

Photoresponsive Ionic Conductivity of Polymer Composite Films Containing Azobenzene Liquid Crystal

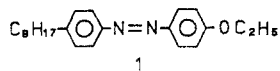
Keiichi Kimura,* Tatsuya Suzuki, and Masaaki Yokoyama

Chemical Process Engineering, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan (Received: December 6, 1989; In Final Form: February 12, 1990)

Ionic-conductivity control by external stimulation was investigated with thin composite films consisting of poly(vinyl chloride), azobenzene liquid crystal **1**, and LiClO₄ (or its 12-crown-4 complex). On heating the composite film, a significant jump in the ionic conductivity was attained around T_{KN} (transition temperature from crystal to nematic states) of **1**. The ionic-conductivity change is attributable to the phase transition of **1**, which in turn enhances the mobility of ionic species in the film. UV light irradiation on the composite film caused photoisomerization from trans to cis forms of the azobenzene derivative, which in turn led to its phase transition from crystal state (below the T_{KN}) or nematic state (above the T_{KN}) to isotropic liquid state, thus augmenting the ionic conductivity of the composite film by more than 2 orders of magnitude compared with that under dark conditions. Visible light irradiation after the UV irradiation promoted cis-to-trans isomerization of **1**, diminishing the UV-enhanced ionic conductivity of the composite film, especially at room temperature, to the initial ionic conductivity. Alternating irradiation by UV and visible lights afforded reversible ionic-conductivity switching in the composite film. A novel type of electrostatic imaging process was realized by using the photoresponsive ion-conducting composite film of **1**.

Ion-conducting organic materials are very attractive for designing of various devices for memory, display, and printing. Considerable attention has been paid to fabrication of highly ion conducting organic materials such as polymer-metal ion composites. Only a few organic materials have been reported that are able to undergo ionic-conductivity switching or jump by external stimulation. Quarternary alkyl halide salts of diazabicyclo[2.2.2]octane (DABCO) are typical, thermally switchable ionic conductors, which exhibit marked crystal-phase transitions based on conformation changes of alkyl chains in DABCO.¹⁻⁴ As the result, abrupt increases in the anion conductivity of the DABCO salt crystals were observed around the phase transition temperatures.

We have attempted to design ion-conducting organic materials that are thermally or photochemically switchable, especially by using liquid crystal compounds. We recently communicated that composite films containing poly(vinyl chloride) (PVC), azobenzene liquid crystal **1**, lithium perchlorate, and 12-crown-4 undergo



significant photoinduced switching in the ionic conductivity, which is based on photoisomerization of the azobenzene derivative.⁵ In this paper, we report in detail the photochemically and thermally induced ionic-conductivity changes in the **1**-containing composite films. Applicability of the resultant photoresponsive ion-conducting films of **1** to electrostatic imaging process is also described.

Experimental Section

Materials. Azobenzene liquid crystal **1**, *p*-ethoxy-*p*'-octylazobenzene, was prepared in the following manner. *p*-Hydroxy-*p*'-octylazobenzene was at first prepared by conventional diazo coupling of *p*-octylaniline and phenol in H₂O/tetrahydrofuran (THF). *p*-Hydroxy-*p*'-octylazobenzene (0.01 mol) and KOH (0.01 mol) were dissolved in ethanol (100 mL) by stirring at 50 °C for 1/2 h. Ethyl iodide (0.023 mol) was added to the

solution, and then the mixture was refluxed for 6 h. After the reaction, the solution was evaporated to dryness and chloroform (100 mL) was added to the residue. The chloroform solution was filtrated, washed successively by dilute HCl, water, 5% NaHCO₃, and water, and then dried over MgSO₄. Evaporation of the solvent gave a crude product of **1**. Silica-gel column chromatography (benzene) and recrystallization from ethanol yielded an orange crystal of pure **1**: mp 39 °C; ¹H NMR(100 MHz, CDCl₃) δ 0.88 (t, 3 H, CH₃(CH₂)₆), 1.2-1.6 (m, 15 H, CH₃(CH₂)₆ and CH₃CH₂O), 2.68 (t, 2 H, PhCH₂), 4.10 (q, 2 H, PhOCH₂), 6.9-7.9 (m, 8 H, aromatic H); M⁺ 338. Anal. Calcd for C₂₂H₃₀N₂O: C, 78.06; H, 8.93; N, 8.28. Found: C, 77.84; H, 8.96, N, 8.21.

