Photoresponsive Ion-Conducting Behavior of Polysiloxanes Carrying a Crowned Azobenzene Moiety at the Side Chain

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ABSTRACT: Three polysiloxane derivatives carrying a crowned azobenzene, that is, an azobenzene derivative with a crown ether moiety, at the side chain have been designed to enhance aggregation of the crowned azobenzene molecules. Crowned azobenzene polysiloxanes 1 and 2 exhibited a smectic liquid crystal phase, whereas their corresponding monomeric crowned azobenzenes did not. Polymer composite films containing one of the crowned azobenzene polysiloxanes and an alkali-metal salt underwent remarkable photoinduced ionic-conductivity switching, which is ascribable to structural changes in its highly-oriented side chains, induced by isomerization of its azobenzene moiety. The ionic conductivity was drastically decreased by UV light and then restored to the initial value by visible light. The photochemical switching tendency of ionic conductivity for the crowned azobenzene polysiloxane systems is opposed to that for the corresponding monomeric systems. The photoresponse mechanism is also discussed.

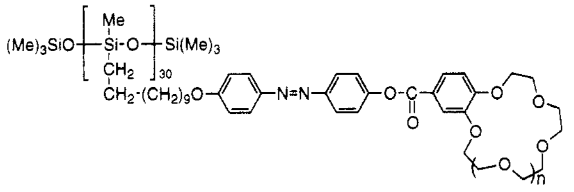
Introduction

Photoinduced isomerism of azobenzene between its trans and cis forms is well-known photochromism,[1] enjoying widespread use for photochemical control of physical properties. The photoisomerization proceeds in macromolecules as well as small molecules. Specifically, in macromolecular photochemistry involving azobenzene moieties, the microstructural changes by trans–cis isomerism of the azobenzene moieties often bring about drastic changes in the macromolecular rheology.[2] Also, *trans*-azobenzene moieties are also useful mesogens for liquid crystal compounds in both small molecules and macromolecules due to their rigid structures.[3] Since *cis*-azobenzene moieties cannot contribute to liquid crystal phases due to their bent structures, photoisomerization of azobenzene derivatives capable of forming liquid crystal phases may cause pronounced phase transition.

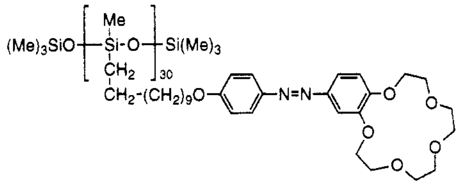
Crown ether derivatives can be sites for hopping of ion-conducting carriers, working as their neutral states for cations and as their cation-bound states for anions. Crown ether polymers, therefore, are candidates for ion-conducting materials.[4–7] If crown ether moieties are arranged so regularly that adjacent crown moieties get close to one another, ion-conducting carriers of either cations or anions may migrate effectively on the crown moieties as seen in biological ion channels. Several attempts have been made to attain ordered arrangements of crown moieties, using rigid polymers,[8,9] and liquid crystals.[10,11]

Using azobenzene derivatives incorporating a crown moiety, what we call crowned azobenzenes, we have been aiming at construction of ion-conducting systems which undergo effective ionic conduction and photoinduced ionic-conductivity switching induced by isomerization of their azobenzene moieties. In polymer composite films containing a lipophilic azobenzene derivative with a monoaza-15-crown-5 moiety, the crowned azobenzene molecules can aggregate orderly, effecting cation-selective conduction.[12] Crowned azobenzenes such **5** and **6**, when isomerized between their trans and cis forms by photoirradiation, underwent abrupt phase transition between solid and liquid states. The photoinduced phase transition has thus led to marked ionic-conductivity changes in composite films containing a crowned azobenzene.[13]

