)

viologen was clearly observed without a supporting electrolyte. These oxidation–reduction potentials were compared with those of *N,N'*-dibutylviologen (But-V) in acetonitrile and in PEO_{200} with 0.1 M $LiClO_4$, respectively. It was confirmed that the introduction of the PEO structure on viologen showed no influence on the redox reaction of viologen. Furthermore, these hybrids showed a good compatibility with not only PEO_{200} but also other organic solvents because of the amphiphilic property of PEO as previously reported[20]. The solubility of $(PEO_m)_2$-V in organic and polymer solvents was increased with increasing M_w of the PEO part. However, even $(PEO_{350})_2$-V and P(PEO_{600}-V) showed a redox response up to the molar ratio of 8 : 2 for PEO_{200}.

Then, the redox activity of $(PEO_{350})_2$-V was analysed in PEO_{200}. The peak current for the first oxidation peak current ($I_{p_{ox}}$) was measured at 60°C with a sweep rate of $10\,mV\,s^{-1}$. The peak current was plotted as the function of the viologen concentration as shown in *Figure 2*. Though the redox response has not been measured in the bulk (100 wt%) because the sample was too rigid to obtain enough contact with the electrodes, $(PEO_{350})_2$-V was miscible in any ratio with PEO_{200} and showed a redox response at high concentration. The $I_{p_{ox}}$ varied with the maximum value as the function of the concentration of $(PEO_{350})_2$-V. This was a diffusion control process, which was confirmed from the dependence of $I_{p_{ox}}$ on the sweep rate. The viscosity of solution was increased with increasing the ratio of $(PEO_{350})_2$-V. The decrease of $I_{p_{ox}}$ at a concentration higher than 50 wt% is explained by the decrease of diffusion coefficient of the viologen unit.

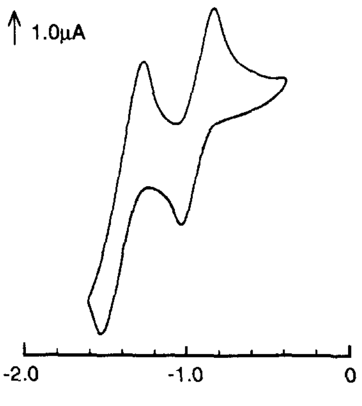


Figure 1 Cyclic voltammogram for $(PEO_{350})_2$-V in PEO_{200} (10 wt%) at 60°C with a sweep rate of $10\,mV\,s^{-1}$

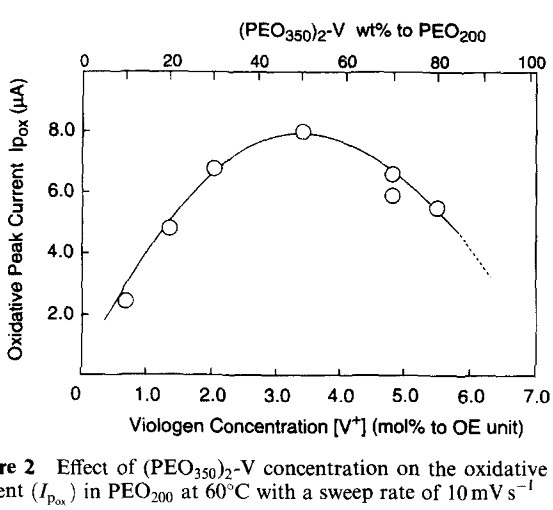


Figure 2 Effect of $(PEO_{350})_2$-V concentration on the oxidative peak current ($I_{p_{ox}}$) in PEO_{200} at 60°C with a sweep rate of $10\,mV\,s^{-1}$

It was our main purpose to prepare amorphous viologens showing redox activity in the bulk. To find the optimum condition, the M_w of the PEO part in $(PEO_m)_2$-V was varied from 350 to 5000. The $(PEO_m)_2$-V for $m > 2000$ showed a crystalline phase at room temperature because of the property of the PEO chain. A drastic decrease in the ionic conductivity was observed in $(PEO_m)_2$-V for $m = 2000$ and 5000 (closed plots in *Figure 3*). The temperature for the ionic conductivity jump corresponding to the freezing point (T_f) of the matrix. The matrix phase was changed from melting state to crystal around this temperature. Similarly, the mobility of bromide and viologen was decreased considerably at this resulting lower ionic conductivity. On the other hand, $(PEO_m)_2$-V for $m < 750$ was confirmed to be amorphous from the ionic conductivity measurement as shown in *Figure 3*, and no transition was found with the d.s.c. measurement from −150°C to +200°C. However, it is difficult to measure the redox response for $(PEO_m)_2$-V with M_w 350 and 550 because of the rigid matrix as previously described. Such a rigid matrix was related considerably to a low ionic conductivity as shown in *Figure 3*. Since these matrices contained high viologen concentration in the bulk, this rigidity seemed to be derived from the characteristics of the viologen unit. Among these materials, $(PEO_{750})_2$-V hybrid gave a viscous liquid with the highest bulk ionic conductivity.

