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Synthesis of Crowned Azobenzene Derivatives and Their Photoresponsive Ion-Conducting Behavior

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Several azobenzene derivatives incorporating a crown ether moiety have been synthesized. Some of them possess liquid-crystal characteristics (nematic), i.e., enantiotropic or monotropic liquid crystal. The phase transition properties depend upon the size of crown ether ring, the length of alkyl chain, and the existence of carbonyl linkage in the azobenzene derivatives. Polymer composite films containing a crowned azobenzene and an alkali-metal salt undergo photoinduced switching of ionic conductivity, which is ascribable to the phase transition of the crowned azobenzene induced by its photoisomerization. Effects of kinds of the alkali-metal salts and the crowned azobenzenes on the ion-conducting behavior of the composite films are also discussed.

Introduction

Azobenzene, a typical photochromic compound, experiences photochemical isomerization; the isomerization from its trans to cis form is caused by UV-light irradiation and vice versa by visible-light irradiation or heating. This photoisomerization can change the physical properties of azobenzene derivatives. We have already designed photoresponsive ion-conducting composite films containing an azobenzene liquid crystal, taking advantage of the photoinduced phase transition of the azobenzene liquid crystal.[1,2] The photoinduced ionic-conductivity switching system has been successfully applied to electrostatic imaging.[3]

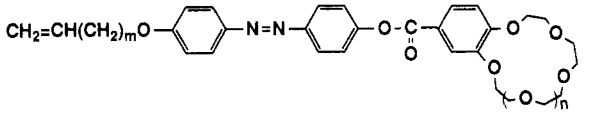
Crown ethers, on the other hand, can be expected to play an important role in ionic conduction, since they complex alkali-metal ions to form separated ion pairs. For instance, addition of crown ethers to ion-conducting systems often enhances their ionic conductivities. This prompted us to combine a crown ether moiety for the cation-binding part with an azobenzene moiety for the photochromic part and to synthesize azobenzene derivatives incorporating a crown ether moiety, what we call crowned azobenzenes.

In this publication, we report the syntheses and phase transition behaviors of crowned azobenzenes **1**–**5** (Chart I) and the photoresponsive ionic conductivity of ion-conducting composite films containing the crowned azobenzenes.

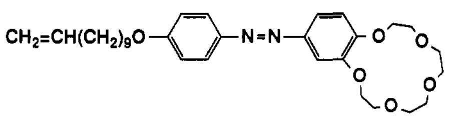
Experimental Section

Syntheses of Crowned Azobenzenes. *General Procedure for Crowned Azobenzenes 1–4.* 4-(Alkenyloxy)-4′-hydroxyazobenzenes were prepared by Williamson reaction of a corresponding alkenyl bromide with 4,4′-dihydroxyazobenzene (KOH, ethanol, reflux), which was in turn obtained by treating 4-nitrophenol with KOH. To a dry chloroform solution (30 cm^3) of 4′-carboxybenzocrown ether (9 mmol) was dropwise added thionyl chloride (22.5 mmol). The mixture was refluxed for 3 h, and then the solvent and excess thionyl chloride were evaporated off to yield 4′-chlorocarbonylbenzocrown ether.[4] The crude chlorocarbonylbenzocrown ether was dissolved in dry benzene (30 cm^3) and then a dry benzene solution containing 4-(alkenyloxy)-4′-hydroxyazobenzene (9 mmol) and dry pyridine (18 mmol) was added dropwise while stirring. The mixture was refluxed for 3 h. After cooling to room temperature, the reaction mixture was filtrated and then evaporated to dryness. The residue dissolved in chloroform (200 cm^3) was washed successively with a 10% citric acid solution and water. The chloroform solution was dried over $MgSO_4$. Evaporation of the chloroform afforded a crude product, which was purified by recrystallization from ethanol.

