Synthesis of Vinyl Polymers Incorporating Different Crowned Azobenzene Moieties and Their Application to Photoresponsive Ion-Conducting System

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Vinyl polymers carrying a crowned azobenzene side chain, which have a crown ether moiety and an azobenzene moiety in two different ways, were synthesized and their ion-conducting behavior investigated. The crowned azobenzene vinyl polymer carrying a crown ether moiety apart from its azobenzene moiety, **1**, exhibited distinct liquid crystal phases, which were stabilized by the addition of alkali metal perchlorates. Ion-conducting composite films containing crowned azobenzene vinyl polymer **1** underwent remarkable photoinduced ionic-conductivity switching. The system of vinyl polymer **2**, which carries a crown-ether ring in the vicinity of its azobenzene moiety, is greater in the magnitude of photoinduced ionic-conductivity change (ionic-conductivity ratio) than the system of vinyl polymer **1**. X-Ray diffraction measurements suggested that the difference in the ionic-conductivity switching between the two crowned azobenzene polymers is derived from the difference in the order–disorder arrangement of the crown ether moiety on the photoisomerization of the azobenzene moiety from its trans form to the corresponding cis one.

We have been aiming at the construction of ion-conducting systems which undergo effective ionic conduction and photoinduced ionic-conductivity switching. As an approach to this aim, liquid-crystalline azobenzene derivatives containing a crown ether moiety, which we call crowned azobenzenes, have been used as key materials for ionic conduction. Azobenzene moieties in the trans form are a useful mesogen for liquid-crystal compounds due to their rigid structures,[1] whereas *cis* azobenzene moieties cannot contribute to liquid-crystal phases due to their bent structures. The photoisomerization of azobenzene derivatives capable of forming liquid-crystal phases may, therefore, cause a pronounced phase transition, which in turn may change the mobility of any ion-conducting carriers. We have already reported that low-molecular-weight and polymeric liquid crystals[2—5] containing crowned azobenzene moieties have shown a photoinduced switching of the ionic conductivity. The incorporation of crowned azobenzene side chains to a polymer main chain brought about stable liquid-crystal formation and caused unique photoresponsive ion-conducting behavior,[5] which was very different from that for the corresponding low-molecular-weight crowned azobenzene derivatives.[2,4] It was obvious that the photoinduced change in the ionic conductivity for the polymer system was due to a change in the ordered arrangement of the crown-ether moiety, which can participate in ionic conduction. It is, therefore, of much interest to compare the photoresponsive ion-conducting behavior among polymers carrying crowned azobenzene side chains which have a crown ether and azobenzene moieties in different ways.

In this study, a vinyl polymer carrying a crowned azobenzene which has its crown moiety apart from its azobenzene moiety **1** was first synthesized. The behavior of the crowned azobenzene polymer in the phase transition and photoinduced ionic-conductivity switching was investigated. The ion-conducting behavior for the polymer was compared with that for vinyl polymer having a crown moiety in the vicinity of its azobenzene moiety, **2**.

Experimental

Synthesis of Crowned Azobenzene Vinyl Monomer. 4,4′-Dihydroxyazobenzene (3). This compound was obtained by the treatment of 4-nitrophenol with KOH.[6] Purple crystals (31%). Mp 219—222 °C; ^{1}H NMR (270 MHz, d^6-DMSO) $\delta = 6.94$ (4H, d, $J = 10.8$ Hz, 3-,3′-,5-, and 5′-H), 7.71 (4H, d, $J = 10.8$ Hz, 2-,2′-,6-, and 6′-H), 10.14 (2H, s, OH).

4-(11-Hydroxyundecyloxy)-4′-hydroxyazobenzene (4). The synthesis was performed by the Williamson reaction of 4,4′-dihydroxyazobenzene with 11-hydroxyundecyl bromide. 4,4′-Dihydroxyazobenzene (5.00 g, 21.6 mmol) was added to an ethanol solution (1 dm^3) of potassium hydroxide (1.21 g, 21.6 mmol). After the addition of sodium iodide (0.22 g), the solution was heated to reflux. An ethanol solution (50 cm^3) of 11-hydroxyundecylbromide (3.61 g, 14.4 mmol) was slowly added while refluxing. The refluxing was continued for 24 h. The ethanol was removed under vacuum. After washing with water, the residue was recrystallized from ethanol twice. Yellow crystals (29.8%). Mp 157—158 °C; ^{1}H NMR (270 MHz, d^6-DMSO) $\delta = 1.10$—1.49 (16H, m, HOCH$_2$(CH_2)$_8$–), 1.64—1.82 (2H, m, –CH_2CH$_2$OPh–), 3.25—3.41 (2H, m, HOCH_2–), 4.04 (2H, t, $J = 6.2$ Hz, –CH$_2$OPh–), 4.29 (1H, t, HO–), 6.92 (2H, d, $J = 8.9$ Hz, 3′- and 5′-H on Ph), 7.07 (2H, d, $J = 9.2$ Hz, 3- and 5-H on Ph), 7.71—7.81 (4H, m, 2-,2′-,6-, and 6′-H on Ph), 10.1 (1H, s, PhOH).

