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Cation Complexation, Photochromism, and Photoresponsive Ion-Conducting Behavior of Crowned Spirobenzopyran Vinyl Polymers

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ABSTRACT: Vinyl polymers incorporating a crowned spirobenzopyran moiety at the side chain were synthesized, and their alkali metal-ion complexation, photochromism, and photoresponsive ion-conducting behaviors were studied in comparison with similar polymers incorporating crown ether and spirobenzopyran moieties independently. The metal-ion complexation by their crown ether moiety significantly affected the photochromism of their spirobenzopyran moiety. The crowned spirobenzopyran polymers are similar to their corresponding monomeric analogue in their metal-ion complexing property and photochromism, with some difference induced by polymer effect. Almost no significant aggregation of the photoinduced merocyanine moiety was found in the crowned spirobenzopyran polymer, unlike the polymers carrying spirobenzopyran and crown ether moiety independently. The crowned spirobenzopyran polymers were applied successfully as components of photoresponsive ion-conducting materials.

Introduction

Considerable efforts have been invested in the design of photochromic compounds.[1] Specifically, organic photochromism has found its wide application in devices for display, memory, and printing. We have applied organic photochromic compounds to photochemical switching of metal-ion complexation and ionic conduction by combining photochromism with the metal-ion binding property of crown ether derivatives.[2] For instance, incorporation of a monoazacrown ether moiety in a nitrospirobenzopyran moiety at the 8-position produced a photocontrol reagent of metal-ion complexation.[3] The crowned spirobenzopyran in the electrically neutral form can bind an alkali metal ion with its crown ether moiety, while its spirobenzopyran moiety isomerizes to the corresponding merocyanine form photochemically. The zwitterionic merocyanine form of crowned spirobenzopyran can bind a metal ion more powerfully by intramolecular interaction of its phenolate anion with a metal ion in the crown ether ring. In the crowned spirobenzopyran, therefore, photoisomerization of its spirobenzopyran moiety brings about a significant change in the metal-ion binding ability. This attractive property of crowned spirobenzopyran prompted us to apply the compound to photoresponsive ion-conducting materials.[4]

Vinyl polymers carrying a crown ether moiety at the side chain exhibit not only powerful cation-binding ability but also attractive polymer rheology.[5−8] On the other hand, polymers incorporating spirobenzopyran side chains are useful tools for photochemical control of polymer rheology.[9−12] Therefore, the combination of crown ether and spirobenzopyran moieties in a polymer molecule is a promising approach. Also, the polymerization of crowned spirobenzopyran provides its polymers with some advantages over their corresponding monomeric analogue in materials applications, i.e., easy immobilization of crowned spirobenzopyran and high processability. An easy way to obtain polymers carrying both crown ether and spirobenzopyran moieties is copolymerization of vinyl monomers carrying the corresponding moieties.[13] The crown ether−spirobenzopyran copolymers, however, lose the original property of photoresponsive metal-ion complexing ability for the monomeric crowned spirobenzopyran, although they undergo photoreversible precipitate formation on the basis of the interpolymer aggregation of photoinduced merocyanine moiety instead.[13]

We have designed vinyl polymers carrying a crowned spirobenzopyran moiety at the side chain **1**, and we call these crowned spirobenzopyran vinyl polymers. Here we describe their metal-ion complexing property, photochromism in the presence of metal ions, and their applicability to photoresponsive ion-conducting materials. A comparison is also made with the corresponding monomeric crowned spirobenzopyran **2** and the copolymers incorporating crown ether and spirobenzopyran moieties independently **3**.

