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ELECTROCHROMIC EFFECT OF VINYL VIOLOGENACETATE COPOLYETHER SOLID ELECTROLYTE

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ABSTRACT

A novel kind of polymeric solid electrolyte, poly[vinyl viologenacetate-*co*-oligo(oxyethylene) methacryate] ($PVAEO_{16}$), which possesses both ion conduction and electrochromic properties, was synthesized. The anion conductivity of the comb viologen copolyether $PVAEO_{16}$ was 1.9×10^{-6} S/cm (25°C). After addition of PEG400 and $KClO_4$ to $PVAEO_{16}$ with EO/K = 18, ion conductivity increases by about one order of magnitude. $PVAEO_{16}$-based ECD displayed yellow and bluish violet reversibly under a voltage higher than 1.7 V. The color-changing response times were 0.6 and 1.3 seconds (± 2.0 V), respectively. The storage time of bluish violet under an open circuit was more than 16 hours.

INTRODUCTION

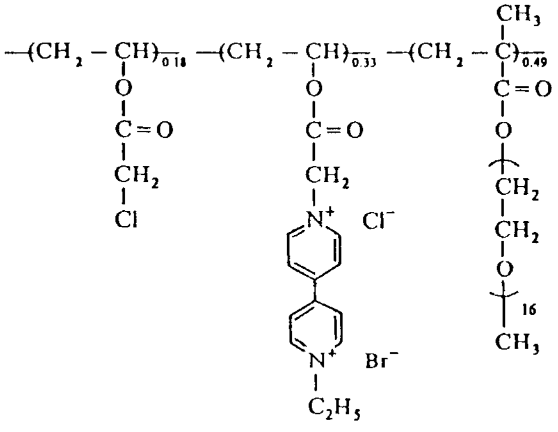
Polymeric solid electrolytes (PSE) have the advantages of high ion conductivity, flexibility, light weight, and easy film-forming ability under the absence of solvent. As new substitution materials for liquid electrolytes, much attention has been paid to the use of PSE in solid batteries, electrochromic display devices, sensors, super capacitors, etc. On the other hand, electrochromic display has the characteristics of no view-angle correlation, good memory, simple constitution, bright color, etc. It is expected to replace liquid crystal in the future. Reports on electrochromism in such materials as tungsten oxide [1], Prussian blue [2], indium oxide [3], viologen [4], polyaniline [5], and polythiophene [6] have appeared over the last few years.

Generally, besides the chromophoric layer in ECD devices, liquid or solid electrolytes must be used to separate two electrodes. However, some problems in leakage and restriction of work space exist if liquid electrolytes are used, and there is slow response when solid electrolyte diagrams are used [7]. Thus, a novel kind of comb viologen copolyether $PVAEO_{16}$, which has both ion conduction and electrochromic characteristics, was synthesized in order to increase the response rate of an all-solid ECD. In this paper the ion conduction and electrochromic behavior of $PVAEO_{16}$ is discussed.

EXPERIMENTAL

Materials

Vinyl chloroacetate (VClA) and 1-ethyl-4,4′-bipyridinium bromide were synthesized according to literature procedures [8, 9]. Poly[vinyl chloroacetate-*co*-oligo(oxyethylene) methacrylate] [P(VClA-MEO_{16})] was synthesized by using the method of radical solution polymerization in which AIBN is used as the initiator. At a temperature between 75 and 80°C and under a nitrogen atmosphere, P(VClA-MEO_{16}) and excess 1-ethyl-4,4′-bipyridinium bromide dissolved in dimethylfulamide react to form a comblike viologen copolyether ($PVAEO_{16}$). After precipitation, washing, and drying, pure $PVAEO_{16}$ was obtained. Infrared spectra showed that $PVAEO_{16}$ has two more absorption peaks (3440 and 1640 cm^{-1}) than does P(VClA-MEO_{16}). The two peaks are the characteristic absorption peaks of viologen salts for $\nu_{-\overset{+}{N}=C-H}$ and $\nu_{C=N}$, respectively. It is clear that the viologen groups have connected with the pendant parts of P(VClA-MEO_{16}). Through the use of elemental analysis data (C, 50.96%; N, 1.71%; H, 6.57%), the molar percentage content for each component in $PVAEO_{16}$ was calculated. The structure of $PVAEO_{16}$ is



