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# Photo-induced Ionic Conductivity Switching in Polymer/Photochromic Liquid Crystal Composite Films Containing Lithium/Crown Ether Complex

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Thin composite films consisting of poly(vinyl chloride), azobenzene liquid crystal, lithium ion / 12-crown-4 complex exhibited reversible photo-induced switching of ionic conductivity based on the photochromic phase transition of the azobenzene derivative. The ionic conductivities increased by more than two orders of magnitude by UV light and then reverted to the initial state by visible light at ambient temperature.

Major efforts have been made in designing high ionic-conducting organic materials, especially polymer - metal salt composites,[1)] to attain efficient organic solid electrolytes. Few organic materials that show pronounced ionic-conductivity switching or jump by light and heat, however, have appeared so far. Nogami and his coworkers have reported drastic ionic-conductivity jump of quaternary alkyl halide salts of diazabicyclo[2.2.2]octane based on their thermal phase transition.[2)] We have tried to design organic thin films of which ionic conductivities can be switched by light, aiming at their applications to various devices. Here we report photo-induced switching of ionic conductivity in thin composite films consisting of poly(vinyl chloride) (PVC), $LiClO_4$/12-crown-4 complex, and p-octyl-p'-ethoxyazobenzene (**1**), which undergoes photoisomerization.

The composite films containing 57.5 wt% PVC, 35.9 wt% **1**,[3)] 6.0 wt% 12-crown-4, and 0.6 wt% $LiClO_4$ were cast on indium tin oxide (ITO) glasses (2 cm X 2.5 cm) from tetrahydrofuran by a spin-coating method. After air drying, the composite film was further dried by a dry nitrogen flow at 40 °C over $P_2O_5$. The composite film of about 1μm thickness was spring-loaded with a platinum disc of 5 mm diameter in a thermostated cell holder, the cell assembly being ITO/film/Pt. The alternating current response of the samples under an argon atmosphere was recorded using Solartron 1253 gain-phase analyzer and Keithley 427 current amplifier, and then the ionic conductivities were evaluated by Cole-Cole plot method.[4)] The photo-irradiation was carried out from the ITO side of the cell assembly. The UV (320-400 nm) and visible (>400 nm) lights were obtained by passing light of a 500 W xenon lamp through Toshiba UV-D35 and V-Y43 glass filters, respectively.

Figure 1 shows the temperature dependence of ionic conductivity[5)] for the thin composite films under dark and photo-irradiated conditions. Without the photo-irradiation, the ionic conductivity increased with temperature and jumped up around 40 °C. Since, in the azobenzene derivative, the trans form is much more stable than the cis form under dark conditions, the ionic-conductivity jump was anticipated to be caused by phase transition of the trans isomer. Differential scanning calorimetry (DSC)[6)] and microscopic examination of trans-**1** indicated that a phase transition occurs from crystal to nematic liquid crystal at 41 °C. The distinct ionic-conductivity increase in the composite films around 40 °C can, therefore, be attributed to enhanced ion mobility based on the phase transition of **1** from crystal to the liquid crystal state. On the UV light irradiation the ionic conductivity increased drastically around 20 °C. The ionic-conductivity jump by the UV light irradiation is more remarkable than that observed under dark conditions. In the absorption spectrum of the composite film, the absorption at 350 nm for the trans form of **1** decreased remarkably with the increase of the absorption around 450 nm for the cis form on the UV light irradiation. The reverse was observed by the visible light irradiation of the sample which had been just irradiated by the UV light for 5 min. Obviously, the UV light irradiation leads to trans-to-cis isomerization of **1**. It was also found by microscopic examination that, on the UV light irradiation at room temperature, **1** underwent phase transition from crystal directly to isomeric state. Thus, the photoisomerization of **1** followed by the phase transition brought about the abrupt enhancement of ionic conductivity on the UV light irradiation. The remarkable ionic-conductivity jump by the UV light irradiation compared with that under dark conditions may be based on the difference in the phase transition and in the dielectric constant between the two isomers of **1**. After finishing the UV light irradiation, the composite