Experimental Section

Synthesis of Crowned Spirobenzopyran Vinyl Polymer. *1′-(2-Hydroxyethyl)-3′,3′-dimethyl-6-nitro-8-[10-(1,4,7-trioxa-10-azacyclododecyl)methyl]spiro[2H-1-benzopyran-2,2′-indoline] or Hydroxyethyl Crowned Spirobenzopyran*. A dry ethanol solution (35 cm^3) of 3a,4,4-trimethyloxazolidino[3,2-*a*]indoline[14] (10 mmol) and 10-(2-hydroxy-3-formyl-5-nitrobenzyl)-1,4,7-trioxa-10-azacyclododecane[3] (10 mmol) was refluxed for 7 h. The reaction mixture was allowed to stand overnight. After filtration of the unreacted substrate, the solvent evaporation yielded a crude product of hydroxyethyl crowned spirobenzopyran. Purification by recrystallization from benzene/hexane(1/10) afforded a dark red glass (78%); mp 71 °C. ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ: 1.17 and 1.42 (3H each, s, $\mathrm{C(CH_3)_2}$), 2.18 (1H, s, OH), 2.81 (4H, m, $\mathrm{N(C\mathit{H}_2CH_2)_2}$), 3.68−3.86 (18H, m, $\mathrm{NCH_2CH_2OH}$, $\mathrm{PhCH_2}$, and $\mathrm{CH_2OCH_2}$), 6.48 (1H, d, $J = 16.2$ Hz, CCH═C*H*Ph), 6.76 (1H, d, $J = 7.6$ Hz, 7′-H of indoline), 6.80 (1H, d, $J = 7.6$ Hz, CC*H*═CHPh), 6.94 (1H, t, $J = 6.5$ Hz, 5′-H of indoline), 7.09 (1H, d, $J = 7.6$ Hz, 4′-H of indoline), 7.17 (1H, t, $J = 6.8$ Hz, 6′-H of indoline), 7.85 (1H, d, $J = 2.7$ Hz, 5-H of benzopyran), 8.29 (1H, d, $J = 2.7$ Hz, 7-H of

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benzopyran). MS, *m/e* (% relative intensity): 540 (M^+, 51), 307 (100). Anal. Calcd for $C_{29}H_{37}N_3O_7$: C, 55.83; H, 6.36; N, 6.70. Found: C, 55.51; H, 5.94; N, 6.45.

1′-(2-Methacryloyloxyethyl)-3′,3′-dimethyl-6-nitro-8-[10-(1,4,7-trioxa-10-azacyclododecyl)methyl]spiro[2H-1-benzopyran-2,2′-indoline] or Methacryloyloxyethyl Crowned Spirobenzopyran. A mixture of hydroxyethyl crowned spirobenzopyran (6 mmol) and triethylamine (9 mmol) dissolved in anhydrous THF (50 cm^3) was cooled in an iced bath under an argon atmosphere. Methacryloyl chloride (7 mmol) was added to the mixture dropwise while stirring. The mixture was then stirred at room temperature for 3 h. After the reaction, the resulting triethylamine hydrochloride was filtered off. The solvent of the filtrate was replaced with chloroform, and the solution was then washed with water and dried over $MgSO_4$. The solvent evaporation afforded a crude product of crowned spirobenzopyran vinyl monomer. Purification by preparative gel permeation chromatography (solvent: $CHCl_3$) yielded dark-red glass (24%); mp 52 °C. ^1H NMR (270 MHz, $CDCl_3$) δ: 1.14 and 1.41 (3H each, s, $C(CH_3)_2$), 2.08 (3H, s, $CH_3C{=}C$), 2.73 (4H, m, $N(CH_2CH_2)_2$), 3.61−3.78 (18H, m, NCH_2CH_2OH, $PhCH_2$, and CH_2OCH_2), 5.87 and 6.44 (1H each, s, $CH_2{=}C$), 6.36 (1H, d, J = 15.8 Hz, $CCH{=}CHPh$), 6.78 (1H, d, J = 8.6 Hz, 7′-H of indoline), 6.87 (1H, d, J = 3.3 Hz, $CCH{=}CHPh$), 6.95 (1H, t, J = 8.1 Hz, 5′-H of indoline), 7.07 (1H, d, J = 7.3 Hz, 4′-H of indoline), 7.17 (1H, t, J = 8.3 Hz, 6′-H of indoline), 8.30 (1H, d, J = 3.0 Hz, 5-H of benzopyran), 8.77 (1H, d, J = 2.6 Hz, 7-H of benzopyran). MS, *m/e* (% relative intensity): 608 (M^+, 100). Anal. Calcd for $C_{33}H_{41}N_3O_8$: C, 65.22; H, 6.80; N, 6.92. Found: C, 64.95; H, 6.71; N, 6.70.