In this study, we have envisaged that crowned azobenzenes, incorporated into a polymer at the side chain, are most likely to be arranged orderly by formation of liquid crystal polymers,[14,15] realizing specific ionic conduction. Then, photoisomerization of the azobenzene moieties may induce a phase transition in the liquid crystal polymers, that is, a collapse of the regularity in crown moiety arrangement, in turn resulting in ionic-conductivity changes. This paper is concerned with the photoinduced phase transition of polysiloxane-type crowned azobenzenes 1–3,and thereby the ionic-conductivity switching in composite films containing one of them and an alkali-metal salt. Comparison of the photoinduced switching of ionic conductivity is also made between the crowned azobenzene



1; n=1
2; n=2



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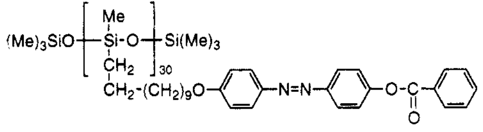

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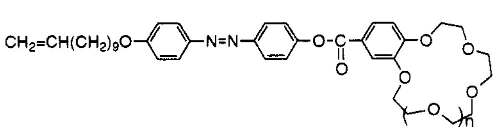
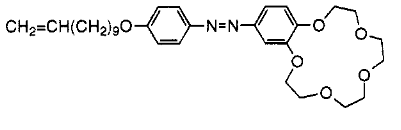


5; n=1
6; n=2



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polysiloxanes and their corresponding monomeric derivatives.

Experimental Section

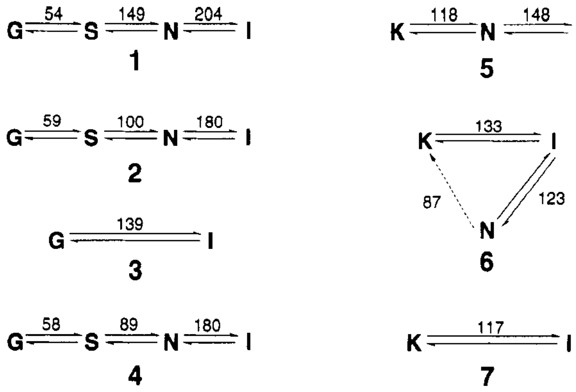
Syntheses of Crowned Azobenzene Polysiloxane. Poly(methylhydrosiloxane) ($M_n = 2270$, average polymerization degree of ca. 30) was used as received from Aldrich. ω-Olefinic crowned azobenzenes **5–7** were prepared by methods reported previously.[13] An olefinic crowned azobenzene (3.5 mmol) was dissolved in freshly distilled toluene (150 cm^3), together with poly(methylhydrosiloxane) (216 mg, 3.2 mmol SiH unit). The reaction mixture was heated to 110 °C under an argon atmosphere, and an aliquot (0.1 cm^3) of a methylene chloride solution of dicyclopentadienylplatinum(II) chloride (1 mg cm^{-3}) was then injected with a microsyringe. The reaction mixture was refluxed under an argon atmosphere for 2 days until ^{1}H-NMR analyses showed that the hydrosilylation reaction was nearly complete. Ethylene was then bubbled in the mixture to react with the residual Si–H units. After the reaction, the mixture was evaporated to dryness. The crude product was purified by preparative gel permeation chromatography to afford a yellow solid of crowned azobenzene polysiloxane, **1** and **2**: ^{1}H NMR (60 MHz, CDCl$_3$) ca. δ 0 (s, Si–CH$_3$), 0.3–0.6 (m, Si–CH$_2$), 1.1–2.2 (m, $(CH_2)_8$CH$_2$O), 3.7–4.4 (m, OCH$_2$CH$_2$O and CH$_2$OPh), 6.8–8.3 (m, aromatic H). **3**: ^{1}H NMR (60 MHz, CDCl$_3$) ca. δ 0 (s, Si–CH$_3$), 0.3–0.7 (m, Si–CH$_2$), 1.1–2.2 (m, $(CH_2)_8$CH$_2$O), 3.6–4.6 (m, OCH$_2$CH$_2$O and CH$_2$OPh), 6.9–8.2 (m, aromatic H). **4**: ^{1}H NMR (60 MHz, CDCl$_3$) ca. δ 0 (s, Si–CH$_3$), 0.3–0.7 (m, Si–CH$_2$), 1.0–2.3 (m, $(CH_2)_8$CH$_2$O), 3.7–4.2 (m, CH$_2$OPh), 6.8–8.5 (m, aromatic H).