Constitution of ECD

By adding a quantity of PEG400, $KClO_4$, and titanium white into $PVAEO_{16}$ (with EO/K = 18) and grinding in an agate mortar, we obtained a well-distributed opaque and white mixture. Drawing and pressing some samples between two pieces of SnO_2 conducting glass gave a film layer with an area of 0.25 cm^2 and a thickness of 60–100 μm. An epoxy resin was used to seal the glass edges. Then a simple electrochromic display device was made (Fig. 1) for testing. The resistance of the SnO_2 conducting layer was 80 Ω/cm^2.

Measurements

The thermal behavior was investigated with the Perkin-Elmer DSC-7 System in the temperature range of −100 to 150°C with a scanning speed of 10°C/min. The glass transition temperature (T_g) was taken as the extrapolated onset of the baseline shift. The crystal melting temperature (T_m) was obtained from the location of the endothermal peak, and the crystallinity (X_c) was derived from the melting enthalpy of 100% crystalline polyether [10].

An ac conductivity measurement was carried out at 1100 Hz with a DDS-11A conductometer and a set of temperature-controlled apparatuses. Then potential step test and cyclic voltammograms of ECD were measured with a WDZ-1 type electrochemical system controlled by a microcomputer. UV-visible absorption spectra were obtained with a Shimadzu UV-260 spectrograph. Storage characteristics under open circuit were determined with a Shimadzu CS-920 high speed TLC Scanner.

RESULTS AND DISCUSSION

Ionic Conductivity of $PVAEO_{16}$

The main chain of the polymer $PVAEO_{16}$, constructed of C—C bonds, endows the polymer with good mechanical and film-forming properties. The pendant chains have two kinds of functional groups. The polar pendant oligoether chain, which includes 16 oxyethylene units, has a low glass transition temperature and acts as a solid solvent to promote dissociation of pendant viologen salt and alkali salt into polycations, alkali cations, and halogen anions. On the other hand, viologen pendant groups act as electroactive groups and ion sources to produce an electrochromic function and ion carriers. The logarithm of ionic conductivity measured in the temperature range from 15 to 70°C is demonstrated in Fig. 2. Curve (a) represents the undoped $PVAEO_{16}$ sample. Its good linear relationship suggests that the

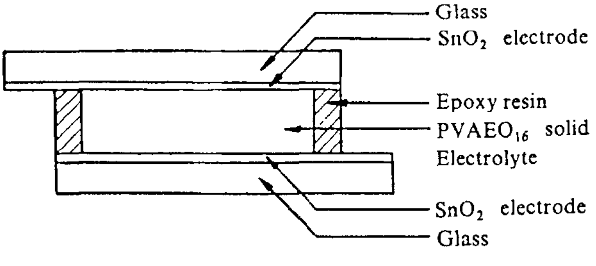


FIG. 1. Cell constitution of $PVAEO_{16}$-based all-solid-state electrochromic display.

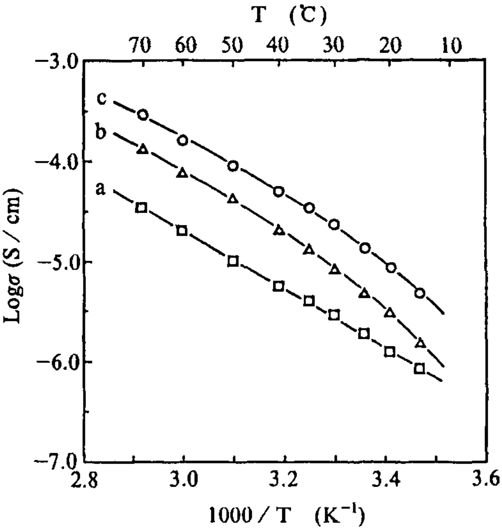


FIG. 2. Log conductivity vs reciprocal temperature for $PVAEO_{16}$-based films with EO/K of 18. (a, □): $PVAEO_{16}$. (b, △): $PVAEO_{16}/KClO_4$ complex, (c, ○): $PVAEO_{16}$/PEG400/$KClO_4$ complex.

ion transport behavior of $PVAEO_{16}$ is of the Arrhenius type. After the viologen salts on the polymer pendant chains have dissociated into polycations and halogen anions, the cations cannot transport because they are fixed onto macromolecules, so only the halogen anions transport in polymer media as carriers. Thus, $PVAEO_{16}$ is a kind of anionic conductor. Anions have great freedom because they do not interact with oxygen atoms in the oligoether, hence the micro-Brownian motion of polymer segments scarcely influence the anionic mobility. Therefore, the anion conductivity was as high as 1.9×10^{-6} S/cm at ambient temperature.