Chart I



	m	n
1	9	1
2	9	2
3	1	1
4	1	2



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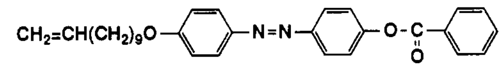

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(4′-{4-(10-Undecenyloxy)phenylazo}phenyl)oxycarbonylbenzo-15-crown-5 (1). The reaction of 4-{4-(10-undecenyloxy)phenylazo}-4′-hydroxyazobenzene with 4′-chlorocarbonylbenzo-15-crown-5 afforded compound **1**. Yellow crystal (39%): δ_H (60 MHz, $CDCl_3$) 1.4–2.4 (16H, m, $(CH_2)_8CH_2O$), 3.9–4.5 (18H, m, OCH_2CH_2O and CH_2OPh), 4.9–5.4 (2H, m, $CH_2{=}CH$), 5.6–6.0 (1H, m, $CH_2{=}CH$), 7.0–8.3 (11H, m, aromatic H); *m/z* (% rel

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[1] Kimura, K.; Suzuki, T.; Yokoyama, M. *J. Phys. Chem.* **1990,** *94,* 6090.

[2] Kimura, K.; Morooka, H.; Yokoyama, M. *J. Appl. Polym. Sci.* **1991,** *43,* 1233.

[3] Kimura, K.; Suzuki, T.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* **1989,** 1570.

[4] Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975,** *97,* 3462.

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intensity) 661 (M^+, 60), 295 (100). Anal. Calcd for $C_{38}H_{48}N_2O_8$: C, 69.07; H, 7.32; N, 4.24. Found: C, 69.33; H, 7.33; N, 4.24.

*(4′-{4-(10-Undecenyloxy)phenylazo}phenyl)oxycarbonylbenzo-18-crown-6 (**2**).* Compound **2** was prepared by the reaction of 4-{4-(10-undecenyloxy)phenylazo}-4′-hydroxyazobenzene with 4′-chlorocarbonylbenzo-18-crown-6. Yellow crystal (73%): δ_H (60 MHz, $CDCl_3$) 1.4–2.6 (16H, m, $(CH_2)_8CH_2O$), 3.8–4.4 (22H, m, OCH_2CH_2O and CH_2OPh), 5.0–.5.5 (2H, m, $CH_2{=}CH$), 5.8–6.6 (1H, m, $CH_2{=}CH$), 7.1–8.4 (11H, m, aromatic H); *m/z* (% rel intensity) 704 (M^+, 5), 339 (100). Anal. Calcd for $C_{40}H_{52}N_2O_9$: C, 68.16; H, 7.44; N, 3.98. Found: C, 68.02; H, 7.42; N, 3.87.

*(4′-(4-(Allyloxy)phenylazo)phenyl)oxycarbonylbenzo-15-crown-5 (**3**).* The reaction of 4-(4-(allyloxy)phenylazo)-4′-hydroxyazobenzene with 4′-chlorocarbonylbenzo-15-crown-5 afforded compound **3**. Yellow crystal (33%): δ_H (60 MHz, $CDCl_3$) 3.7–4.5 (16H, m, OCH_2CH_2O and CH_2OPh), 4.6–4.9 (2H, d, J = 6 Hz, $CH_2{=}CH{-}CH_2$), 5.3–5.8 (2H, m, $CH_2{=}CH$), 6.0–6.5 (1H, m, $CH_2{=}CH$), 7.0–8.3 (11H, m, aromatic H); *m/z* (% rel intensity) 548 (M^+, 11), 295 (100). Anal. Calcd for $C_{30}H_{32}N_2O_8$: C, 65.68; H, 5.88; N, 5.11. Found: C, 65.31; H, 5.81; N, 4.92.

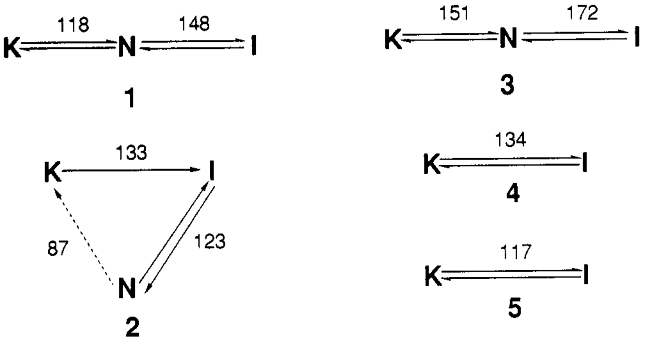
*(4′-(4-(Allyloxy)phenylazo)phenyl)oxycarbonylbenzo-18-crown-6 (**4**).* Compound **4** was prepared by the reaction of 4-(4-(allyloxy)phenylazo)-4′-hydroxyazobenzene with 4′-chlorocarbonylbenzo-18-crown-6. Yellow crystal (35%): δ_H (60 MHz, $CDCl_3$) 3.7–4.5 (16H, m, OCH_2CH_2O and CH_2OPh), 4.6–4.8 (2H, d, J = 6 Hz, $CH_2{=}CH{-}CH_2$), 5.2–5.8 (2H, m, $CH_2{=}CH$), 5.9–6.7 (1H, m, $CH_2{=}CH$), 6.9–8.3 (11H, m, aromatic H); *m/z* (% rel intensity) 592 (M^+, 6), 339 (100). Anal. Calcd for $C_{32}H_{36}N_2O_9$: C, 64.85; H, 6.12; N, 4.73. Found: 64.56; H, 6.08; N, 4.67.