4′-[11-[4-(4-Hydroxyphenylazo)phenoxy]undecyloxycarbon-

yl]benzo-15-crown-5 (5). To a dry chloroform solution (30 cm^3) of 4′-carboxybenzo-15-crown-5 (1.20 g, 3.85 mmol) was added dropwise thionyl chloride (1.15 g, 9.63 mmol).[7] After the mixture was refluxed for 3 h, the solvent and excess thionyl chloride were evaporated off to yield 4′-(chlorocarbonyl)benzocrown ether. The crude 4′-(chlorocarbonyl)benzocrown ether (3.85 mmol) was dissolved in dry THF (20 cm^3), and was then added to a dry THF solution containing 4-(11-hydroxyundecyloxy)-4′-hydroxyazobenzene (1.48 g, 3.85 mmol) and pyridine (0.33 g, 4.24 mmol) while stirring at about 35 °C. The mixture was stirred at 40 °C overnight. After cooling to room temperature, the reaction mixture was evaporated to dryness. The crude product was purified by recrystallization from ethanol, followed by column chromatography with silica gel as the stationary phase and ethyl acetate/chloroform (30/70 vol%) as the mobile phase. Yellow crystals (50.2%): ^{1}H NMR (270 MHz $CDCl_3$) $\delta = 1.20$—1.53 (14H, m, $-OCH_2CH_2(CH_2)_7CH_2CH_2O-$), 1.60—1.86 (4H, m, $-COOCH_2CH_2-$ and $-CH_2CH_2O-$), 3.77 (8H, s, $-OCH_2CH_2O-$), 3.96 (4H, m, $PhOCH_2CH_2O-$), 4.04 (2H, t, $J = 6.8$ Hz, $PhOCH_2-$), 4.17 (4H, m, $PhOCH_2CH_2O-$), 4.26 (2H, t, $J = 9.3$ Hz, $-COOCH_2-$), 6.00 (1H, s, HOPh–), 6.84 (1H, d, $J = 8.7$ Hz, 3′-H on crown Ph), 6.95 (2H, d, J = 8.1 Hz, 3- and 5-H on Ph), 6.97 (2H, d, $J = 8.7$ Hz, 3′- and 5′-H on Ph), 7.51 (1H, m, 6-H on crown Ph), 7.64 (1H, m, 4-H on crown Ph), 7.78 (2H, d, $J = 8.1$ Hz, 2- and 6-H on Ph), 7.84 (2H, d, $J = 8.7$ Hz, 2′- and 6′-H on Ph); MS m/z (% rel intensity) 679 (M^+; 58), 295 (100).

4′-[11-[4-[4-(Methacryloyloxy)phenylazo]phenoxy]undecyloxycarbonyl]benzo-15-crown-5 (6). After a mixture of compound **5** (1.12 g, 1.65 mmol), triethylamine (0.50 g, 4.95 mmol), and THF (20 cm^3) were cooled in an ice bath under an argon atmosphere, methacryloyl chloride (0.26 g, 2.48 mmol) was added dropwise while stirring.[8] The solution was then stirred at room temperature for 18 h. The reaction mixture was evaporated to dryness and the residue was washed with water. The crude product was purified by recrystallization from hexane to yield a yellow solid (78.2%): Mp 101 °C; ^{1}H NMR (270 MHz $CDCl_3$) $\delta = 1.23$—1.54 (14H, m, $-OCH_2CH_2(CH_2)_7CH_2CH_2O-$), 1.65—1.93 (4H, m, $-COOCH_2CH_2$ and $-CH_2CH_2OPh$), 2.09 (3H, s, $CH_2{=}C(CH_3)-$) 3.76 (8H, s, $-OCH_2CH_2O-$), 3.92 (4H, m, $PhOCH_2CH_2O-$), 4.04 (2H, t, $J = 6.8$ Hz, $PhOCH_2-$), 4.17 (4H, m, $PhOCH_2CH_2O-$), 4.28 (2H, t, $J = 9.3$ Hz, $-COOCH_2-$), 5.79 and 6.38 (1H each, s, $CH_2{=}C(CH_3)-$), 6.85 (1H, d, $J = 8.1$ Hz, 3′-H on crown Ph), 7.00 (2H, d, $J = 8.6$ Hz, 3′- and 5′-H on Ph), 7.27 (2H, m, 3- and 5-H on PhOCO), 7.54 (1H, m, 6′-H on crown Ph), 7.68 (1H, m, 4′-H on crown Ph), 7.83—7.99 (4H, m, 2-, 2′-, 6-, and 6′-H on Ph); MS *m/z* (rel intensity) 747 (M^+; 100). Anal. Calcd for $C_{42}H_{54}N_2O_{10}$: C, 67.54; H, 7.29; N, 3.75%. Found: C, 67.39; H, 7.37; N, 3.70%.

4-[11-(Methacryloyloxy)undecyloxy]-4′-hydroxy-azobenzene (7). 4-(11-Hydroxyundecyloxy)-4′-hydroxyazobenzene (2.92 g, 7.6 mmol) and dry pyridine (1.26 g, 16.0 mmol) were suspended in a dry THF solution (145 cm^3) at room temperature under an argon atmosphere. Methacryloyl chloride (0.88 g, 8.4 mmol) was added dropwise while stirring. The mixture was stirred at room temperature for 24 h. The reaction mixture was evaporated to dryness. The crude product was washed with water and then subjected to column chromatography with silica gel and the stationary phase and chloroform as the mobile phase. Yellow crystals (46.6%); ^{1}H NMR (270 MHz $CDCl_3$) $\delta = 1.13$—1.89 (18H, m, $-OCH_2(CH_2)_9CH_2O-$) 1.94 (3H, S, $CH_2{=}C(CH_3)-$), 4.02 (2H, t, $J = 6.5$ Hz, $PhOCH_2-$), 4.14 (2H, t, $J = 6.75$ Hz, $-COOCH_2-$), 5.53 (1H, s, HOPh–), 5.55 and 6.10 (1H each, s, $CH_2{=}C(CH_3)-$), 6.91—7.00 (4H, m, 3-, 3′-, 5-, and 5′-H on Ph), 7.81—7.87 (4H, m, $J = 8.7$ Hz, 2-, 2′-, 6-, and 6′-H on Ph).