Since $(PEO_{750})_2$-V showed enough ionic conductivity to show redox activity around room temperature, the redox reaction for $(PEO_{750})_2$-V was analysed. Relatively high redox activity was observed without any supporting electrolyte in the bulk. The first oxidation and reduction

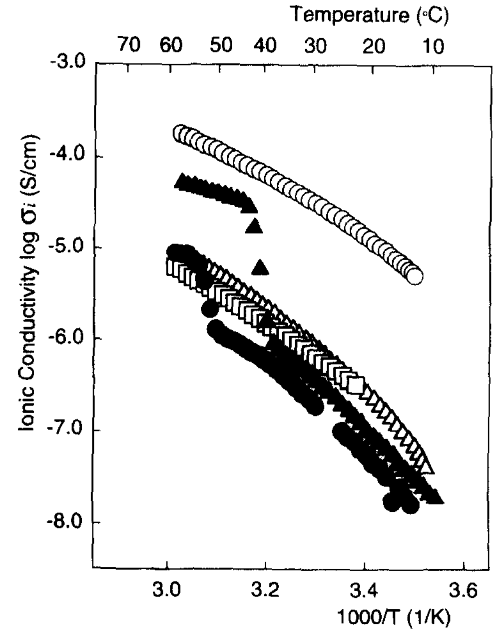


Figure 3 Temperature dependence of the ionic conductivity for $(PEO_m)_2$-V: $m = 350$ (△), 550 (□), 750 (○), 2000 (▲) and 5000 (●), respectively

cycle was confirmed to be reversible. This was clarified to be the diffusion control process from the relation between the I_p and sweep rate. On the other hand, the second redox reaction was irreversible. The nonionic form of viologen is hard to oxidize electrochemically. It is readily adsorbed on the carbon electrode through dimerization. In fact, with the second potential sweep, the peak intensity was decreased gradually and vanished after 10 sweeps. The surface of carbon electrode became insulated owing to the deposition of nonionic viologens. On the other hand, the redox reaction was in a steady state in the first redox sweep, and the initial shape of CV peaks was kept after continuous sweeping. The peak current of the first oxidation ($I_{p_{ox}}$) was measured, and plotted as $I_{p_{ox}}^2 T$ against the inverse temperature as shown in *Figure 4*. Generally, the I_p was known to obey the equation in the reduction step:

$$I_p = 0.043 \cdot 10^{-3} \cdot n^{2/3} F^{3/2} A (RT)^{-1/2} D_R^{1/2} C_R^* v^{1/2} \quad (1)$$

where n is the number of electrons in the redox process, A is the mean electrode area, D_R is the diffusion coefficient for the redox active species, C_R^* is the concentration of the species, and v is the sweep rate. When the sweep rate was fixed, the diffusion coefficient was regarded to be the function of the absolute temperature and I_p;

$$D_R = I_p^2 T \cdot K^{-1}$$

$$K = (0.043 \cdot 10^{-3})^2 n^{4/3} F^3 A R^{-1} (C_R^*)^2 v \qquad \text{(const.)}$$

$I_p^2 T$ was regarded to be proportional to the diffusion coefficient of the redox active species. The temperature dependence of $I_p^2 T$ for $(PEO_{750})_2$-V showed an upper convex curve as seen in *Figure 4*. This behaviour was similar to those of the ionic conductivity. The redox reaction of viologen was required not only for the diffusion of redox active species but also for migration of the counter ion for the charge compensation. These two processes also affected the ionic conductivity of $(PEO_{750})_2$-V.

In the $(PEO_m)_2$-V system, the bulk redox activity was observed only in $(PEO_{750})_2$-V, because a high matrix mobility was necessary for the electrochemical redox reaction of viologen in the bulk. When the M_w of PEO part in $(PEO_m)_2$-V was higher than 2000, the crystal phase was observed at room temperature and the melting point was almost equivalent to that of unsubstituted PEO oligomers. In addition, when $m < 550$ it was very stiff and suggested low bromide ion mobility. It is concluded that $(PEO_{750})_2$-V is a good material as the matrix to provide high ionic conductivity and flexibility. It seems to be quite difficult to design a hybrid with better properties by simply changing the molecular weight of the PEO part.