Other Chemicals. 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 spin coating from chloroform solutions. For instance, polyester (26.3 mg), crowned azobenzene polysiloxane **1** (8.5 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 counterelectrode, a Au disk of 6-mm diameter was evaporated on the composite-film-coated ITO glass before ac impedance measurements. Any composite films with other alkali-metal salts contained an equimolar amount of respective salt. The typical composite film contains about 75.5 wt % polyester, about 24.4 wt % azobenzene polysiloxane, and about 0.06–0.08 wt % alkali-metal salt. The composite films for isothermal transient ionic-current measurements (several tens of micrometers thickness) were cast with the same composition. Corona charging of composite films was carried out with a voltage of 8 kV at 80 °C for 30 min. The films were then cooled to room temperature while corona charging. Unless otherwise stated, any of the composite films was subjected to annealing at 150 °C for 1 h, to assist formation of microdomains consisting of an azobenzene polysiloxane and a metal salt.

Measurements. The procedure and cell setup for the ionic-conductivity measurements were as described elsewhere.[16] The measurement cell was controlled strictly by a thermostated heater combined with an argon stream. Photoirradiation on a composite film during the ac measurements was undertaken from its ITO side. 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 color filters, respectively. Differential scanning calorimetry (DSC) was performed using a Daini Seikousha DSC220C calorimeter equipped with a photoirradiation apparatus (UV-1). Photoirradiation during DSC was made through optical-fiber wave guides, by using UV light of 365 nm with a light intensity of 25 mW cm^{-2}. Isothermal transient ionic-current measurements were carried out at 60 °C in a way similar to a procedure reported previously,[16] using a cell setup with a pair of Pt or Li electrodes for the ionic-conductivity measurements and a programmable electrometer. After application of an appropriate dc voltage (10 V) across a composite film for 5 h, the polarity was switched rapidly and the transient current was then monitored every 10 s.

Scheme 1[a]



[a] G, glassy; K, crystalline; S, smectic; N, nematic; I, isotropic. The temperatures are shown in degrees Celsius.

Results and Discussion

Synthesis and Characterization of Crowned Azobenzene Polysiloxane. In order to enhance ordered aggregation of crowned azobenzene derivatives, liquid crystal polymers carrying a crowned azobenzene moiety at the side chain were designed. Polysiloxane was selected as a flexible main chain for side-chain type crowned azobenzene polymers to facilitate ordered arrangement of their side chains. Thus, hydrosilylation of ω-olefinic crowned azobenzenes with poly(methylhydrosiloxane) was carried out to obtain crowned azobenzene polysiloxanes **1–3**. An azobenzene polysiloxane without any crown moiety, **4**, was also prepared for comparison.

Thermoinduced phase-transition behavior of the crowned azobenzene polysiloxanes was investigated by DSC and optical microscopy. Scheme 1 summarizes the phase transitions for crowned azobenzene polysiloxanes **1–3**, and model polysiloxane **4**, together with those for their corresponding monomeric compounds **5–7**. Crowned azobenzene polysiloxane **1** undergoes a phase transition from glassy successively to smectic, nematic, and isotropic phases. The corresponding monomeric derivative, **5**, does not experience any smectic phase but a nematic one. This may suggest that incorporation of the monomeric crowned azobenzene to polysiloxane allows the higher order of arrangement of crowned azobenzene moieties as can be expected. Similar thermoinduced phase transition was observed in crowned azobenzene polysiloxane **2** and even in the model polysiloxane, **4**. The crowned azobenzene polysiloxane containing no ester linkage, **3**, did not show any significant liquid crystal phase, as is the case with its corresponding monomeric derivative **7**.