The DSC curve of $PVAEO_{16}$ illustrates that the glass transition temperature (T_g) and the crystal melting temperature (T_m) are −51.1 and 95.0°C, respectively. For the lower polymeric degree (n) of the side oligoether [$-(CH_2-CH_2)_{16}-$] and the hindrance of pendant viologen groups to crystallinity of the oligoether, there exists a low crystallinity (X_c) of 7.2% in the polymer.

After adding an inorganic salt, $KClO_4$, to $PVAEO_{16}$ with EO/K = 18 (Curve b), a dual-ion conductor was formed. K^+ cations interacted with oxygen atoms in the oligoether to form coordinate bonds which increase T_g from −51.1 to −43.8°C. However, they destroy the ordered stacking of the oligoether [11], so they hinder crystallization in the polymer. Since the crystallinity (X_c) of $PVAEO_{16}$ is not high, we can see from the DSC curve that the crystalline peak at 95°C disappears. K^+ cationic mobility is affected by segmental motion of macromolecules because of the coordination of oxygen atoms in the oligoether to K^+ cations. Thus, the temperature dependence of conductivity exhibits a positively curved profile, which suggests that the ion conductive behavior is interpretable in the WLF-form [12]. The conductivity of this system increases because of the contribution of K^+ and ClO_4^- to the conductivity. The conductivity at ambient temperature is 4.8×10^{-6} S/cm.

When further PEG 400 is added into the above system (EO/K = 18) (Curve c), T_g degrades from −43.8 to −49.9°C. Because of the polarity and plasticization of PEG that enlarge the ion-transporting tunnels and promote the formation of carriers, conductivity improves by about one order of magnitude compared with undoped polymer. The conductivity at ambient temperature is 1.4×10^{-5} S/cm.

The positive curves (b and c) shown in Fig. 2 reveal a non-Arrhenius behavior, which suggests that a linear relationship may exist in the empirical Vogel-Tammann-Fulcher (VTF) equation. This equation is usually used to describe the transport property in the amorphous state:

$$\sigma = AT^{1/2} \exp\left[-B/(T - T_0)\right] \tag{1}$$

where A and B are constants, T is the absolute temperature, and T_0 is the ideal glass transition temperature. According to Adam-Gibbs analysis, T_0 can be regarded as 50 K below the measured T_g [13]. When it is applied to the data shown in Fig. 2(b and c), a linear relationship indeed appears in Fig. 3, confirming that ion transport occurs preferentially in the amorphous domain.

In order to examine the nature of ion transport in the investigated (b) and (c) systems more closely, the data have been analyzed with the free volume model, which states that the free volume in amorphous polymers above T_g increases in accordance with the polymer segment relaxation. The mode of the micro-Brownian motion is known to obey the Williams-Landel-Ferry (WLF) equation:

$$\log\left[\eta^{-1}(T)/\eta^{-1}(T_g)\right] = C_1(T - T_g)/[C_2 + (T - T_g)] \tag{2}$$

where $\eta^{-1}(T)$ is the mobility of polymer segments at temperature T (K), and C_1 and C_2 are universal constants with $C_1 = 17.40$ and $C_2 = 51.60$. Replace $\eta^{-1}(T)$ by the ionic conductivity, which reflects the mobility of ions in polymer, and Eq. (2) is transformed into the following form:

$$\log\left(\sigma_T/\sigma_{T_g}\right) = C_1(T - T_g)/[C_2 + (T - T_g)] \tag{3}$$

