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Cation-Complexation-Induced Aggregation and Specific Ion Conduction of Lipophilic Crowned Azobenzenes

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Abstract. Lipophilic azobenzene derivatives incorporating a monoazacrown or oligooxyethylene moiety were employed as a component of ion-conducting composite films containing a polyester elastomer and an alkali metal (Li^+, Na^+, K^+) perchlorate. Composite films of monoaza-15-crown-5-containing azobenzene **1** exhibited ionic conductivities following the order of $Na > Li > K$, reflecting the cation-binding selectivity of the 15-crown-5 ring. The ion-conducting behavior of composite films of **1** is quite different from that of composite films containing a 1 : 1 mixture of an azobenzene derivative without any crown moiety and *N*-phenyl-monoaza-15-crown-5 (ionic conductivity order of $Li > Na > K >$). It was suggested that cation and anion migration is predominant in the $LiClO_4$ and $NaClO_4$ systems, respectively. The specific ion conduction can be attributed to ordered aggregation of **1** induced by cation complex formation of its crown moiety. Azobenzene derivatives incorporating a monoaza-12-crown-4, monaza-18-crown-6, or oligooxyethylene moiety cannot afford such aggregate formation and specific ion-conduction as is seen in the **1** system.

Key words. Lipophilic crowned azobenzene, cation complexation, ordered aggregation, specific ion conduction.

1. Introduction

Extensive studies have been made to develop organic ionic conductors (polymer electrolytes), most of which include an oligooxyethylene or polyoxyethylene moiety as ion-conducting sites [1–3]. Crown ethers are cyclic oligooxyethylenes, but only a few examples concerning the applications of crown compounds to organic ionic conductors have been reported until recently. Crown ethers bind alkali metal ions powerfully as compared with their corresponding oligooxyethylene derivatives, thereby promoting separation of the cations and their counter anions. Crown ether complexes of alkali metal salts, therefore, afforded efficient anion conductors [4, 5]. Very recently, several works have appeared describing the use of crown ethers [6–8], cryptands [9], and poly(crown ether)s [10, 11] as a component of ion-conducting composites. The employment of crown compounds in ion-conducting composites affords enhanced solubility and dissociation of metal salts in the composites and lowering of their glass transition temperatures, resulting in an enhancement of the ionic conductivity of the composites.

We have been engaged in designing composite films whose ionic conductivity can be switched by external physical stimuli, such as light and heat. It has

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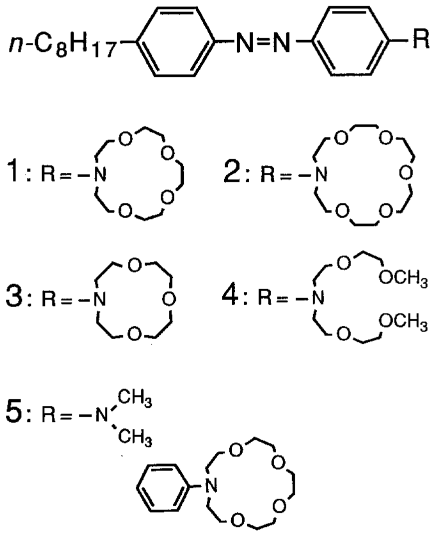
already been found that composite films consisting of poly(vinyl chloride), an azobenzene liquid crystal, $LiClO_4$, and 12-crown-4 undergo photoinduced switching of their ionic conductivity [12, 13], making them promising materials for electrostatic image storage [14]. In the course of designing azobenzene derivatives as the component of switchable ion-conducting films, we have struck on an interesting idea, *i.e.* the incorporation of a crown ether moiety into azobenzene derivatives. Some of the crowned azobenzene derivatives we have synthesized were found to possess liquid crystal characteristics, being applicable to a thermally-bistable ion-conducting composite [15].

We recently found that a lipophilic azobenzene derivative carrying monoaza-15-crown-5 moiety **1**, when incorporated into composite films of a polyester elastomer and an alkali metal perchlorate, enhances conduction of Li^+ which can be complexed weakly by the crown moiety [16]. There is, to the best of our knowledge, no example of such crown-complex-enhanced cation conduction in bi-ionic conduction systems. Similar azobenzene derivatives possessing monoazacrown moieties with different ring sizes and an oligooxyethylene moiety, furthermore, have been synthesized and the resulting composite films have been compared with the **1**-containing films in terms of their ion-conducting behavior. Here we report the full details of the ion-conducting behavior for composite films containing the crowned azobenzene derivatives and their analogs.