Electrochemical redox reaction of poly(PEO$_m$-viologen) [P(PEO$_m$-V)]

In the case of $(PEO_m)_2$-V, the aggregation of the PEO unit or viologen unit was inhibited by the flexible PEO matrix. To reduce the freezing point (T_f) or to make an amorphous phase, steric hindrance was taken into account. The excluded volume effect would make T_f lower even for a high M_w PEO part. It would be possible to prepare an amorphous matrix with a wider M_w range for the PEO part. Thus, we prepared poly(PEO-viologen)s having a repeating PEO_m-V unit.

We prepared the poly(PEO_m-viologen), P(PEO_m-V) with a PEO M_w from 600 to 6000. As expected, the melting (freezing) points of P(PEO_m-V) were lower than those of the corresponding PEO oligomers as shown in the Arrhenius plots of the ionic conductivity (*Figure 5*). The differences in T_f were clear by comparing the data for $(PEO_{2000})_2$-V (▲ in *Figure 3*) with those of P(PEO_{200}-V) (□ in *Figure 5*). The T_f of P(PEO_{2000}-V) was about 10°C lower than that of $(PEO_{2000})_2$-V and showed the same level of ionic conductivity around $4.5 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$ in the melting state. Against this, the matrix containing a high viologen content, e.g. P(PEO_m-V) with M_w of the PEO part lower than 1000, showed a poor ionic conductivity. This seemed to

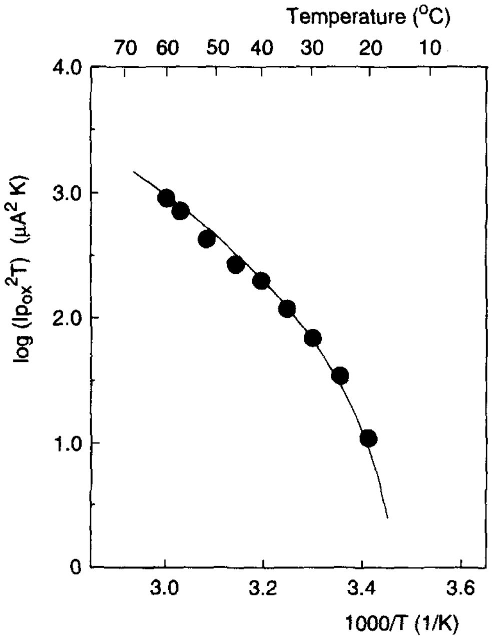


Figure 4 Arrhenius plots of the apparent diffusion coefficient ($I_{p_{ox}}^2 T$) for $(PEO_{750})_2$-V in the bulk with a sweep rate of $10\,\mathrm{mV\,s^{-1}}$

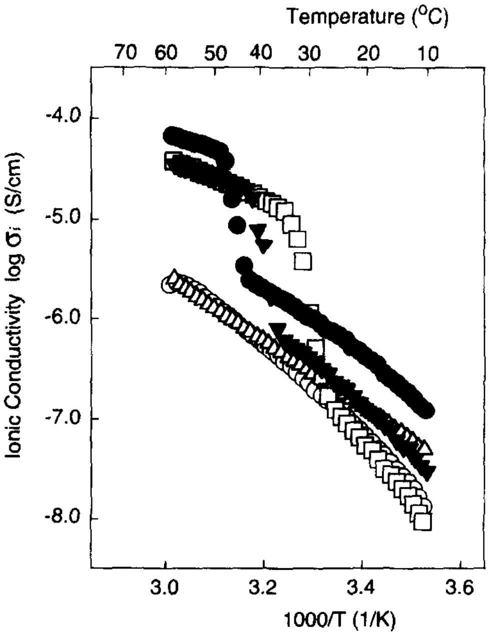


Figure 5 Temperature dependence of the ionic conductivity for P(PEO_m-V): $m = 600$ (○), 1000 (△), 2000 (□), 4000 (▼) and 6000 (●), respectively

originate from their stiff mechanical property. It was, therefore, concluded that the excluded volume of our polymers was effective only when the molecular weight of the PEO unit was larger than 2000.

The redox response was measured in these systems in the melting state. Two oxidation–reduction steps of viologen were clearly observed in the bulk P(PEO$_{4000}$-V), though the peak separation of each reaction was large (*Figure 6*). This large peak separation is attributed to the low diffusion coefficient of P(PEO$_{4000}$-V). It is noteworthy that such a high molecular weight matrix showed clear redox activity even in the bulk. It was confirmed that the diffusion coefficient of the viologen unit was effective in showing a redox response even when it was polymerized. In addition, the first redox response was stable the same as in the case of (PEO$_{750}$)$_2$-V.