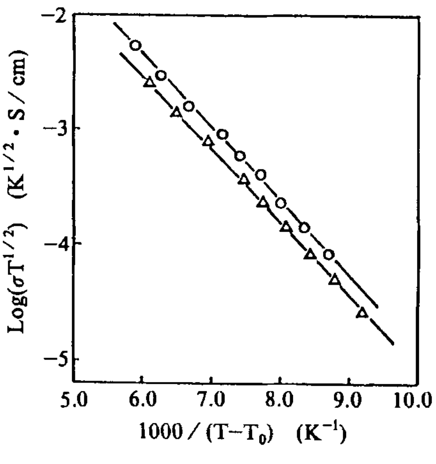


FIG. 3. Vogel-Tammann-Fulcher plots of ionic conductivity for PVAEO$_{16}$-based films with EO/K of 18. (△): PVAEO$_{16}$/KClO$_4$ complex. (○): PVAEO$_{16}$/PEG400/KClO$_4$ complex.

i.e.,

$$\log^{-1}(\sigma_T/\sigma_{T_g}) = C_2/C_1 \cdot (T - T_g) + 1/C_1 \tag{4}$$

Experimental constants C_1 and C_2 are determined by Eq. (4). The results obtained through linear regression with a computer are listed in Table 1. The good approaching of experimental to theoretical values corroborates that ion conduction behavior in the polymer is affected by micro-Brownian motion of the polymer segments.

Coloring/Bleaching Reaction Mechanism of Monolayer ECD

Viologen derivatives (VX_2) are electrochromic substances having redox activities [4, 14]. The coloring/bleaching reaction of chromophoric viologen groups as pendant groups of $PVAEO_{16}$ within the direct current electric field is

$$VX_2 \overset{\text{dissociation}}{\rightleftharpoons} V^{2+} + 2X^- \tag{5}$$

$$V^{2+} \underset{-e}{\overset{+e}{\rightleftharpoons}} V^{+\cdot} \underset{-e}{\overset{+e}{\rightleftharpoons}} V^0 \tag{6}$$

Pendant oligo(oxyethylene) of $PVAEO_{16}$ as a solid solvent promotes partial dissociation of viologen salt (VX_2) into divalent cations (V^{2+}) and halogen anions (X^-) (Eq. 5). Anions X^- could migrate in polymers as carriers, and this makes $PVAEO_{16}$ have ion conduction. When a divalent cation V^{2+} obtains an electron from the cathode, it is reduced to a cation radical $V^{+\cdot}$ (Eq. 6), and it is accompanied by an anion migrating toward the anode in order to keep the ECD film electroneutral so the reaction can proceed. These cation radicals exhibit bright bluish violet, and they could be further reduced to neutral groups (V^0) under much higher voltage. After the voltage polarity is reversed, the above reactions go in the reverse direction in which the viologen groups revert to the original state of divalent cations from zero valence, and anions transport toward the anode simultaneously. This kind of monofilm ECD could have oxidation and reduction, respectively, at the same time on its two electrodes. Thus, the ECD device has a displaying function on its two sides.

Figure 4 is a cyclic voltammogram of ECD with a dielectrode system. The two couples of redox peaks correspond to the one-electron and the two-electron redox

TABLE 1. WLF Parameters of Ionic Conductivity of $PVAEO_{16}$ Samples with EO/K of 18

Samples	T_g, °C	$\log \sigma_{T_g}$, S/cm[a]	C_1	C_2	γ[b]
b	−43.8	−12.69	12.99	52.49	−0.9996
c	−49.9	−12.39	12.18	48.50	−0.9994
WLF eq.			17.40	51.60	1.0000

[a] Derived from the linear regressed VTF equation with $T = T_g$.

[b] Linear factor represents the linearity between $\log^{-1}(\sigma_T/\sigma_{T_g})$ and $(T - T_g)^{-1}$.

