Material Design for Polymer/Azobenzene Liquid Crystal/Metal Salt Composite Films Possessing Thermo- and Photoresponsive Ionic Conductivity

KEIICHI KIMURA,* HISASHI MOROOKA, and MASAAKI YOKOYAMA

Chemical Process Engineering, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

SYNOPSIS

Various azobenzene derivatives and polymers were attempted as materials for thin composite films containing a polymer, a liquid crystal, and lithium perchlorate which can undergo ionic-conductivity switching induced by light or heat. Poly(vinyl chloride)-based composite films containing enantiotropic azobenzene liquid crystals **1** exhibited significant ionic-conductivity change based on thermo- and photoinduced phase transitions of **1**, the temperature dependence on the ionic conductivity reflecting the enantiotropic phase transition behavior of the liquid crystals. Marked, reversible ionic-conductivity switching on alternating irradiation of UV and visible lights was attained with the composite films containing **1**, especially **1** (n = 12). Incorporation of monotropic liquid crystals **3** to the composite films allowed bistability in the temperature dependence on the ionic conductivity. Employment of a polycarbonate resin and poly(methyl methacrylate) as the polymer material of the composite films gave similar ionic-conductivity changes to the poly(vinyl chloride) composite films, whereas polyethyleneoxide brought about some different results in the photoinduced ionic-conductivity change.

INTRODUCTION

Extensive research has been devoted to materials possessing switching character induced by external stimuli, which are attractive for applications to devices for display and memory. We have engaged in designing organic materials which can undergo ionic-conductivity switching by light or heat. It was thus found that polymer composite film consisting of poly(vinyl chloride) (PVC), azobenzene liquid crystal **1** (n = 8), 12-crown-4, and lithium perchlorate, when photoirradiated or heated, exhibit marked ionic-conductivity jump based on phase transitions of the azobenzene derivative.[1,2] In the composite film the ionic conductivity can be switched by irradiation with UV and visible lights at room temperature. This type of thin composite film with photochemically switchable ionic conductivity has been successfully applied to electrostatic imaging process.[2,3]

In order to seek after the higher performance in this type of ionically conducting composite films, we have attempted various azobenzene derivatives including enantiotropic and monotropic liquid crystals and polymers as the film material. In this publication we wish to report the material designing of composite films of polymer/azobenzene liquid crystal/lithium salt and their photo- and thermoresponsive ionic conductivities.

EXPERIMENTAL

Materials

Synthesis of p-octyl-p'-ethoxyazobenzene, **1** (n = 8), has been described elsewhere.[2] Similarly, p-alkyl-p'-ethoxyazobenzenes, **1** (n = 4, 7, 12), and p-alkyl-p'-methoxyazobenzenes, **2** (n = 4, 6), were prepared by conventional diazocoupling of phenol with corresponding alkyl anilines, followed by ethylation of the resulting alkyl azophenols.[2,4,5] The azobenzene derivatives **1** (n = 7 and 12) were de-

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 43, 1233–1239 (1991)
CCC 0021-8995/91/071233-07$04.00

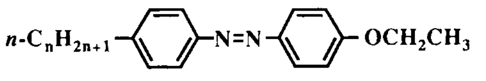
termined as follows. **1**(n = 7): orange crystal; mp: 49°C; ^{1}H-NMR (100 MHz, $CDCl_3$) δ 0.87(t, 3H, $C\underline{H}_3(CH_2)_5$), 1.2–1.8(m, 13H, $CH_3(C\underline{H}_2)_5$ and $C\underline{H}_3CH_2O$), 2.72(5, 2H, $PhCH_2$), 4.11(q, 2H, $PhOCH_2$), 6.9–8.0(m, 8H, aromatic H); M^+: 324.

ANAL. Calcd for $C_{21}H_{28}N_2O$: C, 77.74%; H, 8.70%; N, 8.63%. Found: C, 77.92%; H, 8.76%; N, 8.60%.