Photoresponse in Ion-Conducting Composite Films of Crowned Azobenzene Polysiloxane. First, we tried to fabricate films consisting only of a crowned azobenzene polysiloxane and an alkali-metal perchlorate but found that the film fabrication was difficult due to the film brittleness. Composite films consisting of a polyester elastomer, an azobenzene polysiloxane, and a metal salt were, therefore, fabricated for the ionic-conductivity measurements. Microscopic observation indicated that microdomains, which consist of the crowned azobenzene polysiloxane and, possibly, a high concentration of the salt, are dispersed quite uniformly in the composite films, especially after their annealing. Figure 1 shows the

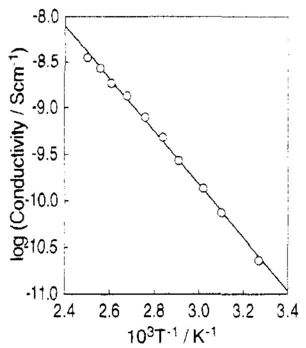


Figure 1. Temperature dependence of ionic conductivity for a composite film containing crowned azobenzene polysiloxane 1 under dark (○) conditions.

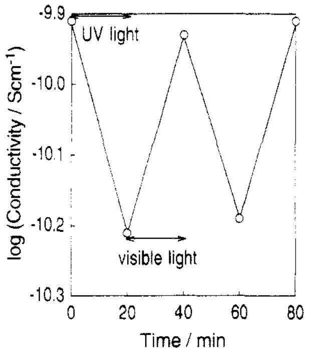


Figure 2. Photoinduced switching of ionic conductivity for a 1-containing composite film at 60 °C. Each point indicates the ionic conductivity of the saturated level after a 20-min photoirradiation.

temperature dependence of ionic conductivity for the composite film containing crowned azobenzene polysiloxane 1 and $LiClO_4$. The relationship between logarithmic ionic conductivity and reciprocal temperature shows linearity, obeying the Arrhenius equation. This means that the composite films of 1 are quite different in ion-conducting behavior from the usual polymer ionic conductors such as poly(oxyethylene)–metal ion composites.[17]

The composite films containing crowned azobenzene polysiloxane 1 and $LiClO_4$ can undergo marked photochemical switching of ionic conductivity (Figure 2). UV-light irradiation decreased the ionic conductivity of the composite films, and the following visible-light irradiation increased it to the initial value. Significant photoinduced changes of ionic conductivity were observed with high reversibility in the temperature range from 40 to 100 °C. Absorption spectra of the composite films containing polysiloxane 1 and $LiClO_4$ were changed by photoirradiation, as demonstrated in Figure 3. That is to say, UV-light irradiation decreased a strong absorption at 350 nm, based on the *trans*-azobenzene moiety of 1, while increasing a broad absorption around 450 nm, based on the corresponding cis form. Obviously, photoisomerization of the azobenzene moiety in the polysiloxane domains can proceed even in the composite film, being closely related to the photochemical ionic-conductivity switching of the composite films containing 1 and $LiClO_4$.

A similar photochemical switching tendency of ionic conductivity was also found with composite films containing crowned azobenzene polysiloxane 2. Composite films of the crowned azobenzene polysiloxane that does not possess any ester linkage in the side chain, 3, however, afforded only slight photoinduced change of ionic conductivity, as compared with the systems of crowned azobenzene polysiloxanes 1 and 2. Since crowned azobenzene polysiloxane 3 cannot form any significant liquid crystal phase, it is suggested that the liquid crystal formation in crowned azobenzene polysiloxanes 1 and 2 contributes to the drastic photoinduced change of ionic conductivity in their composite films.

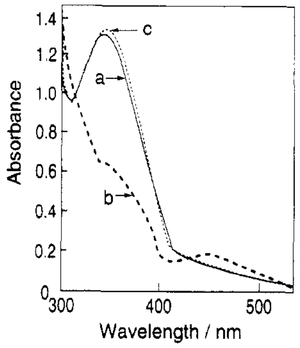


Figure 3. Absorption-spectral changes for a 1-containing composite film on photoirradiation at 60 °C: (a) under dark conditions; (b) on UV-light irradiation for 20 min; (c); on visible-light irradiation for 20 min after the UV-light irradiation.