4′-[4-[4-[11-(Methacryloyloxy)undecyloxy]phenylazo]phenoxycarbonyl]benzo-15-crown-5 (8). Crude 4′-(chlorocarbonyl)-benzocrown ether (1.86 mmol) was dissolved in dry THF (5 cm^3) and then was added to a dry THF solution (10 cm^3) containing 4-(11-methacryloylundecyloxy)-4′-hydroxyazobenzene (0.84 g, 1.86 mmol) and triethylamine (0.188 g, 1.86 mmol) while stirring at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 18 h. The reaction mixture was evaporated to dryness. The crude product was washed with water and purified by recrystallization from ethanol twice. Yellow crystals (69.8%): Mp 95 °C; ^{1}H NMR (270 MHz $CDCl_3$) $\delta = 1.23$—1.89 (18H, m, $-OCH_2(CH_2)_9CH_2O-$), 1.94 (3H, s, $CH_2{=}C(CH_3)-$), 3.78 (8H, s, $-OCH_2CH_2O-$), 3.95 (4H, m, $PhOCH_2CH_2O-$), 4.04 (2H, t, $J = 6.5$ Hz, $-COOCH_2-$), 4.14 (2H, t, $J = 6.8$ Hz, $-CH_2OPh-$), 4.23 (4H, m, $PhOCH_2CH_2O-$), 5.54 and 6.10 (1H each, s, $CH_2{=}C(CH_3)-$), 6.93 (1H, d, $J = 8.4$ Hz, 6′-H on crown Ph), 7.00 (2H, d, $J = 8.9$ Hz, 3′- and 5′- H on Ph), 7.34 (2H, d, $J = 8.4$ Hz, 3- and 5- H on PhOCO), 7.67 (1H, m, 6′-H on crown Ph), 7.86 (1H, m, 5′-H on crown Ph), 7.89—7.97 (4H, m, 2-, 2′-, 6-, and 6′-H on Ph); MS *m/z* (rel intensity) 747 (M^+; 54), 295 (100). Anal. Calcd for $C_{42}H_{54}N_2O_{10}$: C, 67.54; H, 7.29; N, 3.75%. Found: C, 67.36; H, 7.32; N, 3.70%.

Polymerization of Crowned Azobenzene Monomers. Radical polymerization of crowned azobenzene vinyl monomers was carried out in toluene using α,α'-azobisisobutyronitrile (AIBN) as the initiator (1 mol% to the monomer) at 65 °C for 36 h. The polymerization was performed in a glass tube which was sealed after several freeze-pump-thaw cycles under vacuum. The reaction mixture was evaporated to dryness. The crude product was fractionated to appropriate portions by gel-permeation chromatography (JAIGEL-1H and 2H, $CHCl_3$).

Other chemicals. The polyester elastomer, poly(butylene-terephthalate) (Pelprene 40-H, Toyobo) containing an oligo(oxybutylene) moiety with an average molecular weight of about 1000 as the soft segment ($T_g = -80$ °C), was purified by repeated reprecipitation from chloroform in methanol. All other reagents were of 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 (25.0 mg), crowned azobenzene vinyl polymer (8.0 mg), and $NaClO_4$ (0.328 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 room temperature under a nitrogen stream. As a counter electrode, an Au disk of 6-mm diameter was evaporated on the composite-film-coated ITO glass just before ac impedance measurements. The typical composite films contained about 75.0 wt% polyester, about 24.0 wt% crowned azobenzene polymer, and about 0.90—1.1 wt% metal salt. After setting up in the measurement cell, all of the composite films were subjected to annealing at 100 °C in vacuo for 1 h, cooled to 60 °C in an argon stream, and then kept at 60 °C for 3 h until the ionic conductivity did not change any more.

Measurements. The procedure and cell setup for the ionic-conductivity measurements were as described elsewhere.[2] The measurement cell was strictly controlled by a thermostated heater combined with an argon stream. Photoirradiation on a composite film during the a.c. 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

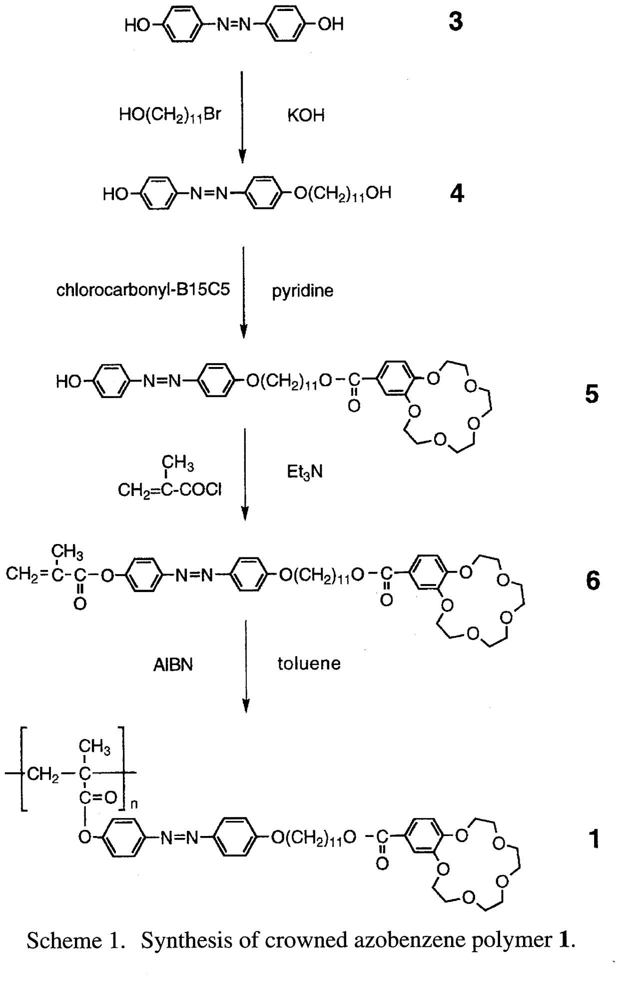
UV-D35 and V-Y43 color filters, respectively. The photoinduced ionic-conductivity changes were recorded after the first cycle of UV- and visible-light irradiation in this study. Differential scanning calorimetry (DSC) was performed using a Daini Seikousha DSC220C calorimeter equipped with a photoirradiation apparatus (UV-1). The temperature-increasing rate was 10 °C min^{-1}. Photoirradiation during the DSC was made through optical fiber wave guides, by using UV light of 365 nm with a light intensity of 25 mW cm^{-2}. X-Ray diffraction experiments were performed on a Rigaku-Denki Rotaflex at room temperature.