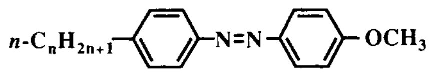
1(n = 12): orange crystal; mp: 55°C; ^{1}H-NMR(100 MHz, $CDCl_3$) δ 0.87(t, 3H, $C\underline{H}_3(CH_2)_{10}$), 1.2–1.8(m, 23H, $CH_3(C\underline{H}_2)_{10}$ and $C\underline{H}_3CH_2O$), 2.72(t, 2H, $PhCH_2$), 4.12(q, 2H, $PhOCH_2$), 6.9–8.0(m, 8H, aromatic H); M^+: 394.

ANAL. Calcd for $C_{26}H_{38}N_2O$: C, 79.14%; H, 9.71%; N, 7.10%. Found: C, 78.90%; H, 9.71%; N, 7.01%.

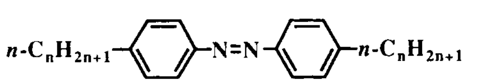
p,p'-Dialkylazobenzenes, **3**(n = 3, 5, 6, 8), were obtained by the procedures reported previously.[6] *p*-Octyl-*p'*-(1,4,7,10-tetraoxanonyl)azobenzene, **4**, was synthesized as follows: To NaH (10 mmol) dispersed in dry tetrahydrofuran (THF) (50 mL) was added a THF (25 mL) solution of *p*-hydroxy-*p'*-octylazobenzene (5 mmol) and then the mixture was stirred at 50°C for 1 h.



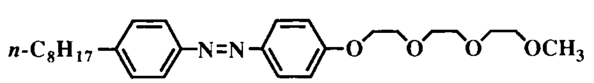
1(n=4,7,8,12)



2(n=4,6)



3(n=5,6,8)



4

To the resulting solution, which had been cooled to room temperature, was added a THF (20 mL) solution of 10-iodo-2,5,8-trioxadecane (5 mmol) dropwise in 1 h while stirring. Stirring of the reaction mixture at 50°C was continued for 24 h. After the reaction the mixture was treated with dilute HCl and the THF was evaporated off. After the chloroform extraction of the residue, silica-gel column chromatography (benzene/chloroform gradient) afforded a pure product of **4**: orange crystal; mp: 37°C; ^{1}H-NMR(100 MHz, $CDCl_3$): δ 0.88 (t, 3H, $C\underline{H}_3CH_2$), 1.2–1.7(m, 12H, $(C\underline{H}_2)_6CH_3$), 2.66(t, 3H, $PhCH_2$), 3.4–4.2(m, 15H, $(CH_2CH_2O)_3CH_3$), 7.0–7.9(m, 8H, aromatic H); M^+: 456.

ANAL. Calcd for $C_{27}H_{40}N_2O_4$: C, 71.02%; H, 8.83%; N, 6.14%. Found: C, 70.86%; H, 8.89%; N, 6.12%.

The mass spectra were taken on a JOEL JMS-DX303 mass spectrometer at the Instrumental Analysis Center.

PVC (polymerization degree of about 1100), bisphenol A-type polycarbonate resin (PC, Panlite L-1250), and poly(methyl methacrylate) (PMMA, MW 93300) were purified by reprecipitation from THF, THF, and 1,2-dichloroethane, respectively, in methanol. Polyethyleneoxide (PEO, MW of 5×10^6) was reprecipitated from acetonitrile in diethyl ether. The crown ether, 12-crown-4 (Aldrich), was used without further purification. Lithium perchlorate of analytical grade was employed.

Film Fabrication

The composite films for alternating-current (ac) conductivity measurements were fabricated by spin coating from THF on an indium tin oxide (ITO)-coated glass (2 × 2.5 cm) and dried overnight at 35°C under nitrogen stream. The composite films based on PVC, PC, and PMMA consist of 57.5 wt % polymer, 35.9 wt % azobenzene derivative, 0.6 wt % $LiClO_4$, and 6.0 wt % 12-crown-4. The typical composition for the PEO-based film was 56.5 wt % PEO, 42.4 wt % azobenzene derivative, and 1.1 wt % $LiClO_4$. The film thickness was about 1 μm unless otherwise noted.

