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Cation-Specific Ionic Conductivity of Polymer Composite Films Incorporating a Crowned Azobenzene Derivative

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Polymer composite films consisting of a polyester elastomer, $NaClO_4$ or $LiClO_4$, and a lipophilic azobenzene derivative containing monoaza-15-crown-5 moiety exhibited higher ionic conductivity than did a similar film containing $KClO_4$, reflecting the ion specificity for cation complexation of the crowned azobenzene itself. The $NaClO_4$- and $LiClO_4$-containing composite films possessed significant domains consisting of aggregates of the crowned azobenzene.

We have already designed azobenzene liquid crystals as a component of polymer composite films which undergo photo-induced ionic-conductivity switching by the phase transition of azobenzene liquid crystals.1) In the course of designing azobenzene derivatives for the ionically-conducting polymer composite films, we have come up with azobenzene derivatives carrying crown ether moiety which is expected to affect the ionic conduction to a great extent by its cation complexation. One of the crowned azobenzene derivatives, *N*-[4-(4-octylphenylazo)phenyl]-monoaza-15-crown-5 (**1**), was found to exhibit an interesting cation dependence of ionic conductivity when incorporated in composite films based on a polyester elastomer and alkali metal perchlorates, although **1** does not possess any liquid crystal phase by itself. Reported herein is the significantly cation-specific ionic conductivity of **1**-containing polymer composite films.

Crowned azobenzene **1** was synthesized by conventional diazo-coupling reaction of 4-octylaniline with *N*-phenyl-monoaza-15-crown-5.2) Polymer composite films which consist of about 63 wt% polyester elastomer (Pelprene 40H), about 37 wt% **1**, a small quantity of $MClO_4$ (0.5 - 0.6 wt%; M = Li, Na, and K) were prepared on indium-tin-oxide-coated (ITO) glasses by the spin-coating technique and then dried at 50 ℃ under a nitrogen stream. The composite films, on which Au electrodes were deposited by vacuum evaporation, were subjected to ac impedance measurements for ionic-conductivity determination.1) Figure 1a shows a temperature dependence on the ionic conductivity of the composite films. At room temperature, the film containing Li^+ possessed quite low ionic conductivity, which was raised with increasing the temperature. The ionic conductivity jumped up at 60 - 70 ℃ due to the phase transition of the crowned azobenzene or its complex from crystal to liquid states. On lowering the temperature, the ionic conductivity was diminished gradually. Below the phase transition temperature, even at room temperature, however, it did not drop drastically due to a very slow phase transition back to crystal state. Allowing the sample to stand at room temperature in a whole day, the ionic conductivity restored to the initial value. Similar hysteresis was observed in the films of Na^+ and K^+.

It should be noted that the ionic conductivity considerably depends on the kind of cation contained in the film. Na^+ provided the best ionic conductivity with the composite films containing the crowned azobenzene, the ionic conductivity decreasing in the order $Na^+ > Li^+ > K^+$. This cation specificity in the ionic conductivity seems to reflect the cation-complexing ability of monoaza-15-crown-5 moiety.3) For comparison, a 1:1 mixture of azobenzene derivative **2** and monoaza-15-crown-5 derivative **3** was employed instead of the crowned azobenzene (Fig. 1b). Interestingly, the ionic conductivity order for the **2**/**3** mixture system just followed the cation size order, $Li^+ > Na^+ > K^+$, the cation specificity being quite different from that for the crowned azobenzene system. The cation specificity in the ionic conductivity of composite films containing **1**, therefore, does not seem to be derived simply from the reduced cation-anion pairing4) by cation complexation with its crown moiety.

Transference numbers of ionic species in the composite films containing the crowned azobenzene, determined by isothermal transient ionic current measurements,5) showed that Li^+ is a main carrier for the ionic conduction in the films containing $LiClO_4$, which possessed an extremely high transference number of 0.97 for Li^+. In the composite film containing the **2**/**3** mixture, on the other hand, a Li^+