2. Experimental

2.1. SYNTHESIS OF CROWNED AZOBENZENES

Lipophilic azobenzene derivatives bearing a monoazacrown or oligooxyethylene moiety, **1**–**4**, were synthesized by the diazo-coupling reaction of 4-octylaniline with corresponding *N*-phenyl-monoazacrowns (such as **6**) and their acyclic analog,



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which were obtained according to a procedure given in the literature [17]. The typical synthetic procedure for the crowned azobenzenes is as follows. To 4-octylaniline (0.04 mol) dissolved in tetrahydrofuran (THF)/water (150/150 mL) was added an aqueous solution (80 mL) of $NaNO_2$ (0.04 mol) in an ice bath. After stirring for a further 30 min, *N*-phenyl-monoazacrown ether (0.04 mol) in THF (200 mL) was added to the mixture while stirring around 3°C. An aqueous solution (300 mL) of $NaHCO_3$ (0.12 mol) was then added dropwise, keeping the temperature at 5°C. The reaction was continued for two more hours at the same temperature. After the reaction, the THF was removed by evaporation and the residual solution was extracted with $CHCl_3$ (200 mL × 3). The $CHCl_3$ solution was dried over $MgSO_4$ and then evaporated to dryness. Silica gel chromatography of the resulting crude product using $CHCl_3$ as the eluent yields an orange crystal or liquid of pure product.

13-[4-(4-Octylphenylazo)phenyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane or *N-[4-(4-octylphenylazo)phenyl]-monoaza-15-crown-5* (**1**)

mp 72°C; ^{1}H-NMR (100 MHz, $CDCl_3$) δ0.88 (*t*, 3 H, CH_3), 1.2–1.8 (*m*, 12 H, $(CH_2)_6$), 2.67(*t*, 2 H, CH_2Ph), 3.6–3.9 (*m*, 20 H, CH_2CH_2O), 6.6–7.9 (*m*, 8 H, aromatic H); MS, *m/z* 511(M^+). *Anal. Calcd.* for $C_{30}H_{45}N_3O_4$: C, 70.42; H. 8.86; N, 8.21. *Found*: C, 70.43, H, 8.80, N, 8.04.

16-[4-(4-Octylphenylazo)phenyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane or *N-[4-(4-octylphenylazo)phenyl]-monoaza-18-crown-6* (**2**)

mp 39°C; ^{1}H-NMR(100 MHz, $CDCl_3$) δ0.88 (*t*, 3 H, CH_3), 1.2–1.8 (*m*, 12 H, $(CH_2)_6$), 2.74 (*t*, 2 H, CH_2Ph), 3.7–3.9 (*m*, 24 H, CH_2CH_2O), 6.7–7.9 (*m*, 8 H, aromatic H), MS, *m/z* 555(M^+). *Anal. Calcd.* for $C_{32}H_{49}N_3O_5$: C, 69.16; H, 8.89; N, 7.56. *Found*: C, 68.98, H, 8.94, N. 7.72.

10-[4-(4-Octylphenylazo)phenyl]-1,4,7-trioxa-10-azacyclododecane or *N-[4-(4-octylphenylazo)phenyl]-monoaza-12-crown-4* (**3**)

mp 49°C; ^{1}H-NMR (100 MHz, $CDCl_3$) δ0.85 (*t*, 3 H, CH_3), 1.2–1.8(*m*, 12 H, $(CH_2)_6$), 2.71 (*t*, 2 H, CH_2Ph), 3.6–4.0 (*m*, 16 H, CH_2CH_2O), 6.7–7.9 (*m*, 8 H, aromatic H), MS, *m/z* 467(M^+). *Anal. Calcd.* for $C_{28}H_{41}N_3O_3$: C, 71.91; H, 8.84; N, 8.99. *Found*: C, 71.94, H, 8.82, N, 9.13.

8-[4-(4-Octylphenylazo)phenyl]-2,5,11,14-tetraoxa-8-azapentadecane (**4**)

Oil; ^{1}H-NMR (100 MHz, $CDCl_3$) δ0.87 (*t*, 3 H, CH_3), 1.2–1.8 (*m*, 12 H, $(CH_2)_6$), 2.73 (*t*, 2 H, CH_2Ph), 3.2–3.8 (*m*, 22 H, $(CH_2)_2O(CH_2)_2OCH_3$), 6.7–7.9 (*m*, 8 H, aromatic H), MS, *m/z* 513(M^+). *Anal. Calcd.* for $C_{30}H_{47}N_3O_4$: C, 70.14; H, 9.22; N, 8.18. *Found*: C, 69.96, H, 9.32, N, 8.14.