Measurements

The ac conductivity measurements of composite films were made under a dry argon atmosphere by using a Solartron 1253 gain-phase analyzer and a Keithley 427 current amplifier. The applied voltage and frequencies were 1 V, and 0.1 Hz–20 kHz, respectively. The setup for measurement cell was as described elsewhere,[2] the cell assembly being Pt/film/ITO. The data was processed *in situ* by a microcomputer and Cole–Cole plot method[7] allowed the ionic conductivity values. The photoirradiation on the composite film was carried out from the ITO side of the cell assembly while being fixed on the cell holder of the measurement setup. Passing a light of a 500 W xenon lamp through color filters of Toshiba UV-D35 and V-Y43 afforded the UV (320–400 nm) and visible (> 400 nm) lights, respectively. The ionic-conductivity measurements for the temperature dependence were performed at increasing temperatures unless otherwise stated.

RESULTS AND DISCUSSION

Design of Azobenzene Derivatives

Various azobenzene derivatives were applied to the composite films of PVC/azobenzene derivative/$LiClO_4$/12-crown-4 and their thermo- and photoresponsive ionic conductivities were investigated. Employed here were azobenzene derivatives **1–4**, the phase transition temperatures of which were determined by differential scanning calorimetry (DSC) as summarized in Table I. Azobenzene derivatives **1** (n = 4, 7, 8, 12) and **2** (n = 4, 6) are enantiotropic liquid crystals and **3** (n = 5, 6, 8) monotropic liquid crystals. An azobenzene derivative carrying a short oligooxyethylene unit, **3**, does not possess any liquid crystal phase.

Table I Phase Transition Temperatures of Azobenzene Derivatives Employed

Azobenzene Derivative		T_{KN} (°C)[a]	T_{KI} (°C)[a]	T_{NI} (°C)[a]
1	n = 4	51	—	86
	7	49	—	89
	8	39	—	79
	12	55	—	82
2	n = 4	32[b]	—	47[b]
	6	40[b]	—	51[b]
3	n = 5	—	49[c]	38[c]
	6	—	38[c]	18[c]
	8	—	47[c]	41[c]
4		—	47	—

[a] Subscripts "K," "N," and "I" stand for crystal, nematic liquid crystal, and isotropic liquid, respectively.
[b] Cited from Ref. 4.
[c] Cited from Ref. 6.

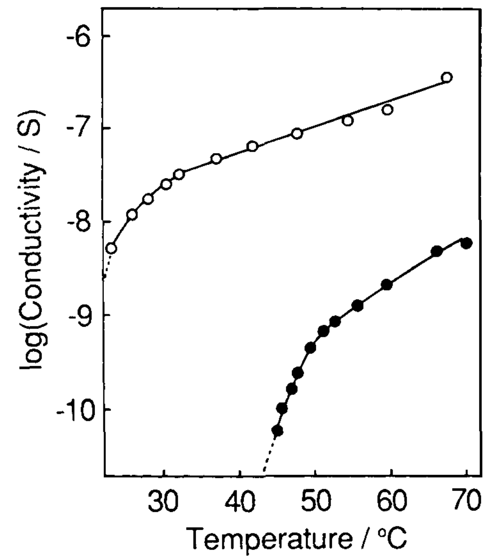


Figure 1 Temperature dependence of ionic conductivity for PVC/**1** (n = 4)-based composite film: (●) in the dark; (○) with UV-light irradiation.

Temperature dependence of ionic conductivity for the PVC-based composite film containing **1** (n = 4) is depicted in Figure 1. Under dark conditions the ionic conductivity was too low to measure below 40°C, but jumped up around 50°C. At higher temperatures than 50°C, the conductivity increased gradually. Definitely, the temperature at which the ionic conductivity is increased drastically corresponds to the phase transition temperature of azobenzene derivative **1** (n = 4) from crystal to nematic liquid crystal states (T_{NI}). The ionic conductivity jump around 50°C can, therefore, be attributed to the significant phase transition of the azobenzene derivative from crystal to liquid crystal states. On UV-light irradiation for 5 min, the ionic conductivity of the composite film was enhanced markedly compared to that without photoirradiation. Even at room temperature, high ionic conductivity was attained which increased monotonously with temperature. Absorption spectra of the composite film showed that under dark conditions *trans* form of azobenzene derivative **1** (n = 4) is predominant over the corresponding *cis* form in the composite film (Fig. 2). The azobenzene derivative in the film isomerizes from *trans* to *cis* forms by UV-light irradiation and vice versa by visible light irradiation. Polarizing-microscopic observation indicated that the UV-induced isomerization of the azobenzene derivative in the composite film from *trans* to *cis* forms results in its abrupt phase transition to isotropic liquid even at room temperature. That is, UV-light irradiation can change the phase of the azobenzene derivative in the composite film from crystal or liquid crystal to isotropic liquid. Thus, the marked phase transition of the azobenzene derivative in the composite film, in combination with a higher dipole moment of the *cis* azobenzene structure than the *trans* one, may cause such huge difference in the ionic con-