*Syntheses of 4′-{4-(10-Undecenyloxy)phenylazo}benzo-15-crown-5 (**5**).* 4′-(4-Hydroxyphenylazo)benzo-15-crown-5 was prepared by diazotization-coupling reaction of 4′-aminobenzo-15-crown-5 and phenol in a way similar to a reported procedure.[5] The (hydroxyphenyl)azobenzocrown ether (7.7 mmol) and KOH (9.1 mmol) were added to dry ethanol (300 cm^3), and the mixture was then refluxed for 1 h. To the refluxing mixture was dropwise added 10-undecenyl bromide (8.5 mmol). The reflux was continued for 4 days. Solvent evaporation afforded crude product, which was purified by recrystallization from ethanol. Yellow crystal (43%): δ_H (60 MHz, $CDCl_3$) 1.1–2.3 (16H, m, $(CH_2)_8CH_2O$), 3.7–4.5 (18H, m, OCH_2CH_2O and CH_2OPh), 4.8–5.3 (2H, m, $CH_2{=}CH$), 5.5–6.5 (1H, m, $CH_2{=}CH$), 6.9–8.2 (7H, m, aromatic H); *m/z* (% rel intensity) 540 (M^+, 100). Anal. Calcd for $C_{31}H_{44}N_2O_6$: C, 68.86; H, 8.20; N, 5.18. Found: C, 68.91; H, 8.25; N, 5.16.

Other Chemicals. The model compound 4-(10-undecenyloxy)-4′-benzoyloxyazobenzene (**6**) was prepared in a way similar to the procedure for **1**. The polyester elastomer poly(butylene terephthalate) (Pelprene 40-H, Toyobo) containing an oligooxybutylene moiety with an average molecular weight of 1000 as a soft segment (T_g = −80 °C) was purified by repeated reprecipitation from chloroform in methanol. All other reagents were the best grade and were employed as received, unless otherwise specified.

Composite Film Fabrication. Composite films for the ionic conductivity measurements were prepared on indium-tin-oxide-coated (ITO) glass plates (2 × 2.5 cm) by a spin-coating technique from chloroform. For instance, polyester (26.3 mg), crowned azobenzene (7.7 mg), and $LiClO_4$ (0.021 mg) were dissolved in 0.42 cm^3 of chloroform, and 0.2 cm^3 of the solution was used for each spin coating to yield a film with a thickness of about 3 μm after drying for a whole day at 50 °C under a nitrogen stream. As a counter electrode, a Au electrode of 6-mm diameter was evaporated on the composite-film-coated ITO glass before the ac impedance measurements. Any of the composite films for other alkali metal salts contained an equimolar amount of respective salt. The typical composite films contain about 77.3 wt % polyester, about 22.6 wt % crowned azobenzene derivative, and 0.1–0.06 wt % alkali metal salt. The composite films for isothermal transient ionic-current measurements (several tens of micrometers thickness) were cast with the same composition.

Scheme I[a]



[a] K, crystal; N, nematic liquid crystal; I, isotropic liquid. The temperatures are given in °C.