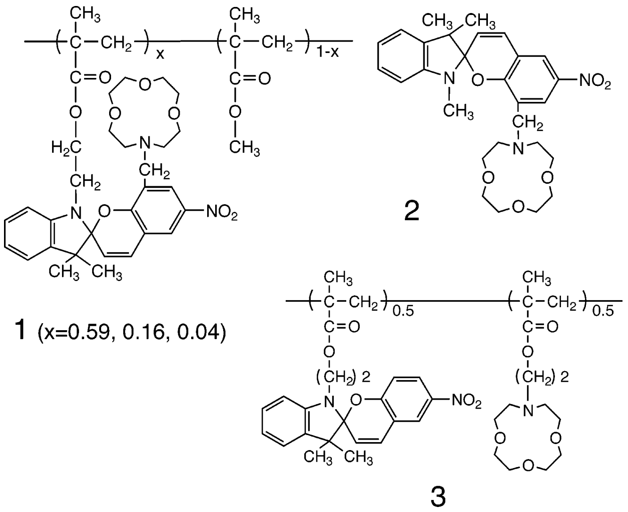
Polymerization. Radical copolymerization of the crowned spirobenzopyran vinyl monomer with methyl methacrylate (MMA) was carried out in toluene at 70 °C for 36 h, using a glass tube sealed after several freeze−pump−thaw cycles under a vacuum. The total monomer concentration ranged from 0.35 to 2.5 mol dm^{-3}. α,α′-Azobis(isobutyronitrile) (AIBN) was used as the initiator (0.5 mol % to the total monomer). After the polymerization, the reaction mixture was evaporated to dryness. The crude polymer was purified by fractionation to appropriate portions by gel-permeation chromatography (GPC, JAIGEL-1H and 2H, $CHCl_3$) to yield dark red or red powder of copolymers. The molecular weights (in polystyrene standard) were determined by GPC (Shodex KF-2003) using THF as the eluent.

Other Materials. Alkali metal salts (perchlorate and hydroxide) and picric acid were of analytical grade. Poly(vinyl chloride) (PVC) (average polymerization degree: 1020) was purified by repeated reprecipitation from THF in methanol. 2-Ethylhexyl sebacate (DOS) was distilled under a vacuum. The solvents used for the measurements and composite film fabrication were of spectroscopy grade (Dojindo Lab., Japan). Water was deionized.

Cation Extraction. Equal volumes (3 cm^3) of 2.1×10^{-3} mol dm^{-3} (concentration of crown ether unit in the case of the polymer) crown ether 1,2-dichloroethane solution and an aqueous solution containing a mixture of 0.1 mol dm^{-3} alkali metal hydroxide and 7.0×10^{-5} mol dm^{-3} picric acid were introduced into a stoppered vial and shaken vigorously by a reciprocating shaker under dark conditions for 15 min.[15] After phase separation, the organic and aqueous phases were subjected to absorption−spectral measurements. The percent of extraction was calculated as $100 \times (A_0 - A)/A_0$, where "A_0" and "A" denote the absorbance of picrate ion (350 nm) for the aqueous phase before and after the extraction, respectively.