Poly(vinyl chloride) (average polymerization degree of 1100) was purified by reprecipitation three times from THF in methanol. The crown ether, 12-crown-4, was employed as received (Aldrich). Lithium perchlorate was of analytical grade. Poly(ethylene terephthalate) (PET) films (Lumirror; 2-, 5-, and 8-μm thickness) employed for the sample fabrication on the application to the electrostatic image storage were kindly given by Toray Co. Ltd.

Composite Film Fabrication. The composite films for alternating current (ac) conductivity measurements were prepared by spin coating from THF on an indium tin oxide (ITO) coated glass (2 × 2.5 cm), unless otherwise stated. The composite films were dried overnight at 35 °C under a dry nitrogen stream. For example, the typical **1**-containing composite film was obtained by spin coating of 100 μL of a solution in which a mixture of 48 mg of PVC, 30 mg of **1**, 0.5 mg of LiClO₄, and 5 mg of 12-crown-4 was dissolved in 1 mL of THF. The composite film, therefore, consisted of 57.5 wt % PVC, 35.9 wt % **1**, 0.6 wt % LiClO₄, and 6.0 wt % 12-crown-4, its thickness being about 1 μm. The **1**-containing composite film for the direct current (dc) conductivity measurements was spin coated on Pt ion sputtered glass in a way similar to that of the film for the ac measurements. The layered composite film of **1** for the application to electrostatic imaging process was prepared by bar coating on the PET film. The ion-conducting-film layer contained 62.49 wt % PVC, 37.50 wt % **1**, and 0.01 wt % LiClO₄, and its thickness was 12 μm. Gold was then evaporated on the composite film, in such way that the ion-conducting layer was sandwiched by the PET film and the Au electrode.

Measurements. The ac conductivity of the polymer composite films was measured by using a Solartron 1253 gain-phase analyzer and a Keithley 427 current amplifier, the cell setup for the measurements being as sketched in Figure 1. The composite film spin coated on ITO glass was spring loaded with a Pt disk, the

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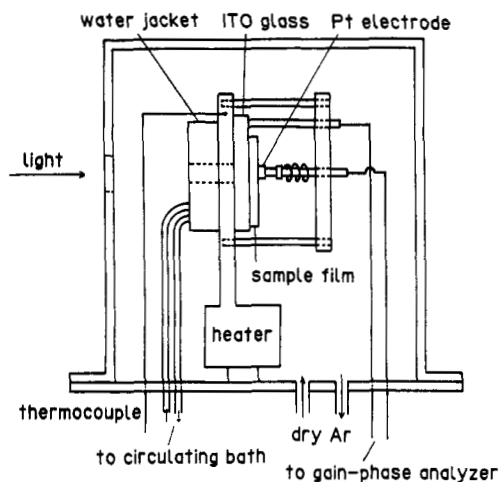


Figure 1. Schematic diagram of cell for ionic-conductivity measurements.

cell assembly being Pt/film/ITO. The ac measurements were performed under a dry argon atmosphere, with an applied voltage of 1 V and frequencies ranging from 0.1 Hz to 20 kHz. The temperature for the measurement cell was controlled by a heater and a thermostated circulating bath and was detected by a copper-Constantan thermocouple and a digital multimeter. The data obtained by the gain-phase analyzer and digital multimeter were processed by a microcomputer (NEC 9801-Vm) through GP-IB boards. The ionic conductivities were computed by the Cole-Cole plot method.⁶ 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) light and visible (>400 nm) light were obtained by passing the light of a 500-W xenon lamp through Toshiba UV-D35 and V-Y43 color filters, respectively.

The dc conductivity of the 1-containing composite film was measured with a dc voltage of 10 V under a dry argon atmosphere, by using a dc power supply (Takeda Riken TR-6141), and electrometer (Keithley 617), and the same measurement cell as for the ac measurements. Lithium metal which was freshly sliced under an argon atmosphere was employed as the counter electrode for the dc measurements.