Measurements. The procedure and cell setup for the ionic conductivity measurements were as described elsewhere.[1] The measurement cell was controlled strictly by a thermostated heater combined with a cool argon stream. The photoirradiation on the composite films during the ac measurements was undertaken from the ITO side of the cell assembly. The UV (320–400 nm) and visible (>400 nm) lights were obtained by passing a light of a 500-W xenon lamp through Toshiba UV-D35 and V-Y43 glass filters, respectively. Differential scanning calorimetry (DSC) of the composite films was undertaken at a scan rate of 5 °C min^{-1} with a Daini Seikosha DSC220C (+UV-1) differential scanning calorimeter. Photoirradiation on DSC was made through optical-fiber wave guides, by using a UV light of 365 nm with a light intensity of 25 mW cm^{-2}. The isothermal transient ionic-current measurements were carried out at 60 °C in a similar way to a procedure reported previously,[6,7] using the cell setup with a Au/Au or Li/Li electrode pair for the ionic conductivity measurements and a programmable electrometer. After application of an appropriate direct-current voltage (5 V) across the films for 3 h, the polarity was switched rapidly and the transient current was then monitored every second.

Results and Discussion

Phase Transition Behavior of Crowned Azobenzenes. Several crowned azobenzene derivatives, **1**–**5**, were synthesized, which carry a long or short aliphatic chain and a 15-crown-5 or 18-crown-6 ring. Crowned azobenzene **5** does not include any ester linkage. A model compound carrying no crown ether moiety **6** was also prepared for comparison.

Phase transition behaviors of the crowned azobenzenes, which are elucidated by DSC measurements and micrographic observation, are summarized in Scheme I. Crowned azobenzene **1**, which carries a 15-crown-5 moiety, shows nematic liquid-crystal phase in both heating and cooling steps, being characteristic of enantiotropic liquid crystal. The phase transition behavior for **1** is essentially the same as that for the corresponding model compound without any crown moiety, **6**. The similar crowned azobenzene incorporating a short aliphatic chain instead of the long one, **3**, also shows enantiotropic liquid crystal. The azobenzene derivative with a 18-crown-6 ring is a little different in the phase transition behavior from the corresponding 15-crown-5 derivatives. Monotropic liquid-crystal formation was found in the crowned azobenzene possessing a long aliphatic chain, **2**; any liquid-crystal phase does not appear on heating, while a nematic liquid-crystal phase does on cooling. Any liquid-crystal phase was not

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(5) Kitazawa, S.; Kimura, K.; Shono, T. *Bull. Chem. Soc. Jpn* **1983**, *56*, 3253.

(6) Greeuw, G.; Hoenders, B. J. *J. Appl. Phys.* **1984**, *55*, 3371.

(7) Watanabe, M.; Rikukawa, M.; Sanui, K.; Ogata, N. *J. Appl. Phys.* **1985**, *58*, 736.

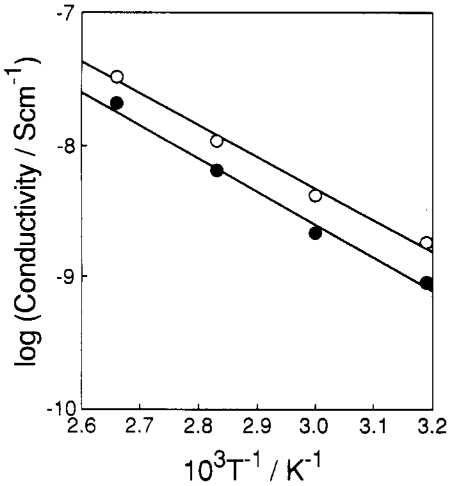

Figure 1. Temperature dependence of ionic conductivity for composite film containing 1 under dark (●) and UV-irradiated (○) conditions.

observed in the corresponding 18-crown-6 derivative with the short aliphatic chain, 4. The difference in the phase transition between the 15-crown-5 and 18-crown-6 derivatives is definitely derived from the crown ether moiety bulkiness, which is likely to prevent ordered aggregation of the crowned azobenzenes and thereby liquid-crystal formation. Thus, the azobenzene derivatives with a 18-crown-6 ring, the bulkier crown ring, are harder to form liquid crystal (nematic) than the corresponding derivatives with a 15-crown-5 ring. The crowned azobenzene derivative not containing an ester linkage, 5, did not show any liquid-crystal phase. This suggests that the ester linkage (carbonyl group) plays a very important role in forming liquid crystal.