Results and Discussion

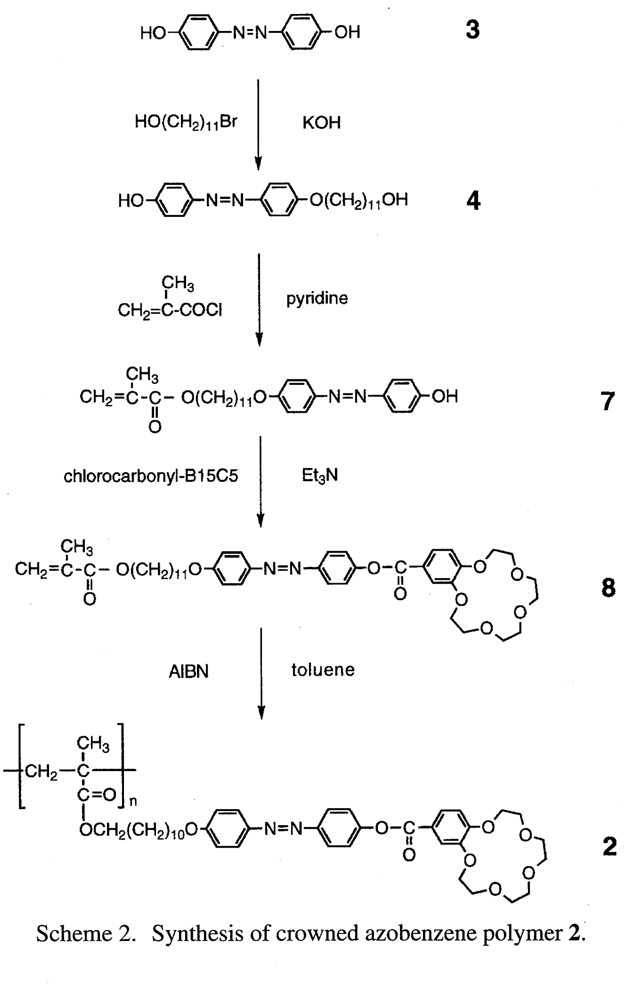
Synthesis of Crowned Azobenzene Vinyl Polymer. The synthetic route for vinyl polymer carrying a crowned azobenzene, which has a benzo-15-crown-5 moiety apart from an azobenzene moiety at the side chain, **1**, is outlined in Scheme 1. The vinyl monomer was synthesized using 4,4′-dihydroxyazobenzene **3** as a starting compound. One of the hydroxyl groups of **3** was reacted with 11-hydroxyundecyl bromide according to the general Williamson synthetic method. The reaction product contained not only the monosubstituted compound, **4**, as the main product, but also the corresponding disubstituted one as the side product. Fortunately, the products was almost insoluble in ethanol, while the starting compound, dihydroxyazobenzene, was readily soluble in it. Therefore, when the starting material, **3**, was employed in excess, monosubstituted compound **4** was easily obtained in a high yield after recrystallization from ethanol. Compound **4** has two different hydroxyl groups, an alkyl alcohol and a phenol group. However, since the alkyl alcohol group has higher nucleophilicity than the phenol one, the following esterification with 4′-(chlorocarbonyl)benzocrown ether occurred selectively at the alkyl alcohol group under mild conditions. The following reaction of **5** with methacryloyl chloride afforded vinyl monomer **6**. On the other hand, vinyl monomer **8** was obtained by reversing the order of the two esterification reactions: first with methacryloyl chloride and then with the chlorocarbonylbenzocrown ether (Scheme 2).

The polymerization of the vinyl monomers was performed using a radical initiator. It was found by gel-permeation chromatography that both vinyl polymers **1** and **2** have average molecular weights (number-average molecular weight, M_n) of about 10000 as polystyrene standards.

Characterization of Crowned Azobenzene Vinyl Polymer. The thermoinduced phase-transition behavior of crowned azobenzene vinyl polymer **1** was investigated by DSC and optical micrography. The DSC thermogram for the first-heating scan shows a broad endothermic peak around 60 °C, which was not reproduced on the second scan. This means that the crowned azobenzene polymer as cast is in a metastable glassy state. The thermogram on the second-heat-



Scheme 1. Synthesis of crowned azobenzene polymer **1**.



Scheme 2. Synthesis of crowned azobenzene polymer **2**.

ing scan was confirmed to be identical with that on the following heating scans. We therefore investigated the phase-transition behavior of **1** based on its DSC thermograms on the second-heating scan. The vinyl polymer **1** successively underwent a phase transition from the glassy state to the crystal state, smectic and nematic liquid crystal states, and then to the isotropic liquid state (Scheme 3). Although the phase transition from a nematic liquid crystal to the isotropic liquid phase could not be detected by DSC, it was observed at around 150 °C by optical microscopy under crossed Nicols. The crowned azobenzene vinyl polymer, **2**, on the other hand, successively underwent a phase transition from the glassy state to the smectic and nematic liquid crystal states, and then to the isotropic liquid state (Scheme 3). Vinyl polymer **2** was found to have a lower phase-transition temperature and a wider temperature region of the liquid-crystal phases than the vinyl polymer carrying an azobenzene moiety, which is a mesogen in this liquid-crystalline system, in the vicinity of the rigid polymer main chain **1**. This suggests that the aggregation of the crowned azobenzene side chains in vinyl polymer **2** is relatively easy due to the flexible spacer between its main chain and mesogen by a long alkyl chain.