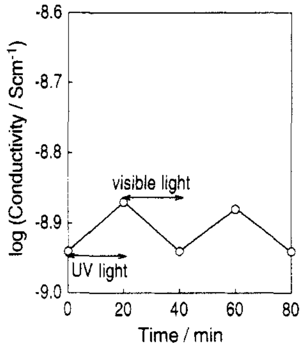


Figure 4. Photoinduced switching of ionic conductivity for a composite film containing polysiloxane without crown moiety 4 at 60 °C. Each point indicates ionic conductivity of the saturated level after a 20-min photoirradiation.

Also, some photoinduced change of ionic conductivity was attained in composite films of the model polysiloxane that does not carry any crown ether moiety but an azobenzene moiety, 4 (Figure 4). In addition, the photoinduced ionic-conductivity change in the 4 system possesses a tendency opposed to the crowned azobenzene polysiloxane systems; i.e., the ionic conductivity is increased and decreased by UV- and visible-light irradiation, respectively. Absorption spectroscopy indicated that UV light isomerizes the *trans*-azobenzene moiety of polysiloxane 4 to its corresponding cis form in a fashion similar to that of crowned azobenzene polysiloxanes 1 and 2. Since *cis*-azobenzene has a greater dipole moment than its corresponding trans isomer does, the local polarizability increase in the composite films containing 4 by photoisomerization of its azobenzene moiety can possibly affect the ion conduction slightly. At any rate, the crown ether moiety takes a very important part in the marked photoinduced ionic-conductivity switching of composite films containing crowned azobenzene polysiloxanes 1 or 2 and $LiClO_4$. This implies that the crown moieties are sites for hopping of ion-conducting carriers in the crowned azobenzene polysiloxane domains in a composite film; that is, the crown moiety itself is for cation migration and the crown-complexed cation for anion migration.

Most noteworthy is that the tendency in the photochemical ionic-conductivity switching system of the corresponding crowned azobenzene derivatives such as 5 and 6 was reversed in the present systems of the crowned azobenzene polysiloxanes. In the composite films containing a monomeric crowned azobenzene derivative and

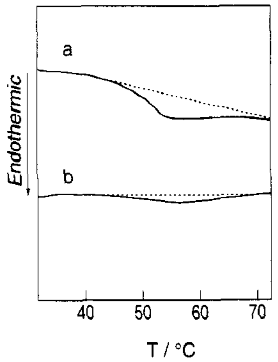


Figure 5. Photochemical DSC thermogram of 1 and comparison with the thermogram under dark conditions: (a) under dark conditions; (b) while irradiating UV light.

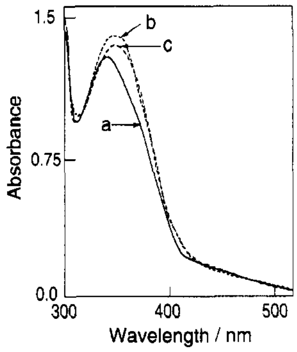


Figure 6. Absorption-spectral changes of 1-containing composite films as prepared (a), after annealing (b), and after corona charging (c).

an alkali-metal salt, as reported previously,[13] the ionic conductivity is increased by UV-light-induced isomerization of the crowned azobenzene from its trans to cis forms, and thereby its drastic phase transition. It is then decreased by the following visible-light irradiation. In the corresponding composite films of the crowned azobenzene polysiloxane, on the other hand, the ionic conductivity was diminished by UV light and then enhanced by visible light.