Figure 7 shows the first oxidation peak current $I_{\mathrm{p_{ox}}}$, for P(PEO$_{2000}$-V) and P(PEO$_{4000}$-V). Since both these matrices had T_f, the I_p decreased considerably at that point, and I_p was not detected below that temperature. T_f in *Figure 7* was slightly different from those in *Figure 5*. This was attributed to the difference between the sweep rate of the cooling process. Ionic conductivity measurement was carried out with continuous cooling (-2.5°C min^{-1}) as opposed to the steady-state CV measurement. The redox reaction of P(PEO$_m$-V) ($m = 400$, 600) was not detected because of its poor mechanical property. As described previously, it is necessary to lower T_f of P(PEO$_{2000}$-V) and P(PEO$_{4000}$-V) for the detection of redox activity in the bulk.

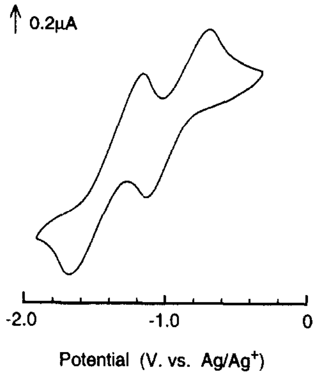


Figure 6 Cyclic voltammogram for P(PEO$_{4000}$)$_2$-V in the bulk at 60°C with a sweep rate of 10 mV s^{-1}

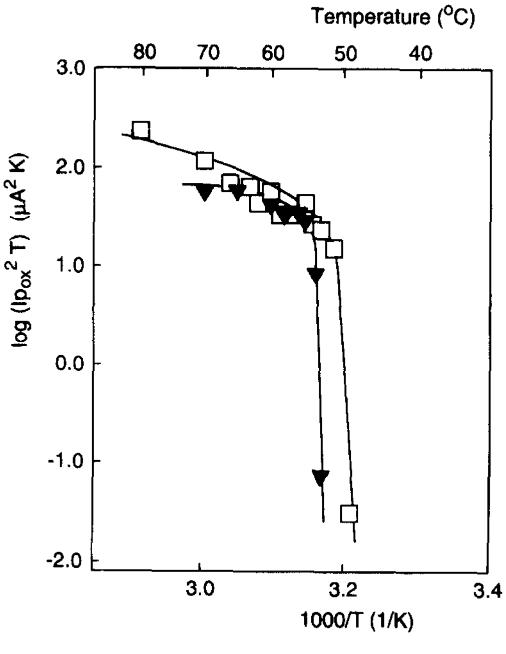


Figure 7 Arrhenius plots of the apparent diffusion coefficient ($I^2_{\mathrm{p_{ox}}}T$) for P(PEO$_{2000}$-V) (□) and P(PEO$_{4000}$-V) (▼) in the bulk with a sweep rate of 10 mV s^{-1}

The depression of freezing point (T_f) by added electrolyte was carried out. The T_f of PEO oligomers was similarly depressed by added salt in PEO[24]. For example, when a large amount of salt was added to PEO oligomers with M_w higher than 1000, the matrix became amorphous through the depression of T_f. At the same time, it is well known that the glass transition temperature (T_g) is increased considerably and the mobility of matrix restrained by the addition of a large amount of salt to PEO derivatives. This is explained by the formation of pseudo-cross linking between the PEO unit and dissociated cation. The matrix with high T_g in the bulk was not preferable for this purpose, because the mobility in the matrix would be low when a large amount of salt was dissolved. Thus the T_g of P(PEO$_m$)-V ($m = 2000$ or 4000) was checked. These matrices had relatively low T_g, -51.4 and -60°C, respectively. Then, the T_f of P(PEO$_{4000}$-V) was analysed by the addition of LiClO$_4$, for example. *Figure 8* shows the d.s.c. thermograms for P(PEO$_{4000}$-V) with and without LiClO$_4$. The T_f of P(PEO$_{4000}$-V) was depressed from 43.4 to 37.8°C when a small amount of LiClO$_4$ (2.35 mol% to OE unit) was dissolved. The endothermic peak of P(PEO$_{4000}$-V) corresponded to the solidifying process diminished with a salt concentration of more than 5.86 mol% to the OE unit. The matrix was shown to be totally amorphous by the salt addition.