The incorporation of an alkali metal salt to crowned azobenzene vinyl polymer **1** promoted liquid-crystal formation due to the cation-complexing property of its crown ether moiety, as exemplified in Fig. 1. Upon changing the ratio of Na^+ to the crown-ether unit from 0 to 0.25, and then to 0.5, the temperature region for the smectic liquid crystal phase was enlarged. Obviously, this phenomenon is concerned with the complexation of sodium perchlorate by the crown-ether moiety of the polymer. It is probably due to an enhancement of the aggregation of the adjacent crowned azobenzene moieties which may form sandwich-type complexes with 2 : 1 stoichiometry of crown ring and Na^+. Further addition of metal salt, however, reduced the temperature region of the smectic liquid crystal phase, as seen in the molar ratios of crown ether and Na^+ of 0.75 and 1. This implies that the formation of 1 : 1 crown ether-Na^+ complexes at high metal-ion concentrations retards the aggregation of adjacent crowned azobenzene side chains, probably because of the electrostatic repulsion among the crown-ether-complexed metal ions.

This interesting phase-transition behavior of crowned azo-

$$\mathrm{G} \overset{19}{\rightleftharpoons} \mathrm{K} \overset{123}{\rightleftharpoons} \mathrm{S} \overset{133}{\rightleftharpoons} \mathrm{N} \overset{150}{\rightleftharpoons} \mathrm{I}$$

1

$$\mathrm{G} \overset{59}{\rightleftharpoons} \mathrm{S} \overset{164}{\rightleftharpoons} \mathrm{N} \overset{186}{\rightleftharpoons} \mathrm{I}$$

2

Scheme 3. Phase-transition behavior of crowned azobenzene polymers **1** and **2**. G, glassy; K, crystalline; S, smectic; N, nematic; I, isotropic. The temperatures are shown in °C.

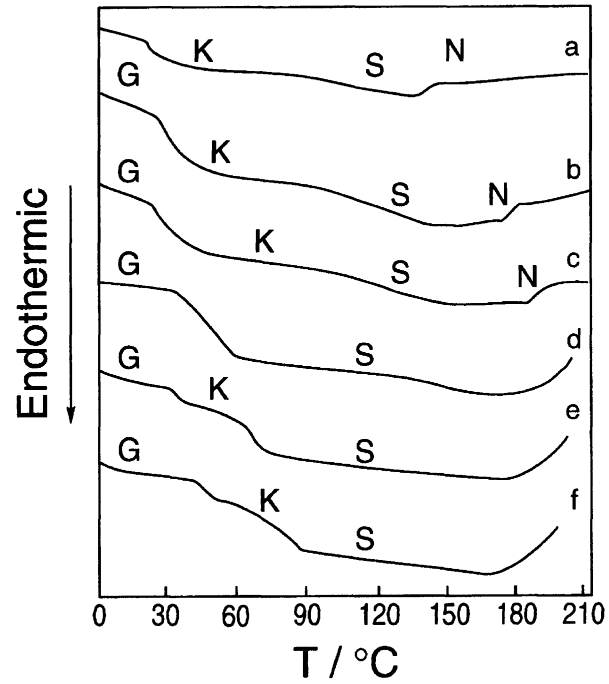


Fig. 1. DSC thermograms for crowned azobenzene polymer **1** in the absence and presence of $NaClO_4$. Molar ratio of Na^+ to crown ether unit: 0 (a); 0.1 (b); 0.25 (c); 0.5 (d); 0.75 (e); 1.0 (f).

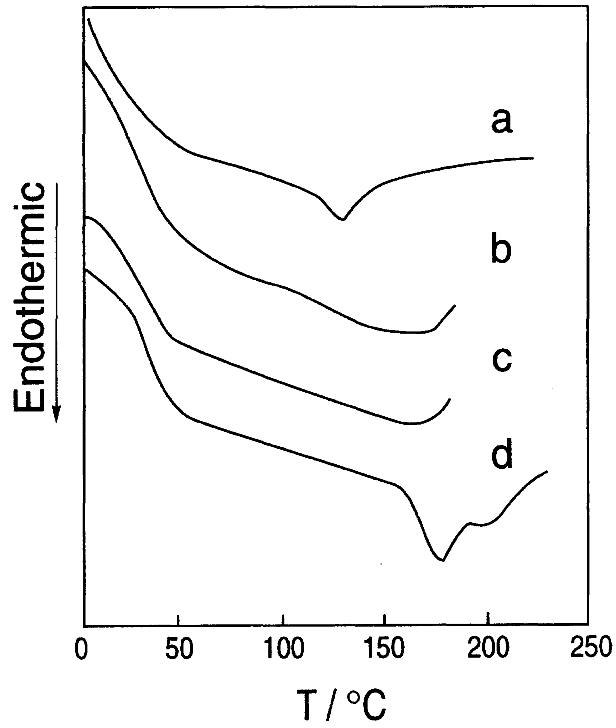


Fig. 2. DSC thermograms for crowned azobenzene polymer **1** containing no salt (a), $LiClO_4$ (b), $NaClO_4$ (c), and $KClO_4$ (d) in a molar ratio of M^+ to crown ether unit of 0.25.

benzene vinyl polymer **1** in the presence of $NaClO_4$ prompted us to compare a system containing $NaClO_4$ with those containing the other alkali metal perchlorates, $LiClO_4$ and $KClO_4$. Figure 2 shows the phase-transition behavior for the crowned azobenzene polymer systems containing a different alkali metal perchlorate at the molar ratio of metal ion to crown ether unit of 0.25. The phase-transition behavior of the Li^+ system is similar to that of the $NaClO_4$ system, whereas the K^+ system is quite different regarding the phase-transition behavior from the two other systems. As can be seen from Fig. 2, the temperature region for the liquid-crystal phase on the K^+ system was shifted to higher temperatures, as compared with the Li^+ and Na^+ systems. It is well known that 15-crown-5 rings form sandwich-type 2 : 1 (crown ether/metal ion) complexes with K^+ much more easily than with Na^+.[9,10] Conceivably, the powerful formation of 2 : 1 complexes causes some crosslinking of the crowned azobenzene vinyl polymer, and thereby a tight orientation of its side chains in the liquid-crystal phase. This differentiates the K^+ system in the phase-transition behavior from the two other systems, and, therefore, in the photoresponsive ion-conducting behavior as described later.