Differential scanning calorimetry (DSC) of the azobenzene derivative and the composite films was carried out at a scan rate of 5 °C min⁻¹, using a Daini Seikosha SSC/560 differential scanning calorimeter. The absorption spectra of the composite films were recorded with the reference of an ITO glass by a JASCO UVVIDEC-660 spectrophotometer. The microscopic observation for phase transition of the azobenzene derivatives was made by a Nikon POH3 polarizing microscope equipped with a Mettler FP-5 thermocontrol system.

Electrostatic Image Storage Experiments. Surface-potential decay in corona-charged samples (the layered composite film) was measured by an electrostatic paper analyzer (Kawaguchi Electric Works, EPA-8100). The photoirradiated composite film was positively corona charged immediately after 5-min photoirradiation unless otherwise noted and was then subjected to the surface-potential measurement. The photoirradiation was carried out from the PET film side of the layered composite film. For comparison of surface potential, initial potential (V_0) was adopted as the surface potential. Image duplication in a conventional xerographic method by using the layered ion-conducting film as a printing master was run in the following manner. The layered composite film for electrostatic image storage was at first exposed to UV light through an appropriate exposure image. The sample was then fixed on an Alumite drum of a xerographic copying machine (Mita DC-162), with the Au electrode of the sample in contact with the drum. The image on the layered film written in by UV light was positively corona charged, developed by negatively charged toner, and transferred to plain paper.

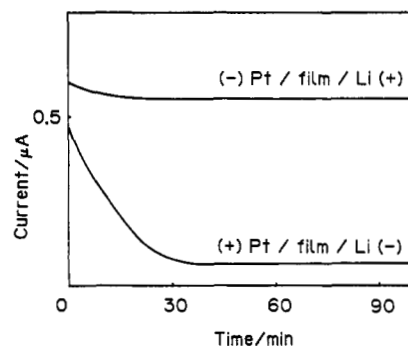


Figure 2. Direct-current measurement for 1-containing composite film sandwiched by Li and Pt metal electrodes.

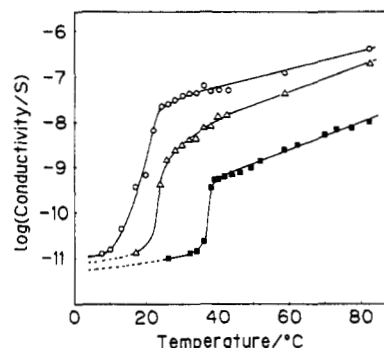


Figure 3. Temperature dependence of ionic conductivity of 1-containing composite film: (■) under dark conditions; (○) with UV light irradiation for 5 min; (△) with visible light irradiation for 5 min after UV irradiation.

Results and Discussion

Thin films possess wide applicability for device application of functional organic materials. We have, therefore, aimed at designing polymer composite films, the ionic conductivity of which can be switched by external stimulation, especially by photoirradiation. An azobenzene derivative was chosen as a photochromic compound. Thus we have fabricated ion-conducting composite films that consist of PVC as the film support, lipophilic azobenzene derivative 1 as the photochromic compound, and LiClO₄ or its crown ether complexes as the ion-conducting carrier. We decided to adopt the composite film containing about 60 wt % PVC and about 35 wt % 1, taking into consideration the mechanical strength and transparency of the resultant composite film.

Direct-current conductivities of the polymer composite film consisting of PVC, 1, LiClO₄, and 12-crown-4 were measured to get some information about conductive carriers of the composite film. Figure 2 depicts the time course of direct current in the 1-containing composite film which was sandwiched by Pt and Li metal electrodes. When the Li electrode was positive and the Pt electrode negative, that is, when Li⁺ was not blocked by the Pt electrode in the electrochemical cell, direct current flew through the composite film without significant current decay. In contrast, when the Pt electrode was positive and the Li electrode negative, that is, when Li⁺ was blocked by the Pt electrode, the dc conductivity was diminished drastically in a short time. It is, therefore, Li⁺ conduction that contributes considerably to the dc conductivity of the composite film. In other words, the polymer composite film of PVC/1/LiClO₄/12-crown-4 system is quite Li⁺ conducting. The ionic conductivity of the composite film was also supported by the fact that the 1-containing composite film without any Li salt exhibits too low conductivity to measure.

