

Photoinduced switching of ionic conductivity by metal ion complexes of vinyl copolymers carrying crowned azobenzene and biphenyl moieties at the side chain

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Vinyl copolymers carrying crowned azobenzene and biphenyl moieties at the side chain were synthesized and their photoresponsive ion-conducting behavior was investigated in the presence of sodium perchlorate. Any of the copolymers or the homopolymer of crowned azobenzene can undergo photochemical switching of ionic conductivity in composite films containing an ion-conducting carrier. UV-light-induced isomerization of the azobenzene moiety causes some disorder in the crown ether moiety (an ion-hopping site), in the liquid crystal state of the polymers, thus decreasing ionic conductivity, and this is reversed by subsequent visible-light irradiation. The highest magnitude in the photoinduced ionic-conductivity changes was attained in polymers containing the highest content of crowned azobenzene moiety, owing to the more efficient photoinduced phase transition. The polymers with the highest content of crowned azobenzene moiety also showed the fastest response in photoinduced switching.

We have been engaged in designing photoresponsive ion-conducting materials possessing a photochromic crown ether moiety;¹ such materials are useful for memory, display, and printing device fabrication. Azobenzene derivatives incorporating a crown ether moiety, 'crowned azobenzenes', can undergo photoinduced switching of ionic conductivity in composite films containing an alkali metal salt. This is based on the photoisomerization-induced phase transition of the azobenzene derivatives between their solid and liquid states and thereby the mobility changes of ion-conducting carriers.² Polymers carrying a crowned azobenzene moiety on the side chain such as **1**, are capable of forming highly ordered liquid crystal phases. On the other hand, the order-disorder cycle in the liquid crystal phase is induced by photoisomerization of the azobenzene moiety between its *cis*- and *trans*-forms. This brings about quite different behavior in the photoinduced ionic-conductivity changes from the corresponding low molecular mass crowned azobenzene derivatives.^{3,4}

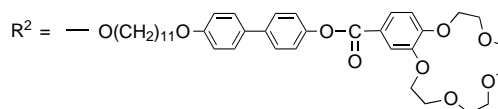
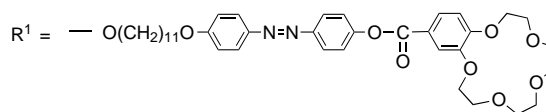
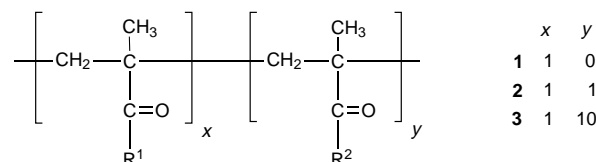
It occurred to us that, in copolymers carrying a non-photochromic mesogen with a crown ether ring as well as a crowned azobenzene moiety, the photoisomerization of the azobenzene moiety also results in such a phase transition in the bulk phase and thereby such ionic-conductivity changes as seen in the homopolymers carrying crowned azobenzene side chains. It is also of much interest to elucidate how efficiently the crowned azobenzene side chains in the copolymers participate in the bulk phase transition and thereby the ionic-conductivity change.⁵ We have therefore designed vinyl copolymers carrying crowned azobenzene and biphenyl moieties at the side chain, **2** and **3**.

This paper deals with the synthesis of the copolymers, **2** and **3** and a comparison with the crowned azobenzene homopolymer, **1**, in photoresponsive ion-conducting behavior. The magnitude and response time in the photoinduced ionic-conductivity switching are described.

Experimental

Materials

The vinyl copolymers containing crowned azobenzene and biphenyl moieties were synthesized as follows. The crowned