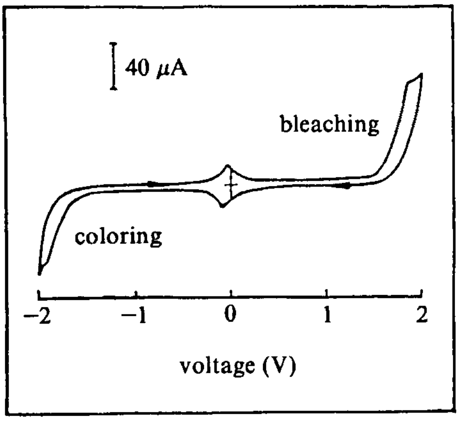


FIG. 4. Cyclic voltammogram of PVAEO$_{16}$-based ECD (film thickness: 100 μm; area: 0.25 cm^2; scan rate: 40 mV/s).

expressed in Eq. (6), respectively. ECD exhibits good stability at the peak current, and the peak area remains the same after 50 cycles of scanning within the range of ±2.0 V. A preliminary life test demonstrates that the polymer film could cyclically carry on the coloring/bleaching process more than 10^4 times. The electrochromic stability is concerned with the microenvironment of chromophoric groups. The exposed cation radical $V^{+\cdot}$ could easily take place in dimerization [15], which influences the reversibility of coloring/bleaching reactions. In PVAEO$_{16}$, V^{2+} groups are surrounded by long oligoether pendant groups. The space effect restrains the dimerization tendency of cation radicals ($V^{+\cdot}$).

Coloring/Bleaching Characteristics of all Solid ECDs

Spectroscopic Properties

Figure 5 indicates the UV-visible absorption spectra of PVAEO$_{16}$-based ECD at oxidation and reduction states. The film has a maximum absorption at 407 nm in the oxidation state, which displays yellow. There are two connected absorption waves at the reduction state. Their maximum wavelengths are located at 550 and 596 nm, respectively. The film shows bluish violet.

Potential Step Response

When a square wave of ±2.0 V is applied across two electrodes of ECD, the relative changes of current (i) and charge (Q) are as shown in Fig. 6. Under the condition of −2.0 V, the current degrades rapidly after it reaches the maximum, but the charge increases. The time when current drops by 90% is about 0.6 second, which is the coloring response time. After the voltage polarity is reversed, the relative time of current diminution, i.e., the bleaching response time, is about 1.3 seconds. These two time lengths are longer than the relative response time of polyviologens for the coloring/bleaching process in liquid electrolytes [16, 17]. The main reason is that the ion conductivity of solid electrolytes is much lower than that of

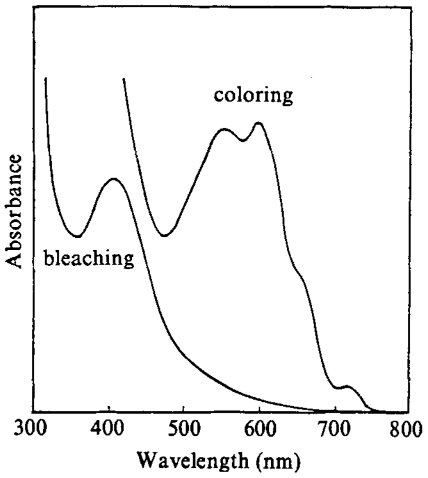


FIG. 5. UV-VIS absorption spectra of PVAEO$_{16}$-based ECD at coloring and bleaching states.

liquid electrolytes. The response time of this monolayer ECD, however, is much shorter than that of ECD using PSE diaphragms [7]. The bleaching response time is longer than the coloring response time because the bleaching process involves two reaction steps, i.e., V^0 to $V^{+\cdot}$ and $V^{+\cdot}$ to V^{2+}, but the coloring process requires just one step, V^{2+} to $V^{+\cdot}$.

Figure 7 exhibits the dependence of charge at the coloring and bleaching states on the applied voltage. The charge rises with an increase of applied voltage.

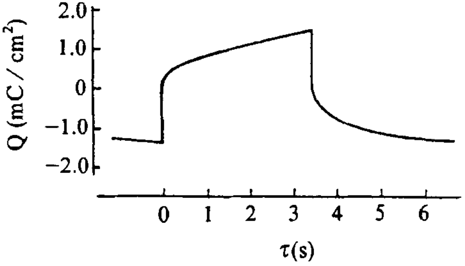


FIG. 6. Electrochromic response of PVAEO$_{16}$-based ECD under −2V to +2V (film thickness: 100 μm; area: 0.25 cm^2).