Photoresponsive Ionic Conductivity of Crowned Azobenzene-Containing Composite Films. Ion-conducting composite films consisting of a polyester elastomer, $LiClO_4$, and crowned azobenzene 1 were first fabricated, and their photoresponsive ion-conducting behaviors were investigated. Figure 1 depicts the temperature dependence of ionic conductivity for the 1-containing composite films, which obeys linear Arrhenius equation under dark conditions. This ion-conducting behavior is quite different from that for typical amorphous polymer electrolytes.[8] The Arrhenius-type relationship implies that the ionic conduction in the crowned azobenzene-containing composite film is not related to segmental motion of the polyester elastomer. It is worth noting that the ionic conductivity is enhanced by UV-light irradiation on the composite film. Visible-light irradiation then restored the ionic conductivity to the initial low value. Alternating irradiation of UV and visible lights on the composite film realized ionic-conductivity switching in the temperature range from 100 °C to room temperature. The photoinduced switching of ionic conductivity is quite reversible (Figure 2).

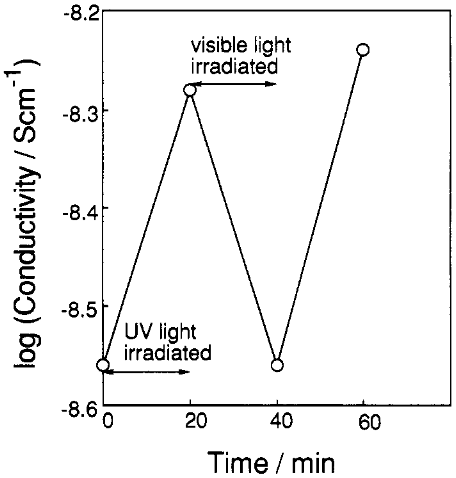

Figure 2. Photoinduced switching of ionic conductivity for 1-containing composite film. Each point indicates ionic conductivity of saturated level after 20-min photoirradiation.

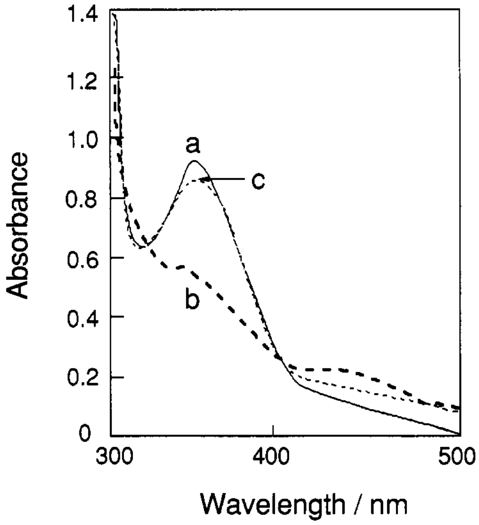

Figure 3. Absorption-spectral changes for 1-containing composite film on photoirradiation: (a) under dark conditions; (b) on UV-light irradiation for 20 min; (c) on visible-light irradiation for 20 min after the UV-light irradiation. Photochemical DSC thermogram of 1 and comparison with thermogram under dark conditions: (a) while irradiating UV light; (b) under dark conditions.

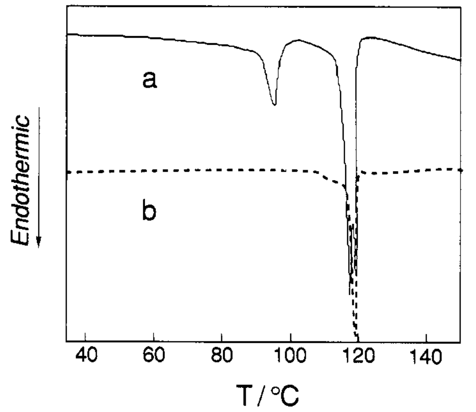

Figure 4. Photochemical DSC thermogram of 1 and comparison with thermogram under dark conditions: (a) while irradiating UV light; (b) under dark conditions.