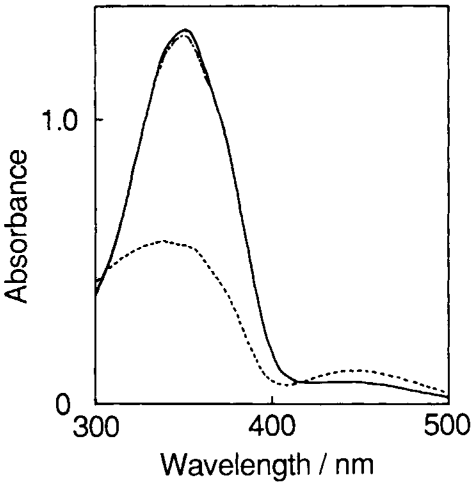


Figure 2 Spectral change in PVC/**1**(n = 4)-based composite film: (——) in the dark; (- - -) with 5-min UV-light irradiation; (- • -) with 5-min visible-light irradiation after the UV-light irradiation.

ductivity between with and without UV-light irradiation as in Figure 1.

The UV-enhanced ionic conductivity of the composite film based on PVC and **1**(n = 4) was decreased by visible-light irradiation accompanied by the *cis*-to-*trans* isomerization of the azobenzene derivative. Specifically, at room temperature, the ionic conductivity of the film could be switched almost reversibly by alternating irradiation of UV and visible lights. The temperature dependence and photoinduced switching of ionic conductivity in the PVC/**1**(n = 4)-based film resemble those in the PVC/**1**(n = 8) system reported previously.[1] Analogous ion-conducting behavior was found with the PVC-based composite films containing azobenzene derivatives with longer alkyl chains, **1**(n = 7 and 12). DSC measurements showed that those composite films possess respective phase-transition temperatures corresponding to those for azobenzene derivatives **1**(n = 4, 7, 8, 12) themselves. The phase transition behavior of the **1**-type azobenzene derivatives was, therefore, reflected in the thermo-induced ionic-conductivity jump in the resulted PVC-based composite films. Some difference was observed in the ionic-conductivity switching at room temperature among the four composite films of **1**(n = 4, 7, 8, 12). In any of the films, UV light enhanced the ionic conductivity drastically and turning off the UV light hardly diminished the high ionic conductivity. Visible light then restored the ionic conductivity to the initial extremely-low value. The composite film of **1**(n = 12) can undergo the most remarkable switching in the ionic conductivity of the four, its ionic-conductivity difference on UV- and visible-light irradiation being more than three orders of magnitude (Fig. 3). Accordingly, the ion-conducting composite film of **1**(n = 12) may be more useful than the previously reported one of **1**(n = 8) in the device applications.

Azobenzene derivatives **2**(n = 4, 6) exhibit a different characteristic from **1**-type azobenzene derivatives in the ion-conducting behavior of the PVC-based composite film. Figure 4 demonstrates temperature dependence of ionic conductivity for the PVC/**2**(n = 4)-based composite film. Any thermoinduced ionic-conductivity jump was not found in the composite film with and without UV-light irradiation, the ionic conductivity being augmented monotonously with rising temperature. The temperature dependence in the ionic conductivity obeys Arrhenius equation in the temperature range of 10–60°C the activation energy being about 30 kcal mol^{-1}. DSC measurements of the PVC/**2**(n = 4) composite film did not afford any endothermic peak corresponding to that for **2**(n = 4) itself, indicating that the azobenzene derivative is highly compatible with PVC. In the opposite sense, significant phase separation between PVC and azobenzene derivatives in the film is required for such thermoinduced ionic conductivity jump as obtained for the PVC/**1**-based composite films, although the azobenzene derivative should be dispersed finely and uniformly in the PVC film for the stable film fabrication. The ionic conductivity on UV-light irradiation was higher than that under dark conditions. Since any significant phase transition of **2**(n = 4) does not occur in this film due to its high compatibility with PVC, the