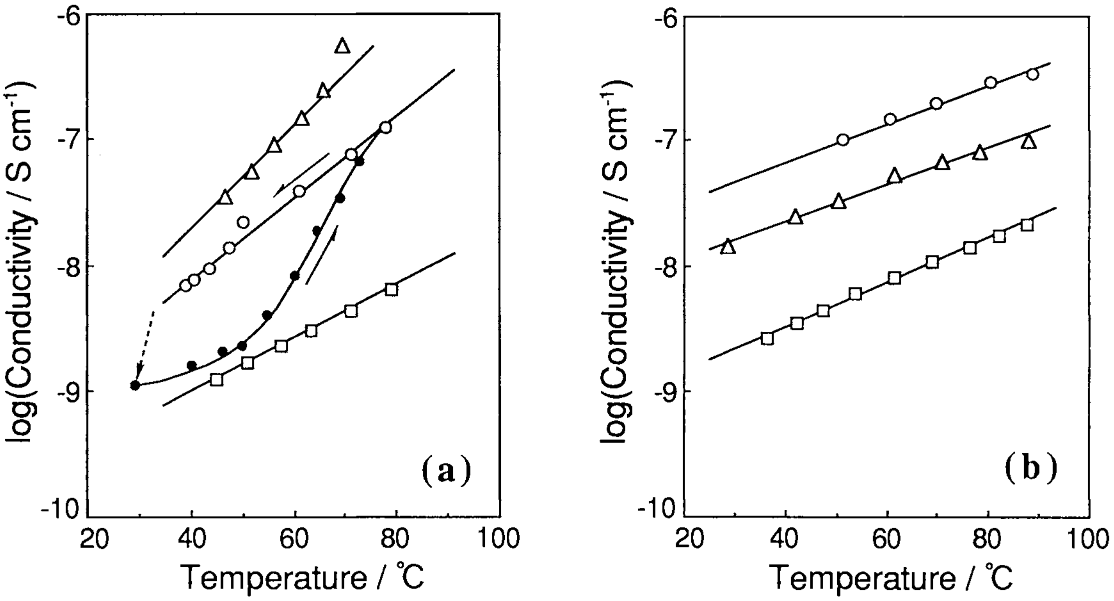
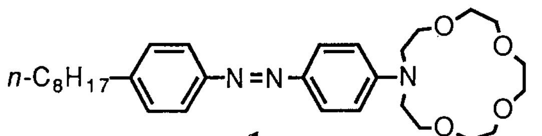


Fig. 1. Temperature dependence of ionic conductivity of composite films containing crowned azobenzene **1** (**a**) and 1:1 mixture of **2** and **3** (**b**). Li$^+$, on ascending (●) and descending (○) temperatures; Na$^+$ (△) and K$^+$ (□) on descending temperatures.



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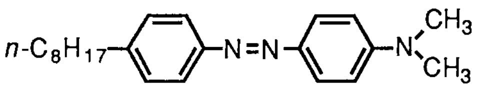

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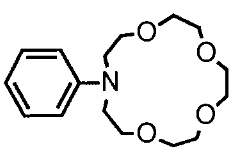

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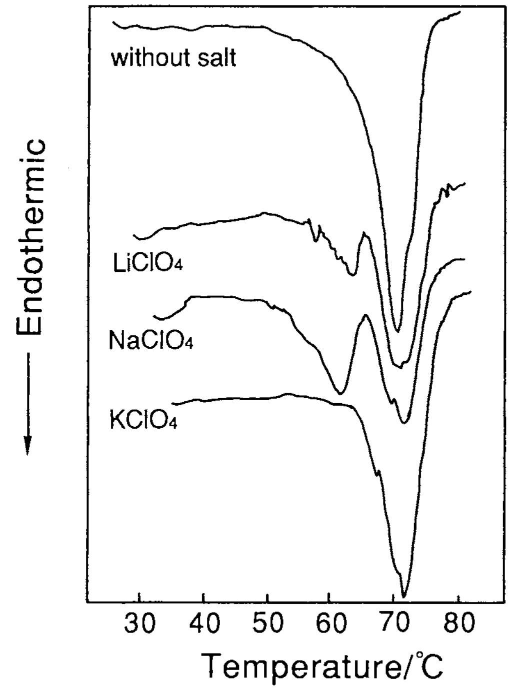

Fig. 2. DSC curves of crowned azobenzene-containing composite films with and without MClO$_4$.

transference number of 0.26 was attained, indicating mixed conduction of the cation and anion with predominant anion conduction.

Differential scanning calorimetry (DSC) of Na^+-containing composite films showed a new endothermic peak around 60 ℃ besides a peak based on the melting of **1** itself at 72 ℃. A similar peak, although weak, was found in DSC for the film of Li^+. By microscopy of the composite films containing $NaClO_4$ and $LiClO_4$, significant domains were observed which can be differentiated from the microcrystals based on **1** itself and actually melted around 60 ℃. The films of the **2**/**3** mixture, however, did not possess such domains. Wide-angle X-ray diffraction photographs of the domains showed Debye-Scherrer rings with ununiform intensities, which are correspondent to Bragg spacings of 3.9, 4.1, and 7.1 Å. The ununiform diffraction clearly indicates some orientational order of the crowned azobenzene molecule in the domain. The Bragg spacing of about 4 Å is typical of that between ordered long alkyl chains. The spacing of 7.1 Å may correspond to that induced by the crown ring with a van der Waals diameter of about 7 Å. Thus, the cation complexation brings about the ordered aggregation of the crowned azobenzene in the composite films consisting of the polyester elastomer, **1**, and $NaClO_4$ or $LiClO_4$, conceivably contributing to the enhanced ion conduction in the composite films.

We are currently studying cation specificities in the ionic conductivity of composite films incorporating similar azobenzene derivatives with different monoazacrown moieties.

References

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