Figure 3 shows absorption-spectral changes of the 1-containing composite film on photoirradiation. Without photoirradiation, the film possesses a strong peak at 350 nm in its absorption spectrum, suggesting that the crowned azobenzene in the film is in trans form. The absorption decreased by UV-light irradiation, while a new peak based on the corresponding cis isomer of 1 appeared around 430 nm. Visible light again caused increase of the 350-nm absorption peak together with disappearance of the 430-

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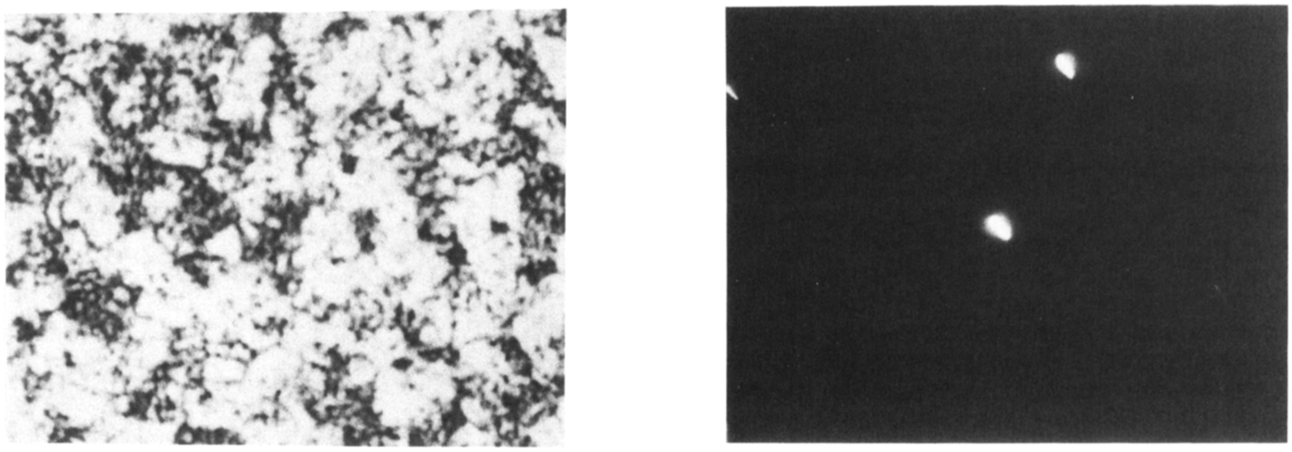
[8] Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.



without photoirradiation

after UV-light irradiation

Figure 5. Optical micrographs of 1-containing composite film under dark and UV-irradiated conditions at 60 °C.

nm peak. The crowned azobenzene can, therefore, isomerize from its trans to cis form by UV-light irradiation and vice versa by visible-light irradiation even in the composite film. What happens by this photoisomerization of the crowned azobenzene in the composite film? Photochemical DSC, which is DSC while irradiating UV light, of crowned azobenzene **1**, gave an important information (Figure 4). In the "dark" DSC thermogram of **1**, a strong endothermic peak was seen which is based on the phase transition of the crowned azobenzene derivative from crystal to nematic phase, as already mentioned. In the photochemical DSC thermogram, on the other hand, a broad peak in the temperature range between room temperature and 100 °C was found besides a sharp peak for the phase transition to nematic liquid crystal. Obviously, this broad endothermic peak is derived from the photoisomerization of the crowned azobenzene derivative from its trans to cis form, being assigned to phase transition of the cis azobenzene derivative and/or a mixture of the trans and cis ones. Optical micrographs of the **1**-containing composite film showed clearly what the phase of **1** for the broad DSC peak is (Figure 5). Under dark conditions at 60 °C, there exists some crystal phase in the composite film. UV-light irradiation, however, brought about a dark sight in the film under crossed nicols, thus resulting in a phase transition of the crowned azobenzene from its crystal to isotropic liquid phase. As a result, the UV-light irradiation led to significant phase transition of **1**, from its solid to liquid state. The drastic phase transition of the crowned azobenzene induced by its photoisomerization probably thus raised the mobility and/or density of the ion-conducting carriers in the composite film and thereby enhanced the ionic conductivity.