2.2. OTHER MATERIALS

The preparation of 4-(*N*,*N*-dimethylamino)-4′-octylazobenzene **5** was performed by a similar diazo-coupling reaction to that used for the crowned azobenzene derivatives [12]. The polyester elastomer (Pelprene 40-H, Toyobo), poly(butylene terephthalate) containing an oligooxybutylene moiety with an average molecular weight of 1000 as a soft segment, was purified by repeated reprecipitation from chloroform in methanol. Poly(vinyl chloride) (PVC, polymerization degree of 1020) was precipitated from THF in methanol. Alkali metal salts employed here were of analytical grade.

2.3. 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 (62.8 mg), crowned azobenzene (36.7 mg), and $LiClO_4$ (0.5 mg) were dissolved in 1 mL of chloroform and 100 μL of the solution was used for each spin coating to yield a film with a thickness of about 4 μm after drying for one day at 50°C under a nitrogen stream. A gold disk electrode of 5 mm diameter was prepared on the composite-film-coated ITO glass by evaporation before a.c. impedance measurements. The composite films for other alkali metal salts contained an equimolar amount of respective salt. The typical film composition was about 63 wt.-% polyester, about 37 wt.-% crowned azobenzene derivative, and 0.5–0.6 wt.% alkali metal salt. Composite films for the transient ionic current measurements were cast on a glass plate (2.5 × 4 cm) from 1 mL of chloroform solutions in the same composition as for the ionic conductivity measurements. The film thickness, which was measured by a dial gauge after each casting, ranged from 50 to 80 μm. Composite films for the X-ray diffraction were obtained by spin coating on a poly(ethylene terephthalate) film (Mylar, 2.5 μm).

2.4. MEASUREMENTS

The procedure and cell setup for the ionic conductivity measurements were as described elsewhere [12]. The isothermal transient ionic current measurements were carried out at 80°C in a similar way to a procedure reported previously [18], using the cell set-up for ionic conductivity measurements and a programmable electrometer (Keithley 617 type) controlled and data-processed by a microcomputer through a GP-IB board. After applying an appropriate d.c. voltage across the films for 3 h, the polarity was switched rapidly and the transient current was then monitored every second. The transference numbers for cation and anion can be calculated from $\tau_+/(\tau_+ + \tau_-)$ and $\tau_-/(\tau_+ + \tau_-)$, respectively, where τ_+ and τ_- represent transient times for the corresponding ions, which were in turn obtained from bumps or shoulders in the logarithmic plots of the current *vs.* time curves. The measurement of transference numbers was performed at least 3 times for each system and the values obtained were averaged. The relative errors for the transference number ranged from 5 to 10%. Differential scanning calorimetry (DSC) of the composite films was undertaken at a scan rate of 5°C min^{-1} with a Daini Seikosha SSC/560 differential scanning calorimeter. Fast-atom-bombardment (FAB) mass spectra of the composite films were taken on a JEOL JMS-DX303 mass spectrometer at the Instrumental Analytical Center, using 3-nitrobenzylalcohol as the matrix. Composite films were soaked in a small quantity of 3-nitrobenzylalcohol for several hours. The extracts were subjected to mass spectroscopy. X-ray diffraction patterns were taken with an evacuated Searle X-ray camera in a specimen-to-film distance of 40 mm, using Ni-filtered Cu-K_α radiation (a Cu anode of the Rigaku FR-B rotating anode X-ray generator operated at 40 kV and 40 mA).