What then happens on UV-light-induced isomerization of the azobenzene moiety from its trans to cis forms in the composite films of crowned azobenzene polysiloxanes? In order to obtain some information about the phase transition for the crowned azobenzene polysiloxane domains in composite films containing 1 or 2 and $LiClO_4$ on UV-light irradiation, we carried out photochemical DSC of 1, which is differential scanning calorimetry while irradiating UV light, and compared it with its corresponding DSC in the dark (Figure 5). A great difference between the DSC thermograms under UV-light-irradiated and dark conditions is in the intensity of the broad endothermic peak around 50 °C which can be ascribed to the thermotropic phase transition of crowned azobenzene polysiloxane 1 from its glassy to smectic states. That is to say, UV-light irradiation on the composite film decreased the peak intensity significantly, thus disturbing the smectic state. In the smectic state of crowned azobenzene polysiloxane, its adjacent side chains consisting of lipophilic crowned azobenzene moiety are closely oriented to one another. In that case, the azobenzene moiety is in the trans form, contributing to the liquid crystal formation as the rigid mesogen. When the *trans*-azobenzene moiety is isomerized to its corresponding cis form, that is, the azobenzene moiety is bent, the close orientation of the crowned azobenzene side chains is disturbed by extending distance between two adjacent side chains. Unfortunately, this photoisomerization-induced structural change in the crowned azobenzene polysiloxane domains could not be detected by X-ray diffraction measurements, probably due to the domain dispersion in composite films.

A plausible mechanism for the photoinduced ionic-conductivity switching in composite films containing a crowned azobenzene polysiloxane and $LiClO_4$ is as follows. When crowned azobenzene polysiloxanes assume a smectic state in a composite film under dark conditions, their adjacent crown moieties at the end of the azobenzene side chain are apt to get close to one another due to their highly ordered orientation. As a result, ion-conducting carriers are easy to migrate on crown ether-based hopping sites, which are the crown moieties themselves for cations and the crown-complexed cations for anions. On the contrary, by UV-light-induced isomerization of the azobenzene moiety, followed by orientation disorder of the side chains, the adjacent moieties are more distant to one another than in the highly oriented state under dark conditions. The ion-conducting carriers are, therefore, harder to hop on the crown moieties under UV-light-irradiated conditions. It is thus considered that photoisomerization-induced disturbance in the highly-oriented smectic state of crowned azobenzene polysiloxanes diminishes ionic conductivity of composite films containing the crowned azobenzene polysiloxane and a lithium salt. The local disturbance of the smectic state is canceled out by visible-light-induced isomerization of the azobenzene moiety back to its trans form, the ionic conductivity being thus restored to the initial value.

If the photoinduced ionic-conductivity change of composite films containing a crowned azobenzene polysiloxane is really based on the disturbance and recovery in the closed orientation of side chains, that is, the polysiloxane smectic state, orientation enhancement in the smectic phase even under dark conditions may raise the ionic conductivity of the polysiloxane-containing composites. For promotion in the smectic orientation of crowned azobenzene polysiloxanes under dark conditions, treatment of the composite films by annealing and corona charging was carried out. In the absorption spectra of composite films containing crowned azobenzene polysiloxane 1, as shown in Figure 6, absorption for its trans isomer was increased by annealing, which caused thermoinduced isomerization of the remaining traces of *cis*-azobenzene moieties to their trans ones. This probably promotes the smectic orientation in the crowned azobenzene polysiloxane. The following corona charging of the composite film decreased the *trans*-azobenzene absorption to some extent. This is probably derived from the decreased molar absorptivity of the absorption, suggesting some enhancement in the smectic orientation of the crowned azobenzene polysiloxane and therefore in the aggregation of adjacent azobenzene moieties. Actually, ionic conductivity of the composite film containing polysiloxane 1 and $LiClO_4$ was increased from 1.3×10^{-10} to 1.6×10^{-10} S cm^{-1} and then to 1.8×10^{-10} S cm^{-1} by the annealing and the following corona charging. These results again support that ionic conductivity of composite films containing crowned azobenzene polysiloxane domains can be modulated by changes in the orientation of its side chains.