azobenzene vinyl monomer, 4'-(4-{4-[11-(methacryloyl)undecyloxy]phenylazo}phenoxy carbonyl)benzo-15-crown-5 was obtained using the procedure reported elsewhere.⁴ The crowned biphenyl vinyl monomer, 4'-[4-(11-methacryloylundecyloxy)-biphenyloxy carbonyl]benzo-15-crown-5 was prepared according to a modified literature procedure.⁶ The only difference was in the reaction of 4-(11-hydroxyundecyloxy)-4'-hydroxybiphenyl with methacryloyl chloride, which was carried out in dry tetrahydrofuran at room temperature for 24 h in the presence of 2 equiv. of pyridine instead of toluene-*p*-sulfonic acid. Radical copolymerization of the vinyl monomers possessing crowned azobenzene and biphenyl moieties was carried out in toluene using α,α' -azobisisobutyronitrile (AIBN) as the initiator (1 wt% of the total monomer) at 65 °C for 36 h, using a glass tube sealed after several freeze-pump-thaw cycles under vacuum. After the polymerization, the reaction mixture was evaporated to dryness. The crude polymer was purified by fractionation to appropriate portions by gel-permeation chromatography (JAIGEL-1H and 2H, CHCl₃).

The polyester elastomer, poly(butylene terephthalate) (Pelprene 40-H, Toyobo), containing an oligo(oxybutylene) moiety with an average molecular mass of 1000 as the soft

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segment ($T_g = -80^\circ\text{C}$) was purified by repeated reprecipitation from chloroform in methanol. All other reagents were of the best available 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 ($2 \times 2.5\text{ cm}$) by spin coating from chloroform solutions. For instance, polyester (25.0 mg) and crowned azobenzene vinyl polymer (8.0 mg), NaClO_4 (0.026 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 $3\text{ }\mu\text{m}$ after drying for 1 d at room temp. 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 75.7 wt% polyester, about 24.2 wt% crowned azobenzene polymer, and about 0.08 wt% metal salt. After being set up in the measurement cell, the composite films were annealed at 100°C *in vacuo* for 1 h, cooled to 60°C under an argon atmosphere, and then kept at 60°C for 3 h until the ionic conductivity value changed no more.

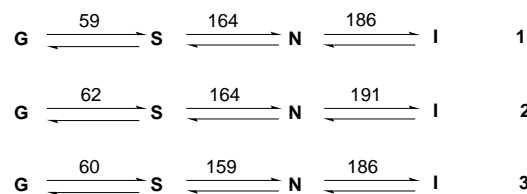
Measurements

The details for the procedure and cell setup for the ionic-conductivity measurements were as described elsewhere.⁷ The measurement cell was held at 60°C by a thermostatted heater combined with an argon stream. Photoirradiation of a composite film during the ac measurements was undertaken from its ITO side. UV (320–400 nm) and visible ($>400\text{ nm}$) light was obtained by passing light from a 500-W xenon lamp through Toshiba UV-D35 and V-Y43 color filters, respectively. Differential scanning calorimetry (DSC) was performed using a Daini Seikousha DSC220C calorimeter with a temperature-increase rate of $20^\circ\text{C min}^{-1}$. The response time for the photo-induced ionic-conductivity switching was measured with composite films similar to those for the ionic-conductivity measurements, by following the real part of the ac impedance at a fixed frequency (resistance) under photoirradiation conditions.

Results and Discussion

Synthesis and characterization of vinyl copolymers carrying crowned azobenzene and biphenyl moieties at the side chain

Radical polymerization of the vinyl monomers of crowned azobenzene and biphenyl was carried out with 1:0, 1:1 and 1:10 molar ratios of the azobenzene and biphenyl moieties. The crude polymers were purified by gel-permeation chromatography to yield the vinyl polymers which have a number-average molecular weight (M_n) of about 10000 based on polystyrene standards. The ratios of M_n to weight-average molecular weight (M_w) were 1.5–1.6 for polymers **1**, **2** and **3**, which means that each of the fractionated polymers has a narrow molecular distribution. Elemental analysis indicated that the mole fractions of crowned azobenzene and biphenyl moieties for the purified polymers almost correspond to the initial mole fraction of the corresponding vinyl monomers, copolymers **2** and **3** carrying 49.5 and 12.4% of crowned azobenzene units, respectively. The thermoinduced phase-transition behavior of the resulted polymers, which was investigated by DSC and optical micrography, is shown in Scheme 1. The copolymers **2** and **3** undergo a phase transition from glassy successively to smectic, nematic liquid crystal, and isotropic liquid phase. Although the homopolymer **1** and the copolymers have a different content of crowned azobenzene and biphenyl moieties, their phase-transition behavior was



Scheme 1 Phase-transition behavior of crowned azobenzene polymers **1**, **2** and **3**. G, glassy; S, smectic; N, nematic; I, isotropic. The temperatures are shown in $^\circ\text{C}$

quite similar to each other. This indicates that the aggregation state of the side chains is almost the same in any of the polymers under dark conditions.