3. Results and Discussion

3.1. ION-CONDUCTING BEHAVIOR OF AZOBENZENE DERIVATIVE WITH MONOAZA-15-CROWN-5 MOIETY

Figure 1 shows the typical ion-conducting behavior of composite films consisting of a poly(butylene terephthalate) elastomer, $LiClO_4$, and crowned azobenzene **1**. At room temperature, the composite film exhibited only a low ionic conductivity. Increasing temperature gradually raised the ionic conductivity, which was still low. The ionic conductivity, however, increased drastically in the temperature range of 60–70°C, obviously owing to ion mobility enhancement by phase transitions of the crowned azobenzene and its cation complex from crystal to liquid states. As the temperature decreased, the ionic conductivity was lowered monotonously. Due to a very sluggish phase transition of **1** back to its crystal state in the film, no abrupt diminution was observed in the ionic conductivity. It took more than 24 h to restore the ionic conductivity to the initial value at room temperature. This type of hysteresis in the temperature-dependent ionic conductivity was also found in similar

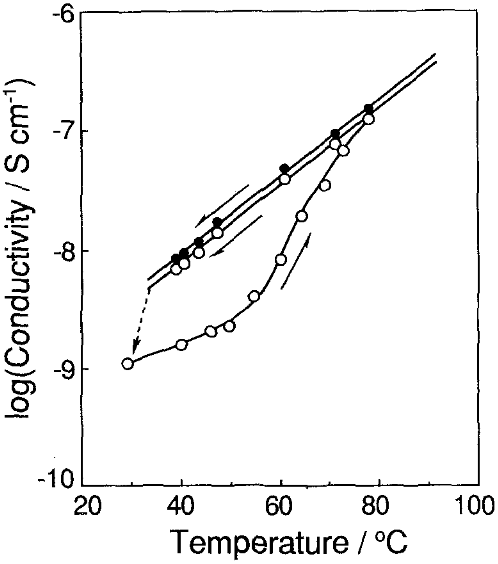


Fig. 1. Thermo- and photoresponse of ionic conductivity for a composite film of polyester/$LiClO_4$/crowned azobenzene **1**. (○) in the dark, (●) with UV light irradiation.

composite films containing $NaClO_4$ and $KClO_4$. Since the azobenzene moiety of **1** is photochromic, a photoinduced ionic conductivity change was expected in the composite film. No significant ionic conductivity change, however, was attained upon photo-irradiation (300–400 nm, light of Xe lamp through a Toshiba UV-D35 filter) on the film, unlike our previous polymer composite systems containing azobenzene liquid crystals [12]. This is mainly because the crowned azobenzene derivative hardly isomerizes to its corresponding *cis* isomer in the composite films.

Figure 2 summarizes the ionic conductivities of the composite films of three alkali metal perchlorates for the decreasing temperature process. It should be noted that the ionic conductivities decrease in the order of Na > Li > K systems, which almost corresponds to the order for the cation-complexing affinity of the monoaza-15-crown-5 moiety. For comparison, a 1 : 1 mixture of azobenzene derivative **5** and *N*-phenyl-monoaza-15-crown-5 (**6**) was employed as an isolated model of crowned azobenzene **1** for the composite film preparation. Ionic conducitivities for the resulting composite films in the decreasing temperature process are depicted in Figure 3. The composite films containing a **5**/**6** mixture clearly differ from those of **1** in that the ionic conductivity follows the order of Li > Na > K systems. Steeper slopes for **1** systems of Li^+ and Na^+ than the **5**/**6** systems in the temperature dependence of ionic conductivity also suggest that the former systems undergo ionic conduction in a different way from the latter ones.

Isothermal transient ionic currents (ITIC) were measured using alkali metal (Li and Na) and Pt electrodes, in order to obtain some information about ionic species that predominates in the ionic conductivity for the crowned-azobenzene-containing

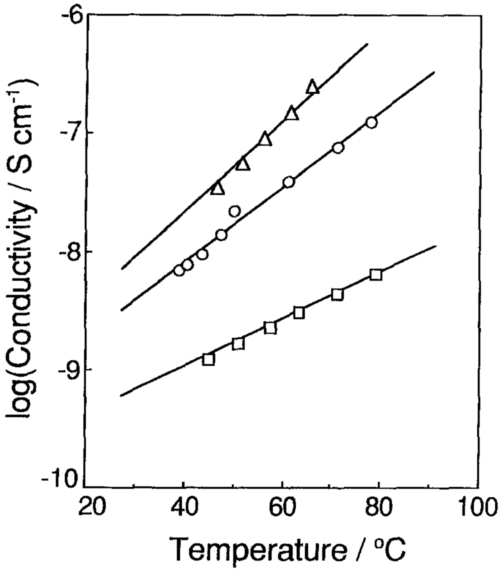


Fig. 2. Comparison of ionic conductivities for composite films of crowned azobenzene **1** containing different alkali metal perchlorates. (○) $LiClO_4$, (△) $NaClO_4$, (□) $KClO_4$.