The Arrhenius plot of the apparent diffusion coefficient in these matrices is shown in *Figure 9*. It was confirmed that the addition of supporting electrolyte did not affect the oxidation–reduction potential for P(PEO$_{4000}$-V). It was observed that the amorphous matrix of P(PEO$_{4000}$-V) containing LiClO$_4$ (5.86 mol%) showed redox activity over a wider temperature range

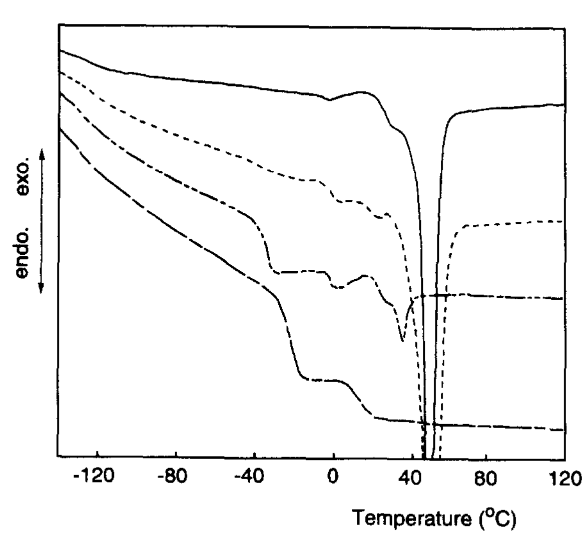


Figure 8 D.s.c. thermograms for P(PEO$_{4000}$-V). LiClO$_4$ concentration: 0 (——), 2.35 (- - - - -), 5.86 (— - - —), and 11.71 (——— – ———) mol% to OE unit

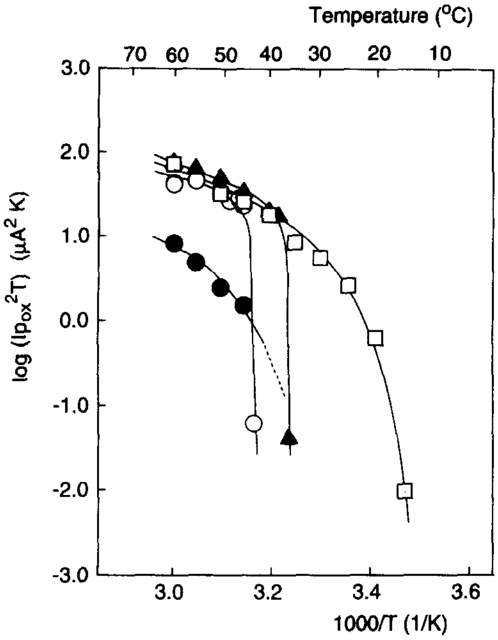


Figure 9 Arrhenius plots of the apparent diffusion coefficient ($I_{p_{ox}}^2 T$) for P(PEO$_{4000}$-V) with a sweep rate of 10 mV s^{-1}. LiClO$_4$ concentration 0 (○), 2.35 (▲), 5.86 (□), and 11.71 (●) mol% to OE unit, respectively

than that without salt. It was suggested that the addition of salt was useful for the preparation of a redox active amorphous matrix. Furthermore, it was indicated that the change of $I_{p_{ox}}^2 T$ reflected the phase change of the matrix and its mobility. The T_g of the P(PEO$_{4000}$-V)/LiClO$_4$ mixture was measured as −55, to −60.2 and −37.1°C for salt concentrations of 2.35, 5.86, and 11.71 mol% to OE unit, respectively. The T_g of P(PEO$_{4000}$-V) containing 11.71 mol% LiClO$_4$ was about 20°C higher than those without salt or with 5.86 mol% LiClO$_4$. It was confirmed that the matrix was flexible at a salt concentration of 5.86 mol% to OE unit. The lower I_p value at the LiClO$_4$ concentration of 11.71 mol% was derived from the low diffusion coefficient of viologen unit and counter ions. A similar tendency was also observed in the temperature dependence of the ionic conductivity for these matrices.

CONCLUSION

The PEO/viologen hybrids showed an electrochemical redox response in PEO$_{200}$ and other organic solvents. The oxidation and reduction potentials were almost equivalent to those of low molecular weight alkylviologen. Bulk redox activity was observed when the matrix showed a totally amorphous phase with low T_g around −50°C. Since the ionic conductivity considerably affected the redox reaction, highly ion conductive matrix should be essential for the electrochemical reaction in the bulk. Furthermore, inorganic salts such as LiClO$_4$ were added to prepare an amorphous phase for viologens having higher PEO molecular weight through the freezing point depression effect. The temperature range which allows the redox response was improved because of the amorphous viologen molecules.

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