Spectrophotometric Measurements. THF solutions containing a crowned spirobenzopyran polymer (4×10^{-4} mol dm^{-3} for spirobenzopyran unit) and an appropriate concentration of an alkali metal perchlorate were prepared, and their absorption spectra were then measured under dark conditions. Photoirradiation was made by using UV light (300−400 nm) and visible light (>500 nm), which were obtained by passing a light from a 500 W Xe lamp through Toshiba UV-D35 and Y-50 color filters, respectively. For the thermal decoloration measurements, crowned spirobenzopyran polymer THF solutions (4×10^{-4} mol dm^{-3} for spirobenzopyran unit) with and without an appropriate concentration of alkali metal perchlorate were irradiated by UV light in a 1 mm quartz cell for 2 min. The absorbance for the corresponding open colored form at 550 nm was followed at 40 °C, immediately after photoirradiation. The first-order rate constants of thermal decoloration (k) were determined from the slope in the plots of $\log[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time (T), where A_t, A_0, and A_∞ are referred to as the absorbance at 550 nm for $T = t$, $T = 0$, and T = infinity, respectively.

Scheme 1. Derivatives Incorporating Crown Ether and Spirobenzopyran Moieties Employed in This Paper



1 (x=0.59, 0.16, 0.04)

2

3

Fluorescence spectra for THF solutions containing a crowned spirobenzopyran polymer (4×10^{-4} mol dm^{-3} for spirobenzopyran unit) with and without an alkali metal perchlorate (4×10^{-4} mol dm^{-3}) were followed by 560 nm excitation at room temperature after UV-light irradiation.

Composite Film Fabrication. PVC-based composite films for ionic conductivity measurements were prepared on indium−tin oxide-coated (ITO) glasses (2 × 2.5 cm) by spin-coating from THF solutions and then dried at 60 °C overnight under a nitrogen stream and thereafter at room temperature for 12 h under a vacuum. An aliquot (0.1 cm^3) of a THF solution (0.6 cm^3) containing PVC (30 mg), DOS (25 mg), crowned spirobenzopyran polymer [0.8 mg for polymers **1**(x = 0.59)], and $LiClO_4$ (0.25 mg) was used for the spin-coating on an ITO glass, affording a composite film with about 2 mm thickness. Composite films containing polymer **3** [PVC (30 mg), DOS (25 mg), crown ether−spirobenzopyran polymer (1 mg), and $LiClO_4$ (0.25 mg) dissolved in THF (1 cm^3), 0.1 cm^3 for each coating] were also fabricated in a similar way. For the self-supporting composite films containing polymer **1**(x = 0.04) (without PVC), 0.2 cm^3 of a THF solution containing polymers **1**(x = 0.04) (9 mg), DOS (2 mg), and $LiClO_4$ (0.5 mg) was used for the spin-coating. For ionic conductivity measurements, gold was evaporated as a disk electrode (4.5 mm diameter, about 40 nm thickness) on the composite films.

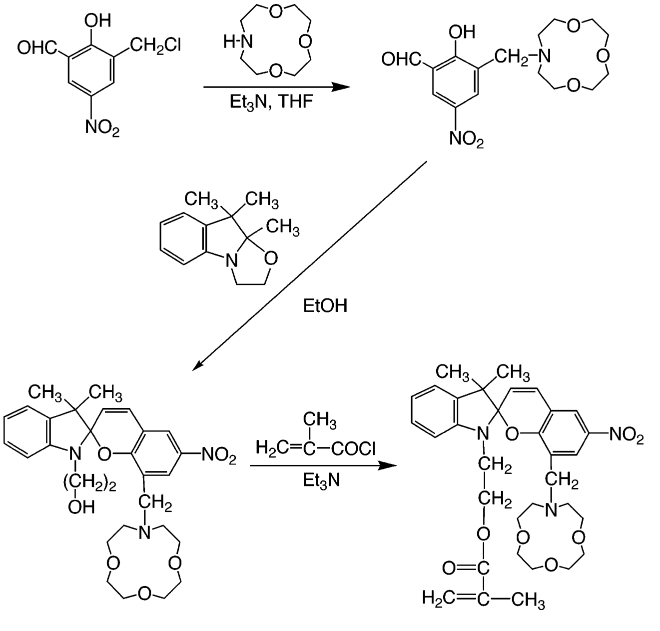
Ionic Conductivity Measurements. Ac impedance of composite films was measured under an argon stream, as reported previously.[16] Ionic conductivity calculation was made by the Cole−Cole plot method.