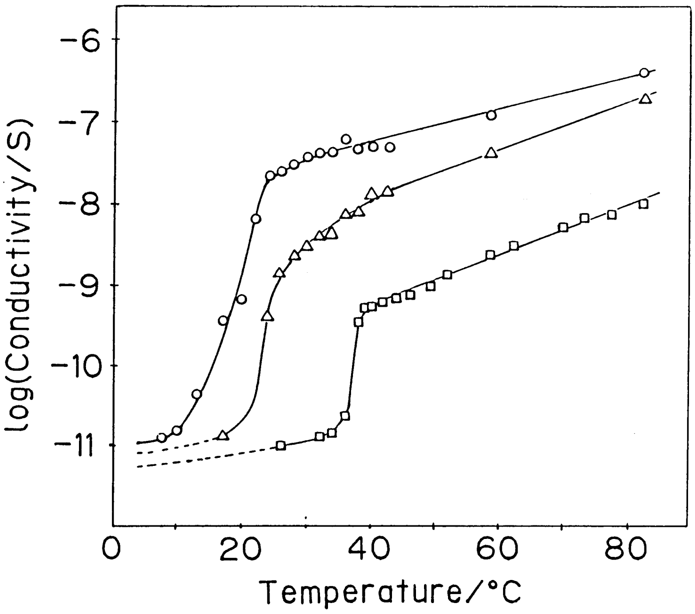

Fig. 1. Temperature dependence of ionic conductivity.
( □ ) under dark conditions, ( ○ ) on UV light irradiation for 5 min, ( △ ) on visible light irradiation for 5 min immediately after the 5-min UV light irradiation.

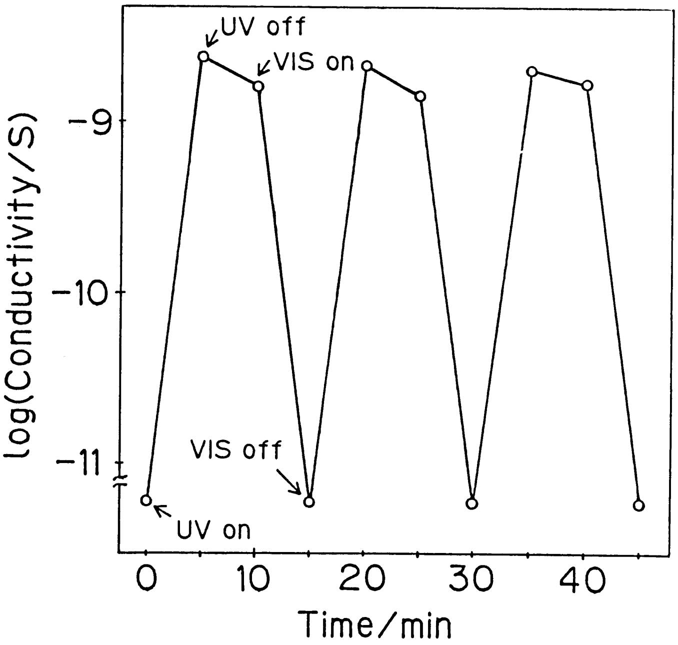

Fig. 2. Photo-induced switching of ionic conductivity at 22 °C. "UV" and "VIS" are referred to as UV and visible lights, respectively.

film was irradiated with the visible light to promote isomerization of the cis-**1** to the corresponding trans form. At room temperature the visible light irradiation allowed immediate reversion of the ionic conductivities to the initial state. At the higher temperature (>30 °C), however, the conductivity reversion proceeded quite slowly. That is to say, there was some memory effect in the photo-induced ionic-conductivity change above 30 °C.

The ionic-conductivity change of the composite film was followed at 22 °C by repetition of successive UV and visible light irradiation. Figure 2 clearly indicates reversible, significant switching of ionic conductivity in the polymeric composite film. Thus, the thin composite film of PVC, **1**, and the $Li^+$-crown ether complex, which exhibited the ionic-conductivity switching at ambient temperature, seems quite promising for device applications. Also, the memory effect of the ionic conductivity at the higher temperature might be applied to light-memory devices. A study is currently under way to apply the present composite film with photo-induced switching ability of ionic conductivity to some devices.

References

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2) J. Shimizu, T. Nogami, and H. Mikawa, Solid State Commun., 54, 1009 (1985); J. Shimizu, K. Imamura, T. Nogami, and H. Mikawa, Bull. Soc. Chem. Jpn., 59, 1443 (1986); K. Imamura, J. Shimizu, and T. Nogami, ibid., 59, 2699 (1986); K. Imamura, T. Nogami, and Y. Shirota, ibid., 60, 111 (1987).

3) Octylazophenol was obtained by conventional diazo-coupling of p-octylaniline with phenol. Compound **1** was then prepared by reaction of the azophenol with ethyl iodide in ethanol in the presence of KOH. The compound was identified by IR and mass spectroscopy and elemental analysis.

4) K. S. Cole and R. H. Cole, J. Chem. Phys., 9, 341 (1941).

5) Direct current measurements using an ion-reversible electrode (Li metal) showed that $Li^+$ is a main carrier for the electrical conductivity.

6) In the DSC measurement of **1** under dark conditions, a strong endothermic peak was observed at 41 °C in both **1** and the composite film. Also, there was a weak endothermic peak at 79 °C in **1**, but no significant peak around 80 °C in the composite film.

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