Ionic conductivities of the composite film were evaluated by ac measurements, followed by analysis of its complex impedance in a Cole-Cole plot. First of all, under dark conditions, ionic conductivities were measured at varying temperatures (Figure 3). The ionic conductivity of the 1-containing composite film increased gradually with temperature, as is generally the case in ion-conducting polymeric materials. It should, however, be noted that

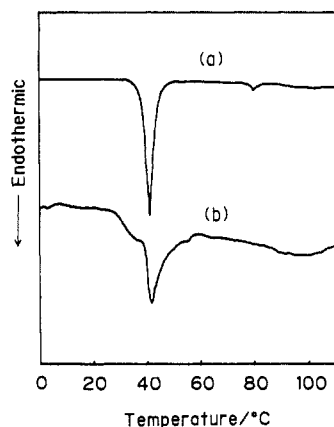


Figure 4. Differential scanning calorimetry of azobenzene derivative **1** (a) and **1**-containing composite film (b).

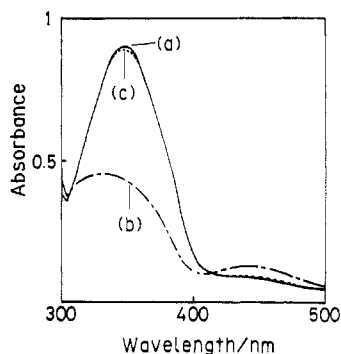


Figure 5. Absorption spectra of **1**-containing composite film: (a) under dark conditions; (b) after 5-min UV light irradiation; (c) after 5-min visible light irradiation on the UV-irradiated film.

under dark conditions the ionic conductivity jumps by more than an order of magnitude around 40 °C. The abrupt ionic-conductivity change in the **1**-containing composite film is most likely to be related to phase transition in the film, especially of the azobenzene derivative which can be expected to have liquid crystal character.⁷ In the DSC data shown in Figure 4, azobenzene derivative **1** exhibits a strong endothermic peak based on the phase transition from crystal to nematic liquid crystal states at 39 °C (T_{KN}) and a weak endothermic peak based on the transition from nematic liquid crystal to isotropic liquid states at 79 °C (T_{NI}). A broad but strong endothermic peak was also observed in the composite film of **1** around 40 °C. It was confirmed by microscopic observation that the strong peak in the composite film is attributed to the phase transition of **1** from the crystal to liquid crystal states. The phase transition in the composite film definitely promotes the ion mobility in the film, thus increasing the ionic conductivity of the composite film drastically.

UV light irradiation enhanced the ionic conductivity of the **1**-containing composite film as compared with that under dark conditions (Figure 3). On photoirradiation around 20 °C, the ionic conductivity of the composite film was augmented by more than 2 orders of magnitude. Absorption spectra of the **1**-containing composite film gave us some information about photoisomerization of the azobenzene derivative **1** in the film (Figure 5). Without photoirradiation, the film showed strong absorption around 350 nm, which indicates that the azobenzene derivative is mainly in trans form under dark conditions. On UV light irradiation for 5 min, the absorption based on the trans isomer decreased, while a broad absorption peak appeared around 440 nm. The spectral change clearly shows that considerable amount of the azobenzene derivative isomerizes from trans to cis forms on UV light irradiation. When the UV-irradiated composite film was further exposed to visible light, the absorption spectrum was almost re-

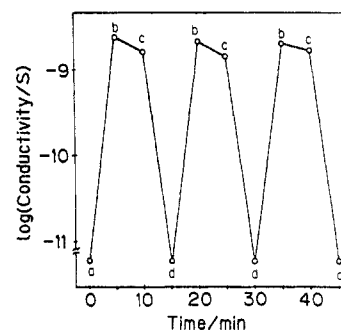


Figure 6. Ionic-conductivity switching of composite film on alternating irradiation of UV and visible lights: (a) UV light on; (b) UV light off; (c) visible light off; (d) visible light off and then UV light on.