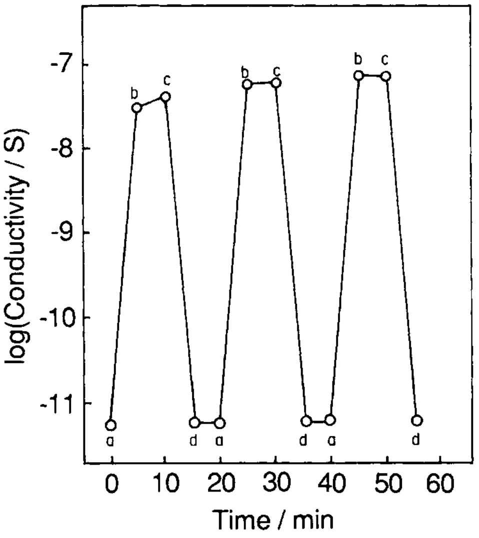


Figure 3 Photoinduced ionic-conductivity switching in PVC/**1**(n = 12)-based composite film: (a) UV light on; (b) UV light off; (c) visible light on; (d) visible light off.

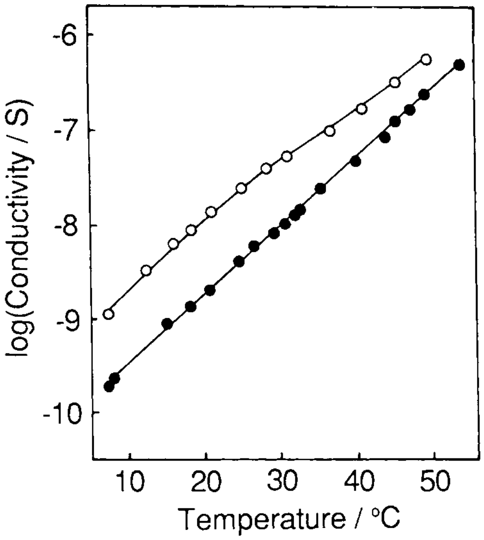


Figure 4 Temperature dependence of ionic conductivity for composite film of PVC/**2**(n = 4)-based composite film: (●) in the dark; (○) with UV-light irradiation.

ionic-conductivity difference between on UV-light irradiation and under dark conditions can be attributed primarily to dipole-moment difference of the *cis*- and *trans*-azobenzene configurations. Such monotonous temperature dependence in the ionic conductivity was also seen for the PVC-based composite film containing **2**(n = 6). Azobenzene derivative **2**(n = 6), however, seems to be somewhat different from **2**(n = 4) in the compatibility with PVC. When the **2**(n = 6) composite film was allowed to stand at 0°C for a whole day, some microcrystals of **2**(n = 6) were formed in the composite film. Once the crystal formation occurred, the **2**(n = 6) composite film exhibited such ionic-conductivity jump based on the phase transition of the azobenzene derivative itself as seen in the **1**-containing composite films. Thus the PVC/**2** composite films are not very much suited for the ionic-conductivity switching based on the phase transitions of the azobenzene derivative in the films.