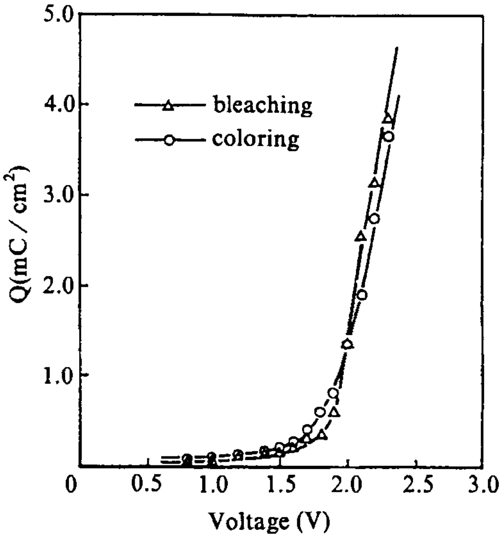


FIG. 7. Relation between applied voltage and charge passing through the cell at the coloring–bleaching process.

Generally, the absorbance change is proportional to the charge applied to the ECD device. So, with an increase of applied voltage, the contrast ratio of color in the coloring/bleaching states grows. When the voltage is below 1.7 V, the Q value is small and the coloring/bleaching process occurs unseen. When the voltage is above 1.7 V, ECD displays bright color changing between yellow and bluish violet. Because of the high ohm resistance of the polymer, the driving voltage must be as high as 2.0 V for ECD to carry on the coloring/bleaching process.

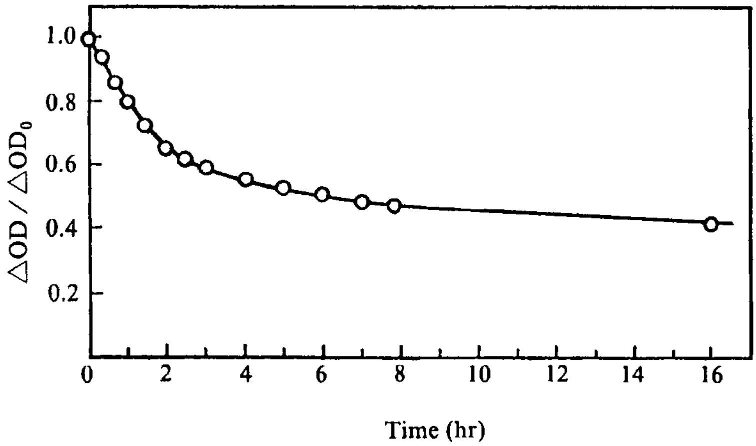


FIG. 8. Result of the storage test of PVAEO$_{16}$-based ECD under open circuit ($\triangle OD_0$ is the optical density difference at t = 0) (film thickness: 60 μm; area: 0.25 cm^2; temperature: 15 °C).

Storage Properties under Open Circuit

One of the advantages of ECD over liquid crystal display (LCD) is the storage properties of ECD in an open circuit. The storage time can be determined by the variation in absorbance of a complex film in the coloring state with time in an open circuit. This is shown as Fig. 8, where ΔOD and ΔOD_0 represent the relative absorbance of ECD at time t and $t = 0$ of an open circuit after coloring at -2.8 V. When the circuit is open, the absorbance diminishes gradually. The half-life period is about 6 hours. After 16 hours, the absorbance decreases to 40% of the initial value. The contrast ratio of color is small, but the pale bluish violet is still distinct. The variation in absorbance involves the relative transference generation of positive and negative ions and the impurities in polymeric solid electrolytes.

CONCLUSION

$PVAEO_{16}$ is a kind of polymeric solid electrolyte which has both ion conduction and electrochromic properties. Its anion conductivity is 1.9×10^{-6} S/cm at ambient temperature. After adding a quantity of PEG400 and $KClO_4$ to $PVAEO_{16}$ with $EO/K = 18$, ion conductivity increases by about one order of magnitude. The ECD device based on $PVAEO_{16}$ has only one layer of film which maintains the oxidation and reduction, respectively, at the same time on two electrodes. Thus, the ECD functions as a double-faced display. ECD reversibly displays yellow and bluish violet under an applied voltage above 1.7 V. When the voltage is between -2.0 and $+2.0$ V, the coloring and the bleaching response times are 0.6 and 1.3 seconds, respectively. The storage time of bluish violet in an open circuit is more than 16 hours.

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