verted to the initial spectrum. This means that the azobenzene derivative in the composite film isomerizes from trans to cis forms by UV light and vice versa by visible light. The photoisomerization of the azobenzene derivative occurs quickly and reversibly even in the film. Moreover, polarizing microscopy of the **1**-containing composite film on UV light irradiation at 30 and 50 °C clearly exhibited two types of phase transitions of the azobenzene derivative induced by its trans-to-cis photoisomerization. That is, the UV-induced isomerization of the azobenzene derivative in the composite film from trans to cis forms at 30 °C, more generally, at the temperatures below the T_{KN} of trans-**1**, causes its phase transition from crystal to isotropic liquid states. At 50 °C, more generally at the temperatures above the T_{KN} , the photoisomerization from the trans to cis forms leads to phase transition of the azobenzene derivative from nematic liquid crystal to isotropic liquid states. Thus, it is the marked phase transition in the composite film, derived from the photoisomerization of azobenzene derivative **1**, that brought about the huge ionic-conductivity enhancement in the film on UV light irradiation. Higher dielectric constant of the cis isomer than the trans isomer, which can be anticipated from their structures, might contribute to the UV-induced jump in the ionic conductivity as well.

Visible light irradiation (5 min) on the UV-irradiated composite film promoted cis-to-trans isomerization of the azobenzene derivative and thereby again lowered the ionic conductivity of the composite film (Figure 3). Specifically, at room temperature below 30 °C, the visible light irradiation allowed the ionic conductivity to revert to the initial values (without the photoirradiation). It is worth noting that alternating irradiation by UV and visible lights at room temperature affords reversible ionic-conductivity switching in the **1**-containing composite film, as illustrated in Figure 6. One may expect that even under dark conditions the UV-enhanced ionic conductivity of the composite film is diminished due to some extent due to thermal isomerization of the azobenzene derivative from cis to trans forms and thereby its phase transition. It should, however, be noted that the reversion of the UV-enhanced ionic conductivity is quite sluggish without visible light irradiation. It is of much interest that, at higher temperatures than 30 °C, there is some memory effect in the photoinduced switching of the ionic conductivity. Visible light irradiation for 5 min above 30 °C could not allow such quick reversion of the ionic conductivity to the initial state as observed at the lower temperature. Since the visible light irradiation on the UV-irradiated composite film above 30 °C gave almost the same absorption spectrum as that under dark conditions, the photoisomerization of the azobenzene derivative occurs quite rapidly even at the high temperatures. Thus the visible light-induced phase transition of the azobenzene derivative from the isotropic liquid state back to the crystal or nematic state seems to proceed very slowly at the high temperatures.

Attempts were made to apply the photoresponsive ion-conducting composite film to electrostatic image storage.⁸ The idea for electrostatic image storage is as follows. On UV light irra-

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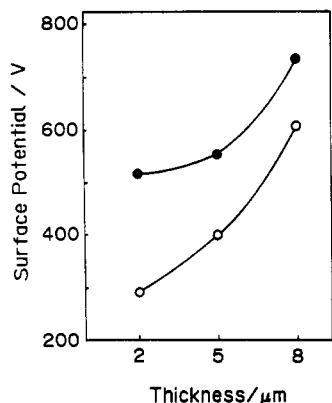


Figure 7. Effect of overlayer film thickness on surface potential induced by corona charging in layered composite film: (●) without photoirradiation; (○) with 5-min UV irradiation.