The PVC-based composite films containing azobenzene derivatives **3**(n = 5, 6, 8) exhibit bistable ionic conductivities, reflecting their monotropic phase-transition behavior. An example for the bistable ionic conductivity is given in Figure 5 which shows temperature dependence of ionic conductivity for the PVC/**3**(n = 6)-based composite film. On increasing temperature under dark conditions, ionic conductivity of the film was too low to measure up to about 30°C. The conductivity jumped up considerably around 38°C, which corresponds to phase transition temperature of **3**(n = 6) from crystal to isotropic liquid (T_{KI}). On decreasing temperature, the enhanced ionic conductivity was reduced gradually down to about 20°C, down to which temperature (even below T_{KI}) any abrupt drop in the ionic conductivity was not observed, reflecting the fact that the azobenzene derivative is still in isotropic liquid state. Around 18°C, the transition temperature of **3**(n = 6) from isotropic liquid to nematic liquid crystal, a small drop in the conductivity occurred. Further cooling of the composite film finally allowed the azobenzene derivative to crystallize in the film, thus bringing about a sudden fall in the ionic conductivity. Similar bistability in the temperature dependence of ionic conductivity was attained under dark conditions for the PVC-based composite films containing the other **3**-type azobenzene derivatives. These PVC/**3**-based composite films possessing the ionic-conductivity bistability are intriguing for device applications. UV-light irradiation of the composite film enhanced the ionic conductivity markedly as seen in the composite films of **1** and **2** systems.

Azobenzene derivative carrying an oligooxyethylene chain, **4**, is an interesting material for the ion-conducting composite film we have been designing, because its oligooxyethylene chain can be expected to participate in the Li^+ conduction in the film. This azobenzene derivative does not have any liquid crystal property and exhibits a phase transition from crystal to isotropic liquid at 47°C. Time dependence of ionic conductivity for the PVC/**4**-based composite film is depicted in Figure 6. Under dark conditions, the ionic conductivity for the film of **4** was extremely low at room temperature but was raised

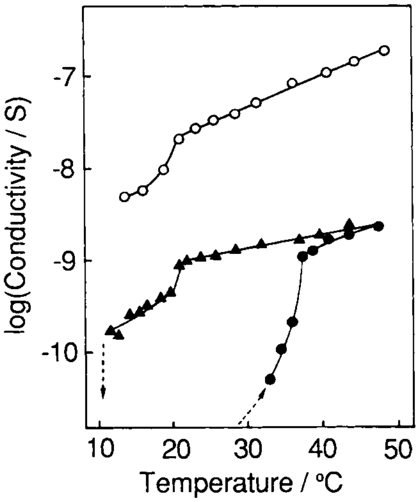


Figure 5 Temperature dependence of ionic conductivity for PVC/**3**(n = 6)-based composite film: (●) on increasing temperature in the dark; (▲) on decreasing temperature in the dark; (○) with UV-light irradiation.

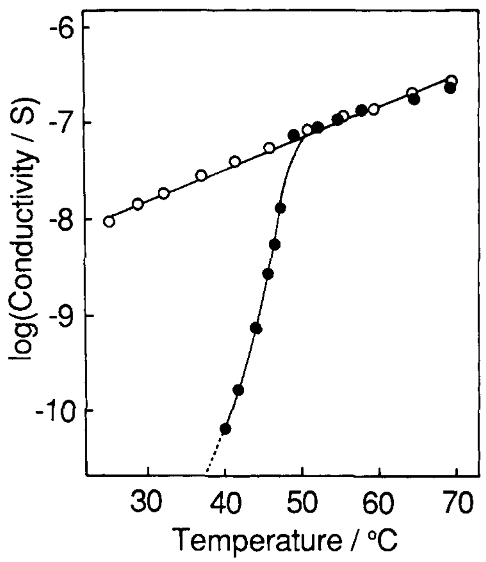


Figure 6 Temperature dependence of ionic conductivity for PVC/**4**-based composite film: (●) in the dark; (○) with UV-light irradiation.