Results and Discussion

Synthesis of Crowned Spirobenzopyran Vinyl Polymers. The synthesis of a spirobenzopyran derivative incorporating a monoaza-12-crown-4 moiety and a methacryloyloxyethyl group at the 8- and 1′-position, respectively, is shown in Scheme 1.

The corresponding 1′-hydroxylethyl derivative was synthesized by the condensation of 1,3,3-trimethyl-2-methyleneindoline with 5-nitrosalicylaldehyde possessing a monoaza-12-crown-4 moiety. The crowned nitro-

Scheme 2. Synthetic Diagram for Crowned Spirobenzopyran Vinyl Monomer



salicylaldehydes were in turn obtained by chloromethylation of 5-nitrosalicylaldehyde,[17] followed by the reaction with a monoazacrown ether[18] in the presence of triethylamine. The reaction of the 1′-hydroxyethyl crowned spirobenzopyran with methacrylic chloride in the presence of triethylamine afforded the methacryloyloxyethyl derivative, that is, the crowned spirobenzopyran vinyl monomer.

Radical polymerization of the crowned spirobenzopyran vinyl monomer was carried out in toluene using a sealed glass tube. We tried homopolymerization of the vinyl monomer, but this failed probably due to the high steric hindrance of the crowned spirobenzopyran side chain on the polymerization. Therefore, we copolymerized the crowned spirobenzopyran monomer with methyl methacrylate (MMA) to obtain three crowned spirobenzopyran polymers with a different composition of crown ether and spirobenzopyran moieties, **1**(x = 0.59, 0.16, and 0.04), the molecular weight of which was 5.7×10^3, 8.1×10^3, and 5.1×10^4, respectively, in polystyrene standards.

Metal-Ion Complexing Property. Alkali metal picrate extraction was used to assay the cation-complexing abilities of crowned spirobenzopyran derivatives toward alkali metal ions. Cation extraction was carried out with a 1,2-dichloroethane solution of a crowned spirobenzopyran polymer, **1**(x = 0.16), from an alkali metal picrate aqueous solution. The results are compared with those for the corresponding monomeric derivative **2** and crown ether–spirobenzopyran copolymer **3** in Figure 1. The metal-ion selectivity for polymer **1**(x = 0.16) is in the order $Li^+ > Na^+ > K^+$. This finding is similar to the metal-ion selectivity of monomeric crowned spirobenzopyran **2** ($Li^+ \gg Na^+ > K^+$).[3] In crowned spirobenzopyran **2**, the crown ether moiety of which binds an alkali metal ion, the isomerization of its spirobenzopyran moiety proceeds even without photoirradiation due to the cation-complexation-induced polarization of the molecule. In the metal-ion complex of the merocyanine form of **2**, the phenolate anion interacts with a metal ion in the crown ether ring, owing to the stable six-membered chelate formation of the oxy anion and the nitrogen atom in the crown ether ring.

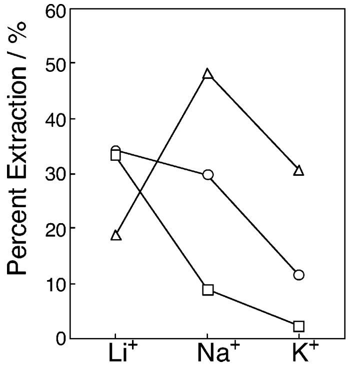


Figure 1. Alkali-metal-ion extraction with crown ether derivatives under dark conditions: circle, **1**(x = 0.16); square, **2**; triangle, **3**.