diation on the composite film containing azobenzene derivative **1** through an appropriate exposure image, the UV-irradiated region of the film becomes highly ion conducting by the above-mentioned photochromic phase transition, while the unirradiated region still remains low ion conducting. When the surface of the photoirradiated film is positively corona charged, the surface charges are easily compensated for by internal polarization based on the UV-enhanced ionic conductivity. On the other hand, the surface of the unirradiated region can be highly charged due to its low ionic conductivity. Thus the surface-potential difference between the photoirradiated and unirradiated regions turns out to be an electrostatic image. For the electrostatic imaging process, we fabricated a relatively thick ($12\ \mu\text{m}$) composite film consisting of PVC, **1**, and a trace amount of LiClO_4 , to keep the dark ionic conductivity of the composite film very low. It is because high surface-potential difference between the photoirradiated and unirradiated regions is required for high contrast in the resulting electrostatic image. Furthermore, the composite film was overlaid with an insulating PET film. Surface potentials of the layered composite films induced by positive corona charging are as shown in Figure 7. The surface potential for the UV-irradiated film was definitely decreased in comparison with that for the unirradiated film (under dark conditions) as expected. The thicker the overlayer film, the smaller the surface-potential difference between the photoirradiated and unirradiated films. It is probably because surface-charge compensation is not very effective in the composite film overlaid with the thick insulating films. The **1**-containing composite film with the overlayer of $2\ \mu\text{m}$ thus afforded the highest contrast in the electrostatic image between the UV-irradiated and unirradiated regions, the surface-potential difference being more than 200 V. Image duplication can be attained readily by toner development in the xerographic method.⁸ The decreased surface potential, based on the UV-induced ionic-conductivity enhancement, was recovered gradually with time (Figure 8). That is, the electrostatic image formed by UV light irradiation on the **1**-containing composite film can be stored for a while at room temperature, unless the film is irradiated with visible light. Even after 2 days, the written-in composite film still kept more than 100 V of surface-potential difference between the photoirradiated and unirradiated regions. Of course, the decreased surface potential can be reverted to the initial potential imme-

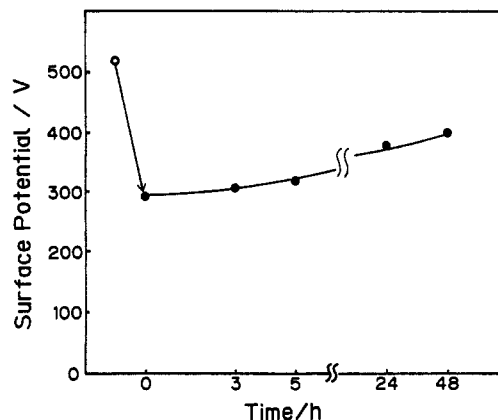


Figure 8. Time course of surface potential induced by corona charging in layered composite film: (○) corona charged without photoirradiation; (●) corona charged at a given time after 5-min UV irradiation.

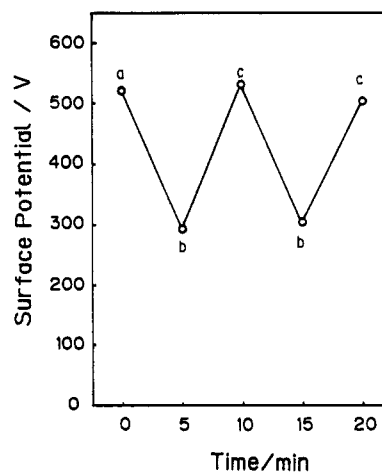


Figure 9. Surface-potential change on alternating irradiation of UV and visible lights: (a) corona charged without photoirradiation; (b) corona charged after 5-min UV irradiation; (c) corona charged after 5-min visible light irradiation.

diately by visible light irradiation at room temperature (Figure 9). This means that the electrostatic image written in the layered composite film is easy to erase with visible light. The write-in and erasing of the electrostatic image by UV and visible light irradiations, respectively, are quite reversible as demonstrated in Figure 9. The write-in process at temperatures higher than $30\ ^\circ\text{C}$ would store the resulting electrostatic image for a longer time due to the memory effect of ionic conductivity observed in Figure 3, although the image erasing by visible light irradiation at the higher temperatures is not so easy as at room temperature.

In conclusion, the composite films that are composed of PVC, azobenzene derivative **1**, and lithium perchlorate (or its crown ether complex) exhibit the ionic conductivities responsive to light and heat. The composite films can undergo reversible switching in the ionic conductivity by UV and visible light irradiations at room temperature. The photoresponsive ion-conducting composite films with azobenzene **1** are very promising for various devices, especially of image storage.