It is of much interest to compare the crowned azobenzene system with the corresponding system of its model compound containing no crown ether moiety in the molecule, **6**. The composite films which contain 1:1 mixture of **6** and benzo-15-crown-5 instead of crowned azobenzene **1** exhibited similar photoresponse of ionic conductivity to the **1**-containing system. That is to say, alternating irradiation of UV and visible lights on the composite film of the **6**/benzo-15-crown-5 mixture increased and decreased its ionic conductivity, respectively. The magnitude in the photoinduced ionic-conductivity change (ratio of UV-light-enhanced and visible-light-attenuated ionic conductivities) is, however, about 1.6 for the system containing the mixture of **6** and benzo-15-crown-5, being lower than that (about 2.0) for the corresponding system containing crowned azobenzene **1**. In general, crown ether moiety promotes ion-pair separation by its cation complexation, which in turn enhances the ion conduction. Naturally, the ion-conducting carriers exist on the periphery of the crown ether moiety. For the system containing the crowned azobenzene, where its crown moiety is connected with the azobenzene moiety forming a domain for the photoinduced phase transition, the ion-conducting carriers are almost always in the domain participating the photoinduced ionic-conductivity change. Significant ionic-conductivity switching is, therefore, considered to occur in the crowned azobenzene system. On the other hand, for the system containing the mixture of the model compound and benzo-15-crown-5, where crown-separated ions (the ion-conducting carrier) are not necessarily in the azobenzene domain, the photoinduced ionic-conductivity change becomes less intensive.

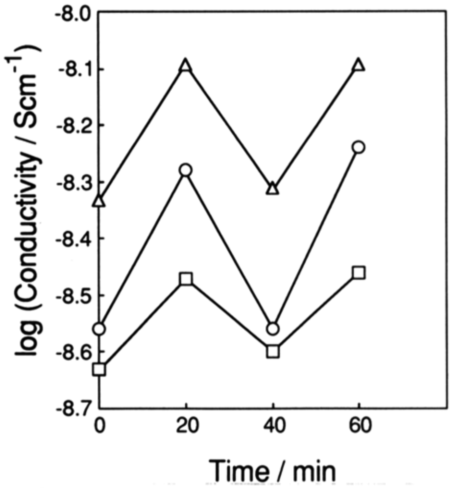


Figure 6. Comparison in behavior of photoinduced ionic-conductivity switching among 1-composite films containing $LiClO_4$ (○), $NaClO_4$ (△), and $KClO_4$ (□).

Variation of alkali metal perchlorates in the composite films of polyester/crowned azobenzene **1**/metal salt did not modify significantly the behavior for the $LiClO_4$-containing film in the photoinduced switching of ionic conductivity (Figure 6). This implies that the metal cations do not contribute to the ionic conductivity and the switching very much. Isothermal transient ionic-

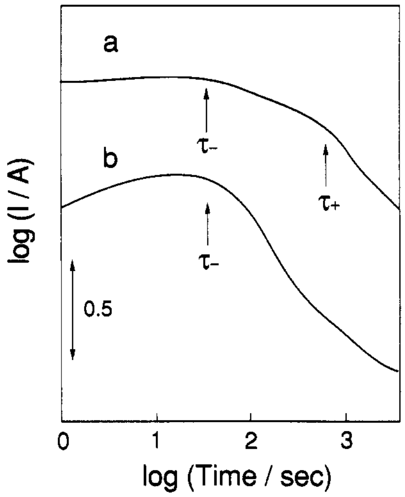


Figure 7. Isothermal transient ionic-current measurements for composite films containing 1 and $LiClO_4$. (a) Au/sample/Au system; (b) Li/sample/Li system. τ_+ and τ_- stand for transient times of the cation and anion, respectively.

current measurements shows that anions migrate much faster than cations in the composite film containing 1 and $LiClO_4$ (Figure 7). The transport number of the anion (ClO_4^-) in the composite film can be estimated as 0.8–0.9. The anion contribution was also supported by the fact that such a great ionic-conductivity change cannot be induced by photoirradiation in a single-ionic (cationic) conducting system which is composed of lithium poly(perfluorosulfonate) (Nafion Li^+ salt) and crowned azobenzene 1.

Similar behavior in the ionic conduction and the photoinduced switching as seen in Figures 1 and 2 was also found in the polyester/$LiClO_4$ composite films containing other crowned azobenzenes 2 and 3. However, the composite films containing crowned azobenzene 4 or crowned azobenzene with no ester linkage 5 hardly exhibit any significant ionic-conductivity change on photoirradiation. This is due to the fact that crowned azobenzenes 4 and 5 cannot undergo the phase transition from crystal to liquid state irrespective of their distinct photoisomerization from the trans to cis form.

In conclusion, the crowned azobenzene derivatives 1–3 are useful key materials for photoresponsive ion-conducting composite films.