markedly in the temperature range of 40–50°C. The conductivity enhancement is, of course, derived from the phase transition of **4** from crystal to liquid. After the phase transition temperature the ionic conductivity increased gradually. UV-light irradiation augmented the ionic conductivity at room temperature, probably due to the phase transition of **4** from crystal to isotropic liquid based on its *trans*-to-*cis* photoisomerization. At higher temperatures than 50°C, with and without UV-light irradiation, the composite film possesses almost the same temperature dependence of ionic conductivity. This **4**-containing composite film is definitely different from those of the other azobenzene derivatives in which the *cis*-abundant state of the azobenzene derivatives afford higher ionic conductivity than the corresponding *trans*-abundant state even when they both are in isotropic liquid state. This implies that the ionic conductivity in the composite film of **4** is affected greatly by its oligooxyethylene unit rather than its *cis–trans* configuration above 50°C, at which temperature **4** is in isotropic liquid state irrespective of its configuration. It is worth noting that the composite film of **4** is much more remarkable in the ionic-conductivity jump induced by heat under dark conditions than that for the composite films of **1**, **2**, and **3**, realizing a conductivity jump of 3 orders of magnitude. The PVC/**4**-based composite film may be promising for a device using thermoinduced switching of ionic conductivity.

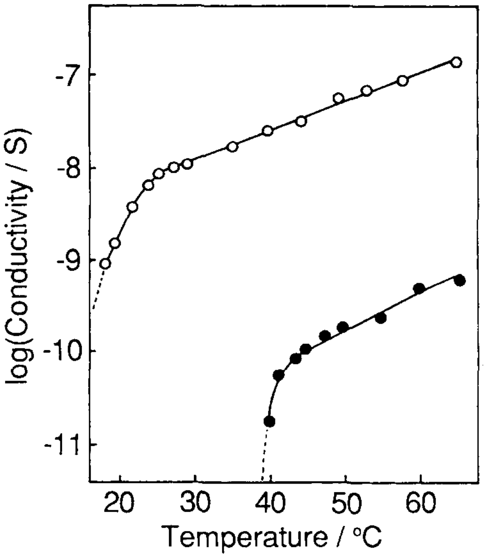


Figure 7 Temperature dependence of ionic conductivity for PC/**1**(n = 8)-based composite film: (●) in the dark; (○) with UV-light irradiation.

Selection of Polymeric Material

PC and PMMA, well-known optical organic materials, were attempted for their usefulness as an alternative of PVC for the composite film possessing thermo- and photoresponsive ionic conductivity. Employed as the azobenzene derivative was **1**(n = 8) and the composition of polymer, azobenzene derivative, $LiClO_4$, and 12-crown-4 was the same as the typical composition for the above-mentioned PVC-based films (see the Experimental section). Figure 7 shows temperature dependence of ionic conductivity for the PC/**1**(n = 8)-based composite

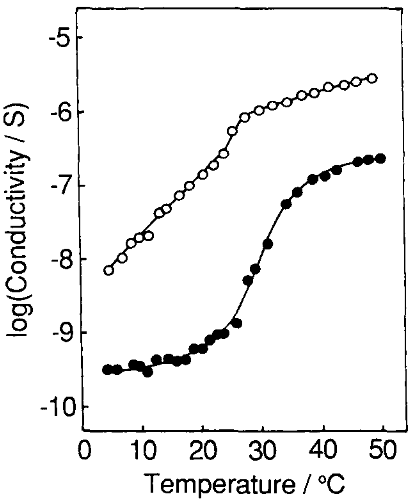


Figure 8 Temperature dependence of ionic conductivity for composite film of PEO/**1**(n = 8)/$LiClO_4$(56.5/42.4/1.1 wt %): (●) in the dark; (○) with UV-light irradiation.

film, which is quite similar to that for the corresponding PVC/**1**(n = 8)-based composite film.[1] The ionic conductivity for the PC/**1**(n = 8)-based film was enhanced appreciably by phase transition of the azobenzene derivative from crystal to liquid crystal states. Also, UV light allowed the ionic conductivity to increase markedly, especially at room temperature. This was the case for a corresponding PMMA/**1**(n = 8)-based composite film. A difference between the PVC-based film and PC- and PMMA-based films is that the ionic conductivity for the former composite film is generally low than the latter ones, probably due to the lower dielectric constants for PC and PMMA.