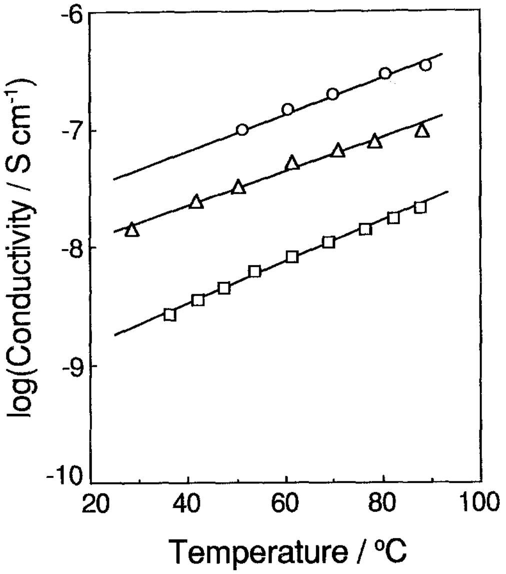


Fig. 3. Comparison of ionic conductivity for composite films **5**/**6** mixture containing different alkali metal perchlorates. The symbols are identical with those of Fig. 2.

composite films (Figure 4). When a pair of Pt electrodes was used for the transient current measurements, the d.c. current was reduced immediately after the polarity switching in composite films containing **1** and $LiClO_4$, because Pt electrodes are ion-blocking for both the cation and anion. On the other hand, when a pair of Li electrodes was used instead, the current remained almost unchanged. Since Li electrodes are ion-reversible for Li^+, the unchanged transient ionic current indicates

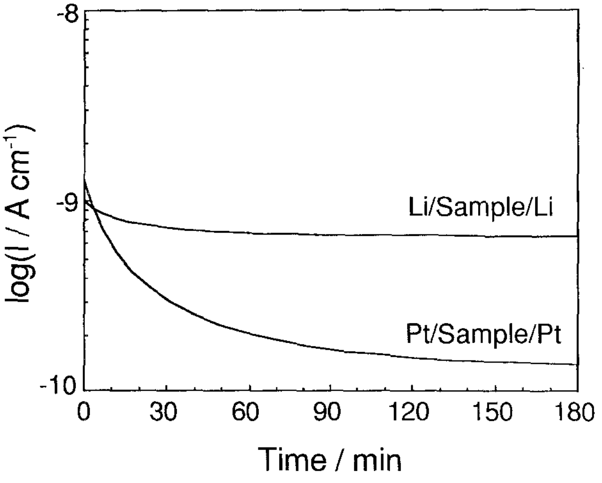


Fig. 4. Isothermal transient ionic currents for composite films containing **1** and $LiClO_4$ with applied voltage of 1 V.

that Li^+ is a main carrier for the conductivity of composite films of polyester elastomer/$LiClO_4$/crowned azobenzene **1**. Estimation of transference numbers for the ionic species was made by ITIC measurements. Well-defined bumps were observed in the logarithmic ITIC curves for composite films of polyester/crowned azobenzene **1**/$LiClO_4$ (Figure 5). Taking account of the maximal current time for the anion (ClO_4^-) in the Li electrode (cation-reversible) system, the early and late bumps in the Pt electrode (ion-blocking) system can thus be assigned to the cation and anion, respectively. It is worth noting that the composite film containing crowned azobenzene **1** and $LiClO_4$ possesses a high transference number for the cation ($\tau_+ > 0.9$), undergoing specific cation (Li^+) conduction. Similarly, transference numbers for the **1**/$NaClO_4$ system were obtained by its logarithmic ITIC curves (Figure 6), the pattern of which is dramatically different from that for the corresponding $LiClO_4$ system. The transference number for the anion, this time, in the **1**/$NaClO_4$ system is very high ($\tau_- > 0.9$), indicating that the anion migrates specifically in the composite film. This predominant anion conduction in the **1**/$NaClO_4$ system presents a striking contrast to the predominant cation conduction in the **1**/$LiClO_4$ system. On the other hand, the transference numbers in the composite films containing a **5**/**6** mixture and $LiClO_4$ (or $NaClO_4$) show that both the cation and anion participate in the ionic conduction ($\tau_- =$ ca. 0.7 for $LiClO_4$ and $\tau_- =$ ca. 0.8 for $NaClO_4$). In the composite film of **5**/**6** mixture, the crown ether probably contributes to dissolution of alkali metal salts and thereby to separation between the cation and anion, which in turn promotes ion migration across the films, as is the case with crown-assisted ionic conduction reported so far [6–9]. It is certain that the present results distinguish the ion-conducting behavior of the polyester/**1**/$MClO_4$ films from the simple crown-assisted ionic conduction.