Li^+ not only fits well into the 12-crown-4 ring but also interacts strongly with the phenolate anion due to its high charge density. This is the reason why crowned spirobenzopyran **2** possesses high Li^+ selectivity, which is also true in crowned spirobenzopyran polymer **1**(x = 0.16). On the other hand, crown ether–spirobenzopyran polymer **3** exhibited a different metal-ion selectivity from that for crowned spirobenzopyran polymer **1**, having a selectivity order of $Na^+ > K^+ > Li^+$. Since the crown ether and spirobenzopyran moieties are not very close to each other in the polymer carrying the two moieties independently at the side chain, **3**, the moieties have difficulty in cooperating on the metal-ion binding, unlike crowned spirobenzopyran derivatives **1** and **2**. The high Na^+ selectivity for crown ether–spirobenzopyran polymer **3** suggests that the neighboring crown ether rings cooperate on the metal-ion binding to form sandwich-type 2:1 (crown ether ring/metal) complexes instead. Actually, this was the case with polymers carrying a 12-crown-4 moiety at the side chain[19] and their corresponding dimers, bis(12-crown-4) derivatives.[20]

The absorption spectra for organic phases after the cation extraction explains the cooperation of the crown ether and spirobenzopyran moieties on the metal-ion complexation. The absorption spectra for the extraction system with crowned spirobenzopyran polymer **1**(x = 0.16) are shown in Figure 2, together with those for the extraction systems with **2** and **3** for comparison. Figure 2a shows that there is significant absorption between 500 and 600 nm for the **1**(x = 0.16) system even under dark conditions, which can be assigned to the merocyanine form of the crowned spirobenzopyran moiety. The organic phase after cation extraction with both **1**(x = 0.16) and **2** turned purple. The merocyanine absorption was the most intense on Li^+ extraction with crowned spirobenzopyran polymer **1**(x = 0.16), as was the case with the system of the monomeric derivative **2**. On the contrary, there was hardly any significant absorption based on the merocyanine in an organic phase of crown ether–spirobenzopyran polymer **3** in extracting any metal ion. This means that in crown ether–spirobenzopyran polymer **3** the metal-ion complexation with its crown ether moiety does not induce the isomerization of its spirobenzopyran moiety to the corresponding merocyanine form and thereby the additional ionic interaction between its phenolate anion and a metal ion in the crown ether ring.

Thus, the polymeric and monomeric derivatives containing a crowned spirobenzopyran moiety show Li^+ selectivity due to the efficiently cooperative action of the

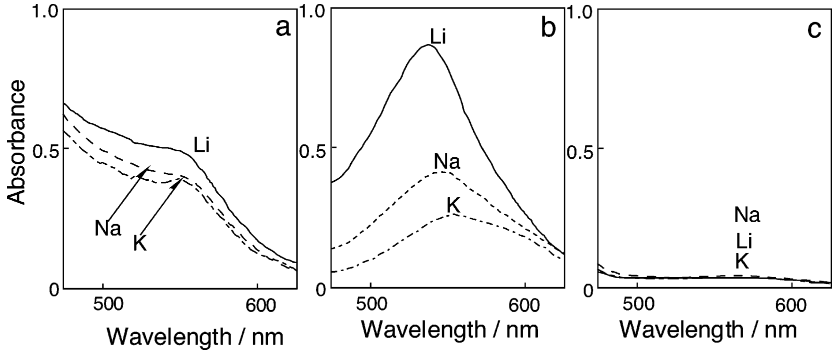


Figure 2. Absorption spectra for the organic phase after alkali-metal-ion extraction without photoirradiation: (a) crowned spirobenzopyran polymer **1**(x = 0.16); (b) monomeric crowned spirobenzopyran **2**; (c) crown ether−spirobenzopyran polymer **3**.