Measurements of isothermal transient ionic current by polarity switching were made to obtain some information about ion-conducting carriers and their mobilities in composite films containing crowned azobenzene polysiloxane 1 and $LiClO_4$ (Figure 7). When a pair of Li electrodes, that is, Li^+-reversible ones, was employed for the transient current measurements under dark conditions,

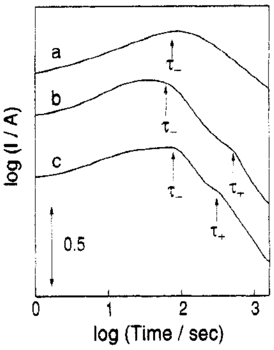


Figure 7. Isothermal transient ionic-current measurements for composite films containing 1 and $LiClO_4$ at 60 °C. (a) Li/sample/Li system, under dark conditions; (b) Pt/sample/Pt system, under dark conditions; (c) Pt/sample/Pt system, on UV-light irradiation. τ_+ and τ_- stand for transient times of the cation and anion, respectively.

the transient curve possesses a well-defined bump, which can be attributed to the anion (ClO_4^-) migration in film. Two peaks (a bump and a shoulder) were observed in the curve with a pair of Pt electrodes that are ion-blocking against both the cation and anion. By comparison of the two transient ionic current curves, the early bump and late shoulder in the transient current curve with the ion-blocking electrodes can be assigned to the anion and cation migration, respectively. This indicates that the anion conduction is predominant to the cation one in the ion-conducting composite films of crowned azobenzene polysiloxane 1. Since the total ionic conductivity of the composite film is possibly contributed by ionic conduction in both the crowned azobenzene polysiloxane domains and the polyester elastomer area, one cannot estimate transport numbers of the cation and anion only for the domains by the transient current measurements. UV-light irradiation on the composite films modified the transient current curve for dark conditions. Drift mobilities for the ions, which were calculated from the corresponding transient times, were changed by UV-light irradiation from 3.3×10^{-8} to 2.6×10^{-8} cm^2 s^{-1} V^{-1} for the anion (μ_-) and from 2.9×10^{-9} to 4.2×10^{-9} cm^2 s^{-1} V^{-1} for the cation (μ_+), with a decrease of the total mobility ($\mu_+ + \mu_-$) from 3.6×10^{-8} to 3.0×10^{-8} cm^2 s^{-1} V^{-1}. Thus, a photoinduced ionic-conductivity decrease in the crowned azobenzene polysiloxane system is considered to be derived from the disturbance in the polysiloxane smectic orientation, which in turn lowers drift mobilities of the ion-conducting carriers.

Since the relationship between crown moieties and cations employed sometimes dominates migration of cations and their counteranions in solution chemistry, one may also anticipate some effect of the kind of the crown moiety and cation on the ion-conducting behavior of composite films containing a crowned azobenzene polysiloxane and an alkali-metal perchlorate. In the system of 15-crown-5-containing polysiloxane 1, hardly any significant difference in the tendency and magnitude of the photochemical ionic-conductivity switching was found among the composite films containing three different alkali-metal perchlorates (Li^+, Na^+, and K^+) as the ionic species. In the system of 18-crown-6-containing polysiloxane 2, the $LiClO_4$-containing composite films showed the lower switching magnitude as compared to the films of other alkali-metal salts (Na^+ and K^+), although they are the same in the switching tendency (Figure 8). This is probably due to the fact that Li^+ is too small to fit into the 18-crown-6 ring cavity, therefore possessing low complexing ability toward the metal ion. As a result, the crown ether effect was especially small in the photoinduced ionic-conductivity changes of crowned azobenzene polysiloxane-containing composite films.

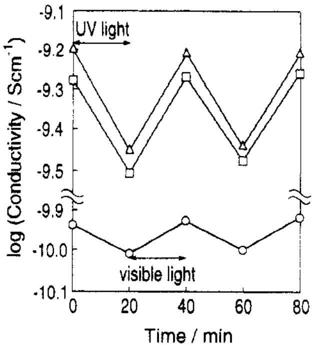


Figure 8. Comparison of the behavior of photoinduced ionic-conductivity switching among 2–composite films containing $LiClO_4$ (○), $NaClO_4$ (△), and $KClO_4$ (□) at 60 °C.

In conclusion, composite films containing a crowned azobenzene polysiloxane 1 or 2 and an alkali-metal salt were found to undergo remarkable photochemical ionic-conductivity switching, the tendency of which is completely the opposite to that for composite films containing their corresponding monomeric crowned azobenzene derivatives.

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