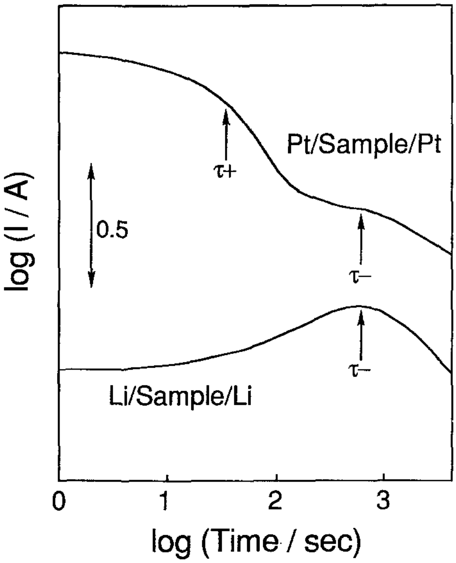


Fig. 5. Logarithmic plots of isothermal transient ionic currents for composite films containing **1** and $LiClO_4$ with applied voltage of 5 V.

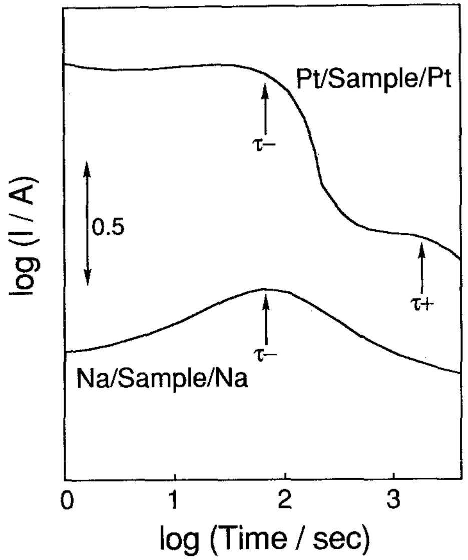


Fig. 6. Logarithmic plots of isothermal transient ionic currents for composite films containing **1** and $NaClO_4$ with applied voltage of 3 V.

3.2. AGGREGATE FORMATION OF AZOBENZENE DERIVATIVE WITH MONOAZA-15-CROWN-5

Figure 7 shows DSC data for the **1**-containing composite films with different alkali metal perchlorates. The composite films without any alkali metal perchlorate and with $KClO_4$ possess a single endothermic peak around 70°C which corresponds to the melting point of **1**, while the films containing $LiClO_4$ and $NaClO_4$ exhibited another endothermic peak around 60°C, besides the 70°C peak. By microscopic observation, significant domains, which actually melted around 60°C, were found in both of the $LiClO_4$ and $NaClO_4$ systems. As the content of $LiClO_4$ or $NaClO_4$ was increased in the composite films, the 60°C peak was intensified in the DSC. This implies that complexation of the crowned azobenzene **1** with $LiClO_4$ and $NaClO_4$ is responsible for the domain formation in the composite films. The cation complexation of **1** in the composite films is evidenced by a FAB mass spectrum for extracts of composite films containing the three alkali metal perchlorates simultaneously (Figure 8). There are appreciable fragment peaks based on **1**$-Li^+$ and **1**$-Na^+$ complexes, but only a tiny peak for the **1**-K^+ complex. The relative peak intensities for the complex cations confirm the cation-complexing selectivity of crowned azobenzene **1**, *i.e.*, $Na^+ > Li^+ > K^+$. Nevertheless, the domains, observed in composite films containing **1** and $NaClO_4$ (or $LiClO_4$), do not seem to consist merely of 1 : 1 **1**$-M^+$ ($M = Li$, Na) complexes. In a separate experiment, we prepared a 1 : 1 **1**/$NaClO_4$ complex, which melted around 120°C, and then dispersed the complex in the polyester elastomer. The resulting composite of polyester and the **1**$-NaClO_4$ complex, however, did not exhibit any 60°C peak for what we call domains, but a weak 70°C peak for the crowned azobenzene itself.