Photoresponse of ionic conductivity

We fabricated ion-conducting composite films consisting of one of the crowned azobenzene polymers (**1**, **2** and **3**), NaClO_4 and also a polyester elastomer as the film support for the ionic-conductivity measurements. Fig. 1 shows the ionic-conductivity changes for the composite films on alternating irradiation of UV and visible light at 60°C . Significant photochemical switching of ionic conductivity was observed in the composite films. UV-light irradiation reduced the ionic conductivity and following visible-light irradiation increased it for the polymer systems. The azobenzene moiety can isomerize photochemically between its straight *trans*-form and bent *cis*-form with a change in the aggregation of crown ether moieties which is an ion-hopping site, as already discussed in our previous paper concerning the homopolymer of crowned azobenzene.⁴ Since the crowned azobenzene polymers assume a smectic liquid crystal phase at 60°C in composite films, which was annealed at 100°C just before the measurement, under dark conditions, its adjacent crown ether moieties at the end of the azobenzene side chain are likely to get close to each other owing to the highly ordered orientation of the side chains. The ion-conducting carriers, therefore, migrate comparatively efficiently on crown ether-based hopping sites. When the azobenzene moiety is isomerized from its *trans*- to *cis*-forms, orientation disorder of the side chains occurs. Thus the adjacent crown ether moieties are further apart than in the highly

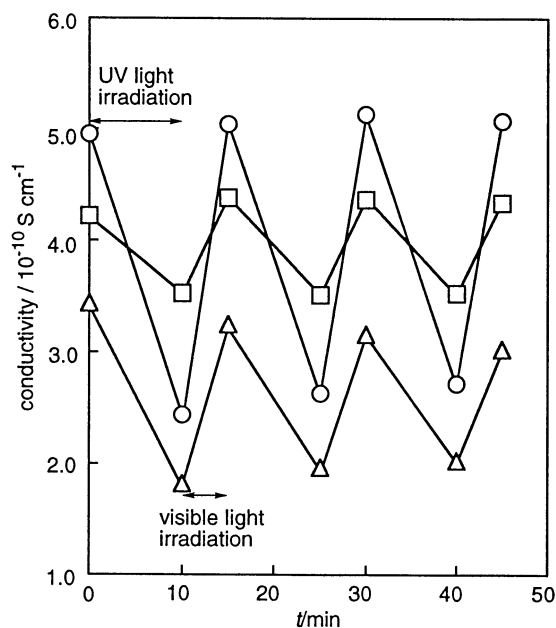


Fig. 1 Photoinduced switching of ionic conductivity for composite film containing crowned azobenzene polymers **1** (○), **2** (△) and **3** (□) at 60°C

oriented state under dark conditions, and thereby ionic conduction is suppressed. This results in the remarkable ionic-conductivity changes.

This is probably the case with the photoresponsive ion-conducting systems incorporating the copolymers of crowned azobenzene and biphenyl, **2** and **3**. However, it is worth noting that the magnitude of the photoinduced ionic-conductivity change is increased with increasing azobenzene content in the polymers. This suggests that the photoisomerization of azobenzene moieties leads to a more extensive structural change in homopolymer **1** than in copolymers **2** and **3**, because the photoinduced structural changes occur only in the vicinity of the crowned azobenzene side chains. Conceivably, the aggregation of crown ether moieties can be perturbed effectively by photoirradiation of the polymer systems containing a higher azobenzene content.