We investigated the photoisomerization of the azobenzene moiety in crowned azobenzene vinyl polymer **1** by the absorption spectra (Fig. 3). The polymer, as cast on a glass substrate, possesses an absorption peak at about 350 nm based on the π–π^* transition of the trans-azobenzene moiety. The absorption peak was decreased by annealing at 150 °C, which corresponds to the phase-transition temperature of **1** from its nematic liquid crystal to an isotropic liquid. Taking into consideration that the azobenzene moiety often has an anisotropy at around 350 nm,[11,12] this remarkably decreased absorptivity of the azobenzene moiety suggests that the crowned azobenzene side chains of the polymer are reoriented by annealing. UV-light irradiation increased the absorption peak around 450 nm based on the cis form with a decrease of the trans-form peak. The following visible-light irradiation causes back isomerization from the cis form to the trans one. This clearly indicates that crowned azobenzene polymer **1** undergoes photoisomerization of its azobenzene moiety between its trans and cis forms, even in polymer film. Interestingly, the absorption peak based on the trans azobenzene moiety for polymer **1** after subsequent UV- and visible-light irradiation is slightly greater than that for the polymer just after annealing. The first cycle of UV- and visible-light irradiation also alters, more or less, the orientation of the crowned azobenzene moiety in the polymer.

In any case, the photoisomerization of the azobenzene moiety in the crowned azobenzene polymer, after annealing followed by the first cycle of UV- and visible-light irradiation, proceeds almost reversibly.

Photoresponsive Ionic Conductivity of Crowned Azobenzene Vinyl Polymer. We first tried to fabricate ion-conducting films consisting only of crowned azobenzene vinyl polymer **1** and an alkali metal perchlorate. However, no stable films could be obtained due to the film brittleness. Composite films containing a polyester elastomer were therefore fabricated by a spin-coating method. Figure 4 shows a typical temperature dependence of the ionic conductivity for composite films consisting of a polyester elastomer, crowned azobenzene polymer **1**, and $NaClO_4$ with a molar ratio of $NaClO_4$ to crown ether unit of 0.25. It should be noted that this curve has two breaking points, the temperatures for which nearly correspond to those for the two

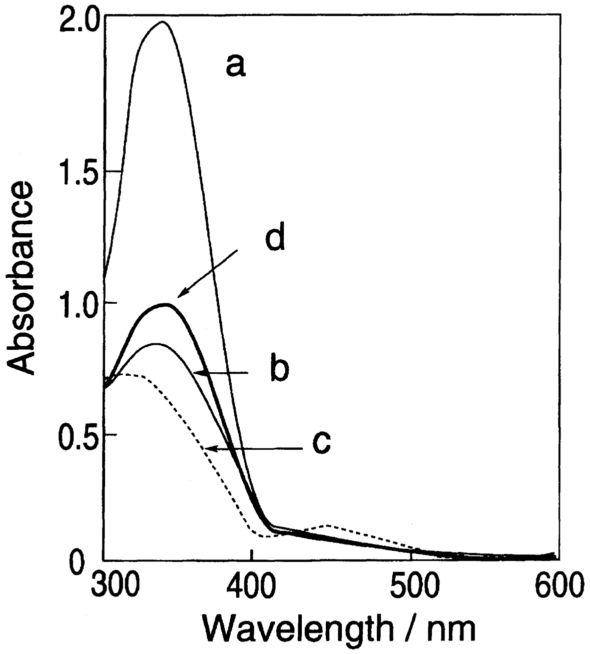


Fig. 3. Absorption-spectral changes of crowned azobenzene polymer **1** as cast (a), after annealing (b), on UV-light irradiation (c), on visible-light irradiation after UV-light irradiation (d).

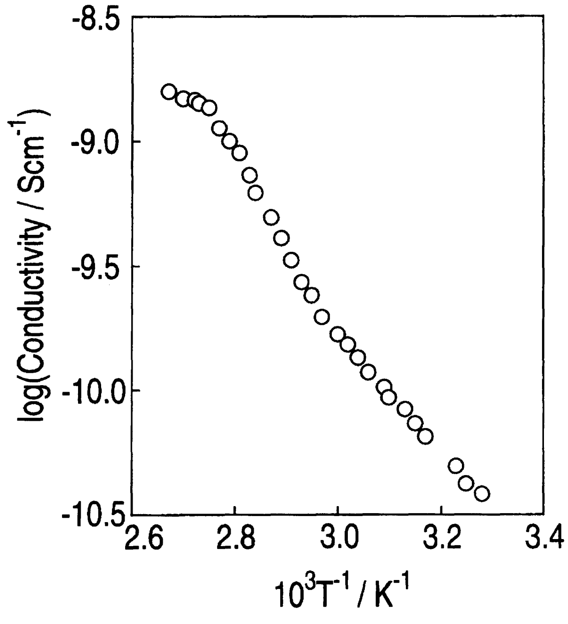


Fig. 4. Temperature dependence of ionic conductivity for composite film of polyester elastomer (75.0 wt%)/**1** (24.0 wt%)/$NaClO_4$ (1.0 wt%).

types of phase transitions of the crowned azobenzene polymer: The lower, middle, and higher regions may be assigned to the regions for the glassy, crystalline, and smectic liquid-crystalline states of the crowned azobenzene polymer. The gentle slope in the higher temperature region means low activation energy for the ionic conduction in composite film. This suggests that efficient ion migration occurs in the smectic liquid-crystal phase. This is probably because the adjacent crown-ether moieties, which are ion-hopping sites, can approach each other when the polymer forms the smectic liquid-crystal phase.

The composite films containing crowned azobenzene vinyl polymer **1** and $NaClO_4$ can undergo marked photochemical switching of ionic conductivity at 60 °C (Fig. 5). UV-light irradiation decreased the ionic conductivity of the composite film, and the following visible-light irradiation increased it. UV-light-induced isomerization of the azobenzene moiety in the polymer from the trans to cis forms brings about some disturbance in the ordered orientation of the side chain, and, therefore, of the crown ether moiety, which in turn prevents ionic conduction among the adjacent crown-ether rings. The reverse occurs upon following visible-light irradiation.