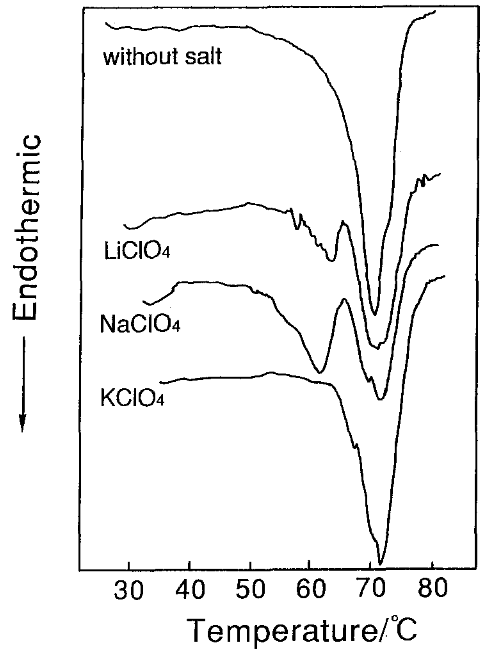


Fig. 7. DSC curves for composite films of polyester/crowned azobenzene 1/$MClO_4$.

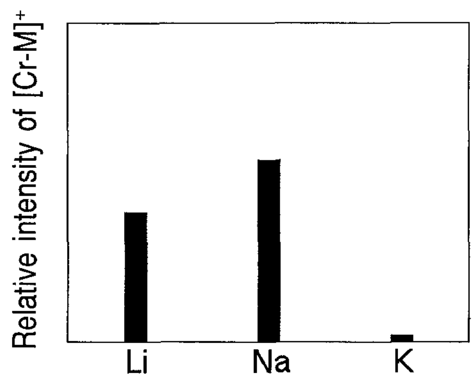
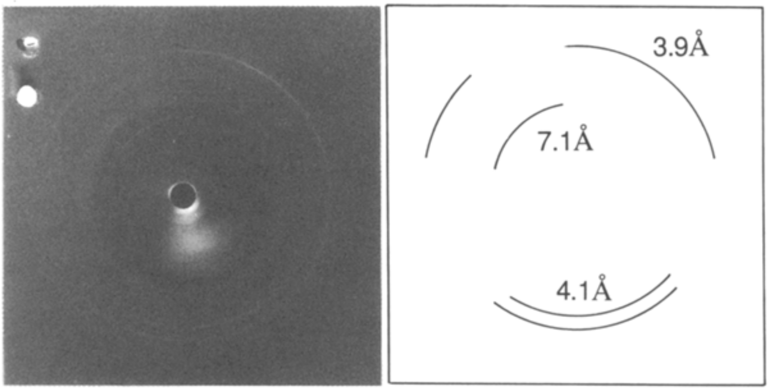
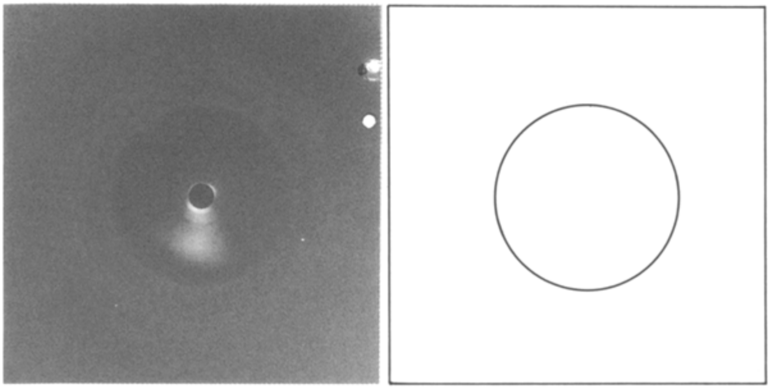


Fig. 8. Relative intensities for crown-complexed metal cations in FAB mass spectrum of composite films of polyester/crowned azobenzene 1/perchlorate salts of Li, Na, and K.