It is of much interest to see how the ion-conducting composite film works if PEO, which itself is an efficient ion-conducting polymer,[8] is employed as the polymer material of the film instead of PVC. In the temperature dependence of ionic conductivity for the PEO/**1**(n = 8)/$LiClO_4$(56.5/42.4/1.2 wt %) composite film, a thermoinduced jump of ionic conductivity was also found which is based on the crystal-to-liquid crystal phase transition of the azobenzene derivative (Fig. 8). The thermoinduced jump of ionic conductivity was considerably attenuated in a PEO/**1**(n = 8)/$LiClO_4$(65.8/32.9/1.3 wt %), which possesses a lower content of azobenzene derivative, although its polymer/azobenzene derivative ratio is comparable to that for the composite films based on the other polymers (Fig. 9). This fact suggests that the ion-conducting ability of PEO, the polymer material for the composite film, contributes to the ionic conductivity of the PEO-based composite films to a certain extent unlike the PVC-based composite films. The PEO/**1**(n = 8)/$LiClO_4$(65.8/32.9/1.3 wt %) also can undergo photoinduced ionic-conductivity switching at room temperature as demonstrated in Figure 10. In the ionic-conductivity switching, too, the PEO-based composite film differs from the corresponding PVC-based films in that the UV-enhanced ionic conductivity can be switched off only by turning off the UV light without further visible-light irradiation.

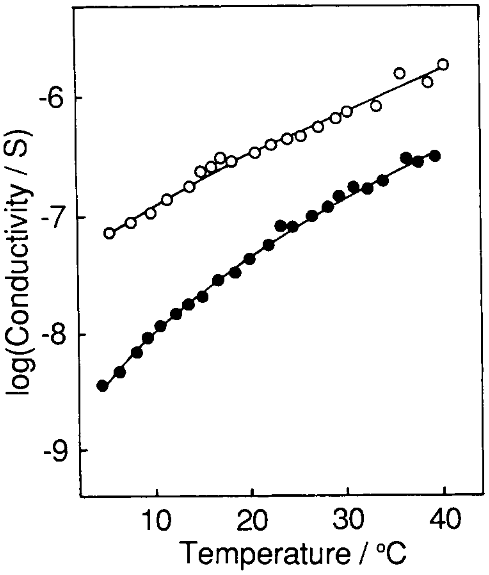


Figure 9 Temperature dependence of ionic conductivity for composite film of PEO/**1**(n = 8)/$LiClO_4$(65.8/32.9/1.3 wt %): (●) in the dark; (○) with UV-light irradiation.

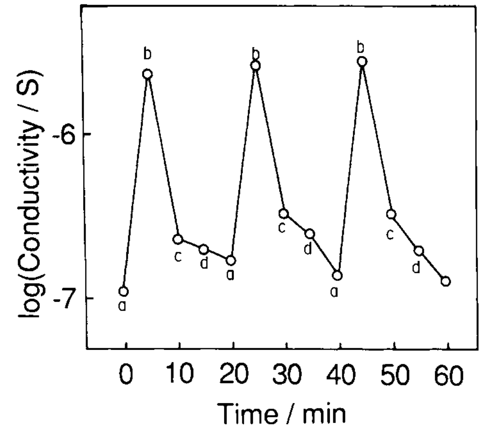


Figure 10 Photoinduced ionic-conductivity change in composite film of PEO/**1**(n = 8)/$LiClO_4$(56.5/42.4/1.1 wt %): (a) UV light on; (b) UV light off; (c) visible light on; (d) visible light off.

REFERENCES

1. K. Kimura, T. Suzuki, and M. Yokoyama, *Chem. Lett.*, **1989,** 227.
2. K. Kimura, T. Suzuki, and M. Yokoyama, *J. Phys. Chem.*, **94,** 6090 (1990).
3. K. Kimura, T. Suzuki, and M. Yokoyama, *J. Chem. Soc. Chem. Commun.*, **1989,** 1570.
4. R. Steinstrasser and L. Pohl, *Z. Naturforsch.*, **26b,** 577 (1971).
5. L. E. Knaak and H. M. Rosenberg, *Mol. Cryst. Liq. Cryst.*, **17,** 171 (1972).
6. W. H. de Jeu and J. van der Veen, *Philips Res. Repts.*, **27,** 172 (1972).
7. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9,** 341 (1941).
8. J. M. Parker and P. V. Wright, *Polymer*, **14,** 589 (1973).

Received August 14, 1990
Accepted January 3, 1991