Similar measurements for the photoinduced ionic-conductivity switching were also carried out for composite films containing $LiClO_4$ or $KClO_4$ instead of $NaClO_4$ (Fig. 6). It is worth noting that the photoresponsive ion-conducting behavior for the K^+ system was opposite to that for the Na^+ system, while the Li^+ system was similar to the Na^+system; that is, UV-light irradiation increased the ionic conductivity, and following visible-light irradiation decreased it for the K^+ system, unlike the two other metal-ion systems. As mentioned above, some crosslinking of the polymer chains occurs in the presence of K^+, thus resulting in a tight arrangement of the crowned azobenzene side chains, which is not very easy to collapse by UV-light-induced isomerization of the azobenzene moiety irradiation as in the corresponding Li^+ and Na^+ systems. In the K^+ system, therefore, the ion-conducting behavior may be mainly governed by the dielectric constant of the film based on the dipole-moment change induced by the azobenzene isomerization.

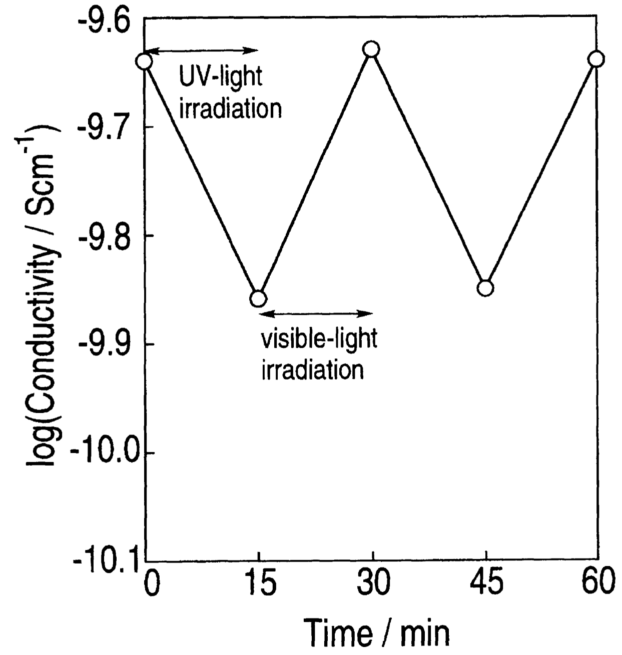


Fig. 5. Photoinduced switching of ionic conductivity for composite film of polyester elastomer (75.0 wt%)/**1** (24.0 wt%)/$NaClO_4$ (1.0 wt%) at 60 °C.

For a comparison, composite films containing crowned azobenzene vinyl polymer **2**, which carries a crown ether moiety in the vicinity of an azobenzene moiety at the side chain, was also investigated for the photoinduced switching of ionic conductivity (Fig. 7). UV-light irradiation decreased

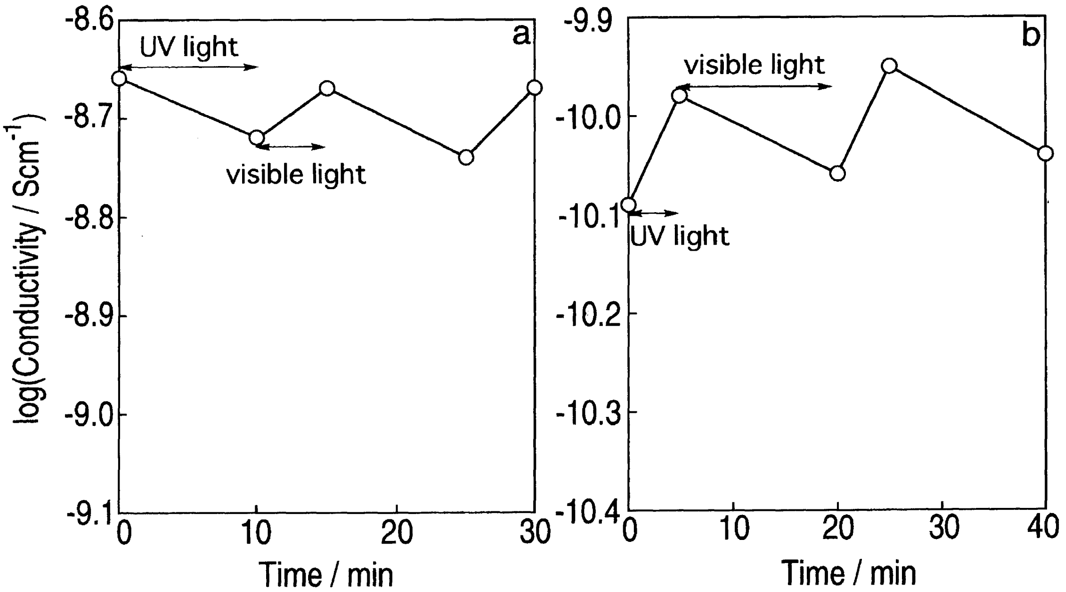


Fig. 6. Photoinduced switching of ionic conductivity for composite films containing $LiClO_4$ (a) and $KClO_4$ (b). The composition in films are the same as that for Fig. 4.