A probable component of the domains in composite films containing **1** and $NaClO_4$ (or $LiClO_4$) is a crown-complexation-induced aggregate of crowned azobenzene **1**. X-ray diffraction photographs of a composite film containing **1** and $NaClO_4$ offer valuable information about the structure of the domains. Debye–Scherrer rings observed in the photograph for the domains have nonuniform diffraction intensities, their Bragg spacings being ca. 4 and 7 Å (Figure 9). Such nonuniformity in X-ray diffraction was not found in the non-domains of the



domain

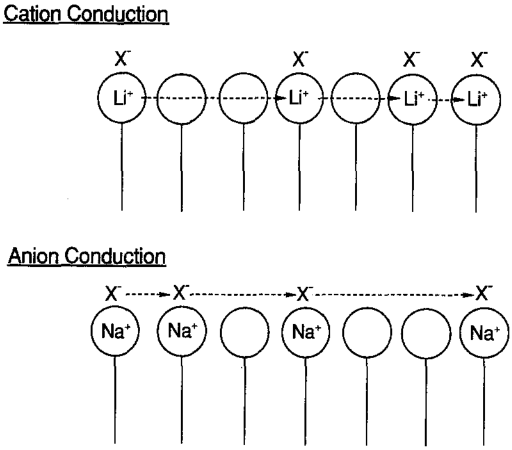


non-domain

Fig. 9. X-ray diffraction of domains and non-domains for a composite film of polyester/crowned azobenzene **1**/$NaClO_4$.

composite film. The nonuniform diffraction suggests that the domains bear a rather ordered structure. The Bragg spacings of 4 and 7 Å may be derived from ordered aggregation of the long alkyl chains and crown moieties, respectively, of crowned azobenzene **1**.

Thus composite films of polyester elastomer/crowned azobenzene **1**/$NaClO_4$ (or $LiClO_4$) were found to contain some domains that are possibly composed of aggregates of the crowned azobenzene induced by cation complexation of its monoaza-15-crown-5 moiety. The domain formation might explain the predominant cation and anion conduction in the **1**-containing composite films with $LiClO_4$ and $NaClO_4$, respectively, as speculated in Figure 10. Li^+ is easy to migrate through the crowned azobenzene aggregate in the **1**/$LiClO_4$ system, just like a sort of ion channel. In the **1**/$NaClO_4$ system, on the other hand, Na^+ is bound so powerfully by the crown moiety that the cation is hard to migrate. Instead, the anion, ClO_4^-, is able to move efficiently along the cations fixed in the aggregate.


Cation Conduction

Anion Conduction

Fig. 10. Plausible mechanism for predominant cation and anion conduction along a crowned azobenzene aggregate.

3.3 ION-CONDUCTING BEHAVIOR OF OTHER CROWNED AZOBENZENES

It is of great interest to see how the kind of crown moiety affects ion-conducting behavior of crowned azobenzene derivatives. In order to elucidate a ‘crown effect’ on the ionic conduction, we also synthesized similar azobenzene derivatives with a monoaza-18-crown-6 or monoaza-12-crown-4 moiety, and with an acyclic model of the monoaza-15-crown-5 azobenzene, **2**–**4**, and then fabricated polyester composite films similar to the above-mentioned composite films containing **1** and alkali metal perchlorates. In the composite films of **2**–**4**, such domain formation or crowned azobenzene aggregation as observed in the **1** systems could not be detected by DSC, microscopy, and X-ray diffraction. The ionic conductivity of the polyester composite films of crowned azobenzene **2** follows the order $\mathrm{K} > \mathrm{Li} > \mathrm{Na}$ systems, the ionic conductivity order reflecting the cation-complexing specificities of the crown moiety. This was the case with the **3** systems, the ionic conductivity being in the order of $\mathrm{Li} > \mathrm{Na} > \mathrm{K}$ systems. ITIC measurements for their $LiClO_4$ and $NaClO_4$ systems suggested mixed conduction of the cation and anion in the **2** and **3** systems. It is probable in these cases that cation complexation by their crown moieties merely promotes cation–anion separation, thus assisting migration of ions, especially the counter-anions of crown-complexed cations, in the composite films. The composite films of **2** and **3** seem to resemble the **5**/**6** mixture systems and the previous crown-assisted bi-ionic conduction systems in the ion-conducting behavior [6, 7, 9]. Similarly, composite films of acyclic model compound **4** and $LiClO_4$ undergo mixed ion conduction. The oxyethylene units are considered to act as cation-hopping sites as seen in composite films of poly-oxyethylene/alkali metal salts [3]. Accordingly, it is easier for smaller cations to move in the composite films, resulting in the ionic conductivity order of $\mathrm{Li} > \mathrm{Na} > \mathrm{K}$ systems.

In conclusion, only the lipophilic azobenzene derivative incorporating the monoaza-15-crown-5 moiety **1** afforded the specific ion conduction in polyester composite films also containing $LiClO_4$ and $NaClO_4$, respectively, probably owing to the formation of domains based on the crowned azobenzene aggregation.

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