Response time for photoinduced ionic-conductivity switching

The response time for the photoinduced ionic-conductivity switching was also measured to obtain more information about the effect of the azobenzene content on the photoisomerization-induced rearrangement in the liquid crystal phase of the homopolymer and copolymers of crowned azobenzene. Fig. 2 and 3 show the time-course changes in the conductance (reciprocal value for the real part of ac impedance) and the isomerization degree of the azobenzene moiety, respectively, for the ion-conducting composite films containing **1** and **3** on photoirradiation. The values for response time (t_{90}), the time in which the value reached 90% of its corresponding final value, are summarized in Table 1. The response times for the photoinduced conductance changes are closely related to those for the photoisomerization of the azobenzene moiety of crowned azobenzene polymers. This means that the rate-

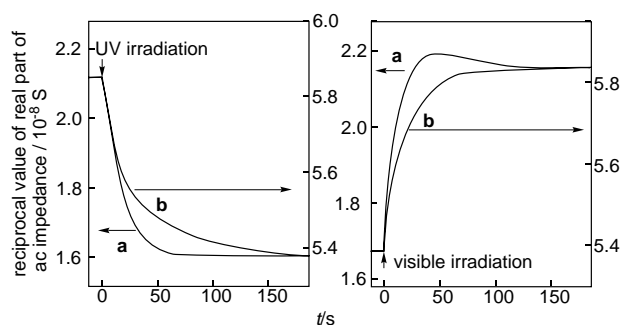


Fig. 2 Time-course changes of conductance for polymers having different contents of azobenzene moieties on photoirradiation: **1** (a), **3** (b) at 60 °C

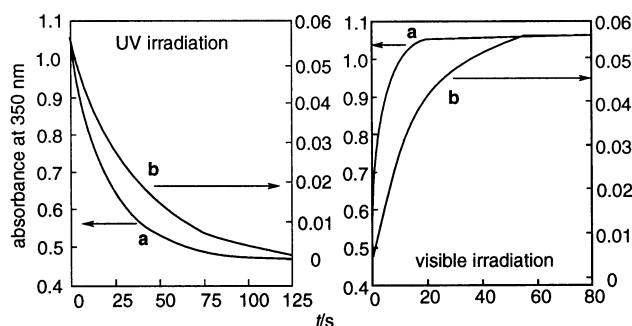


Fig. 3 Time-course changes of absorbance at 350 nm for polymers having different contents of azobenzene moieties on photoirradiation: **1** (a), **3** (b) at 60 °C

Table 1 Response time (t_{90}) for photoinduced change of conductance and isomerization for crowned azobenzene polymers **1** and **3**

polymer system	response time/s			
	conductance		isomerization	
	UV light	visible light	UV light	visible light
1	40	16	52	10
3	91	47	79	35

determining step for the photoinduced ionic-conductivity changes in composite film of the crowned azobenzene polymers is the photoisomerization of their azobenzene moiety. On the whole, the response times on UV-light irradiation causing *trans*–*cis* isomerization of the azobenzene moiety are longer than those on visible-light irradiation leading to the opposite isomerization. This is probably due to the fact that UV-light-induced isomerization of the azobenzene moiety from its straight *trans* form to the corresponding bent *cis* form requires considerable free-volume expansion in the highly ordered crowned azobenzene side chain. In contrast, the visible-light-induced isomerization from the *cis* to *trans* forms, accompanying free-volume contraction, takes less time than the UV-light-induced one. It should be noted that the shortest response times were obtained with crowned azobenzene homopolymer **1** on both UV- and visible-light irradiation. In the crowned azobenzene homopolymer **1** the high azobenzene content facilitates its photoisomerization accompanied by free-volume changes probably due to the cooperative action of adjacent azobenzene moieties. In the copolymer with only 10% of crowned azobenzene moiety **3**, on the other hand, its isomerization may not be very easy due to the isolation of the azobenzene moiety in the bulk of the ordered biphenyl side chains. Also, the reorientation of the crowned biphenyl side chains induced by the photoisomerization of azobenzene moieties proceeds slowly in the copolymer.

In conclusion, in the copolymers containing crowned azobenzene and biphenyl moieties, the photoisomerization of their azobenzene moiety perturbs the ordered orientation of their crown ether-containing side chains in the vicinity of the azobenzene moiety, resulting in the change of the ionic conductivity in the bulk phase. Thus, the homopolymer carrying a crowned azobenzene moiety at the side chain brings about a greater magnitude and a shorter response time of the photoinduced ionic-conductivity change than that seen for the copolymers also containing crowned biphenyl moieties, due to the effective isomerization of the azobenzene moiety and thereby the effective reorientation of the side chains.

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