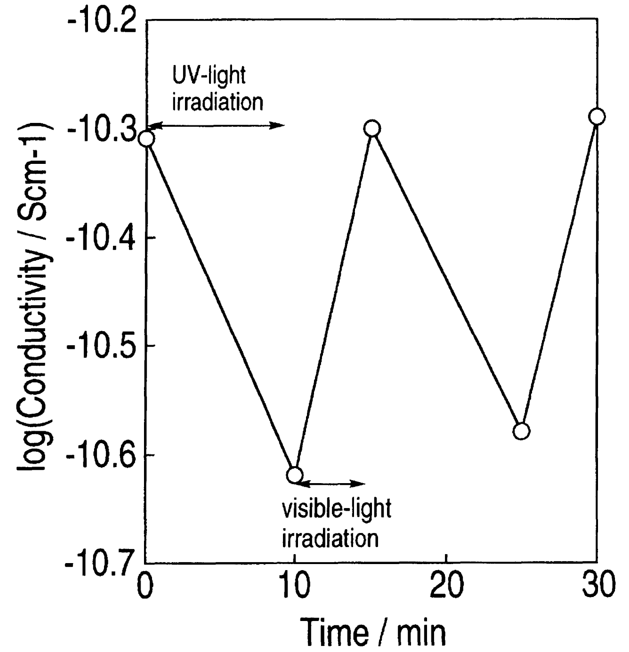


Fig. 7. Photoinduced switching of ionic conductivity for composite film of polyester elastomer (75.7 wt%)/**2** (24.2 wt%)/$NaClO_4$ (0.07 wt%) at 60 °C.

the ionic conductivity of the composite film, and the following visible-light irradiation increased it in the **2** systems, as is the case with the **1** system. However, the polymer carrying a crown-ether moiety in the vicinity of azobenzene moiety **2** is greater in the magnitude of photoinduced ionic-conductivity change (ionic-conductivity ratio) than the polymer carrying a crown ether moiety apart from an azobenzene moiety, **1**. It is thought to be due to some difference in the photoinduced structural change of the azobenzene moiety.

X-Ray diffraction (XRD) patterns of the crowned azobenzene polymers were measured at room temperature after annealing at 150 °C to obtain some information about the structural changes induced by photoirradiation (Fig. 8). Both of the polymers have a broad peak at around 20 °C and around 1.5—5° at room temperature under dark conditions. Its XRD pattern is typical for smectic liquid crystals.[13)] The scattering-angle peak of 20° means a Bragg spacing of 4.3 Å which corresponds to the distance between the adjacent crowned azobenzene side chains on liquid crystal formation. This indicates that the ordered orientation for the smectic liquid crystal phase is retained stably at room temperature. Obviously, UV-light irradiation brings about the marked disappearance of the peak around 20° for the both polymers. That is to say, the ordered arrangement of the crowned azobenzenes was disturbed considerably by the light irradiation. Such peak disappearance also occurred in the low-angle region for the crowned azobenzene polymer **2**, which carries a crown ether moiety in the vicinity of its azobenzene moiety. In the polymer carrying a crown ether moiety apart from azobenzene moiety, **1**, on the other hand, any significant photoinduced peak change in the low angle region was hardly found. This suggests that the photoisomerization of azobenzene moiety of **1** does not affect the change of liquid crystal phase so much as that of **2**. In other words, the terminal crown ether moiety in **1** is not perturbed so much as that in **2** by the photoinduced structural change of the azobenzene moiety. Thus, the difference in the photoinduced ionic-conductivity switching between the two polymers, **1** and **2**, can be ascribed to the difference in the location of their crown ether moiety.

In conclusions, the vinyl polymers carrying a crowned azobenzene moiety at the side chains, **1** and **2**, can form smectic liquid-crystal phases. Composite films containing a crowned azobenzene polymer and an alkali metal salt were found to undergo remarkable photochemical ionic-conductivity switching, based on a significant change in the smectic liquid-crystal phase, and, thereby, of the orientation of the crown-ether moiety. Most interestingly, the location of the crown-ether and azobenzene moieties in the polymer side chain significantly affects the photoresponsive ion-conduct-

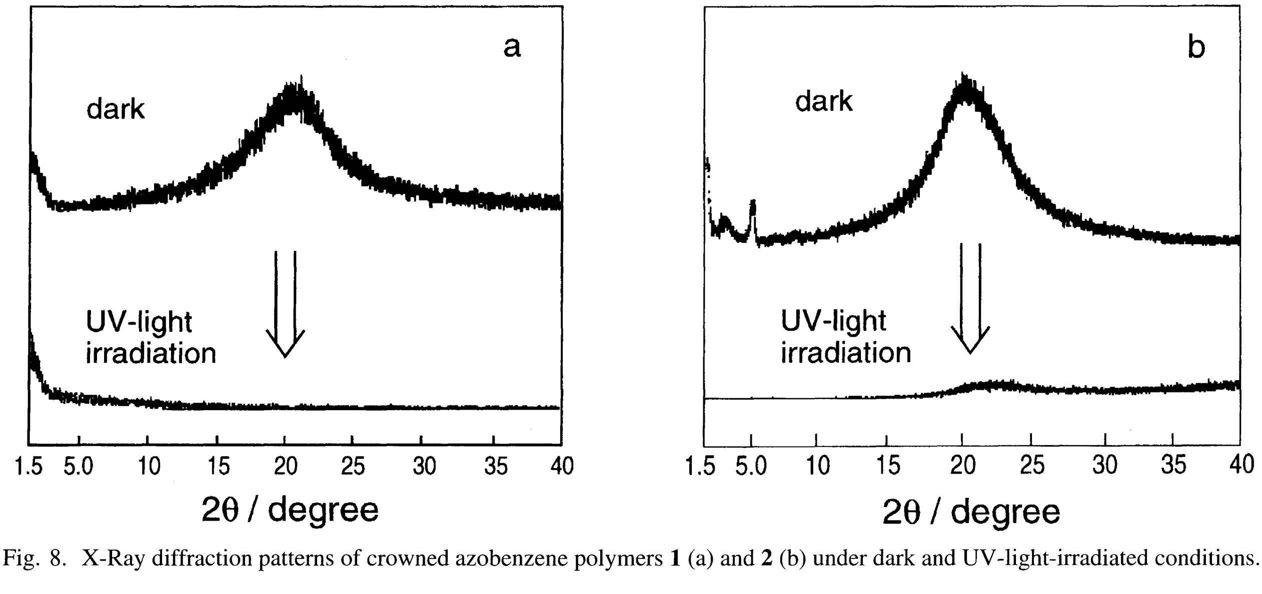


Fig. 8. X-Ray diffraction patterns of crowned azobenzene polymers **1** (a) and **2** (b) under dark and UV-light-irradiated conditions.

ing behavior.

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