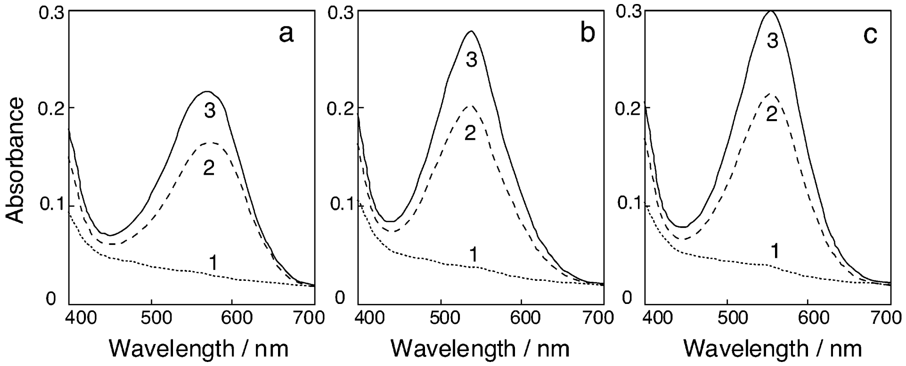


Figure 3. UV-light-induced absorption−spectral changes for THF solutions of crowned spirobenzopyran polymer **1**(x = 0.16) without metal ion (a), with Li^+ (b), and with Na^+ (c). Photoirradiation time: (1) 0 min; (2) 1 min; (3) 3 min.

crown ether and spirobenzopyran (merocyanine) moieties. Such cooperative action cannot be realized in polymer carrying crown ether and spirobenzopyran moieties independently **3**. Instead, the cooperation of two adjacent crown ether rings resulted in Na^+ selectivity in polymer **3**. A similar cooperative effect by two neighboring crown ether rings might contribute to the enhanced Na^+ extractability by crowned spirobenzopyran polymer **1**(x = 0.16) as compared to that by its corresponding monomeric analogue **2**.

Photochromism in the Presence of Alkali Metal Ions. The spirobenzopyran moiety of crowned spirobenzopyran polymers **1** isomerizes photochemically in the absence and presence of an alkali metal ion, as demonstrated by the typical UV-light-induced absorption-spectral changes of polymer **1**(x = 0.16) THF solution (Figure 3). However, hardly any significant blue shift (time-course changes of the absorption peak) in the merocyanine peak was observed in any system of the crowned spirobenzopyran polymers **1**. The present crowned spirobenzopyran polymers are very different from crown ether−spirobenzopyran polymer **3** in that a marked blue shift, assigned to the merocyanine aggregate formation, can be found in the prolonged photoirradiation of THF solutions of polymer **3**, especially in the presence of Li^+ or Na^+. Also, no polymer precipitation induced by the merocyanine aggregation as seen in polymer **3** was observed in any of the crowned spirobenzopyran polymers **1**. Probably, the merocyanine aggregation in polymers **1** is suppressed by the steric hindrance of their crown ether moiety and/or by the powerful interaction between their phenolate anion and a metal ion in the crown ether ring.

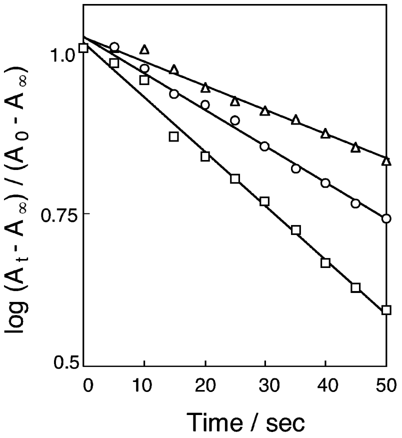


Figure 4. Plots of $\log[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time for thermal decoloration **1**(x = 0.16) without metal ion (square), with 4×10^{-4} mol dm^{-3} Li^+ (triangle), and with 4×10^{-4} mol dm^{-4} Na^+ (circle). Concentration of **1**(x = 0.16): 4×10^{-4} mol dm^{-3} (for spirobenzopyran unit).

After UV-light irradiation on THF solutions of polymers **1**, turning off the light caused the thermal isomerization from the merocyanine to return to its spiropyran form, and the purple color of the solutions disappeared with time. The thermal decoloration reaction was followed in order to estimate the thermal stability of the merocyanine forms in the absence and presence of an alkali metal ion. The slopes in the plots in Figure 4 indicate first-order rate constants for the thermal decoloration. Adding an equimolar amount of Na^+ to a THF solution of polymer **1**(x = 0.16) decreased the thermal decoloration rate, and the addition of Li^+ enhanced the reaction depression. The rate constants for polymers **1**(x = 0.59, 0.16, and 0.04), monomeric derivative **2**, and polymer **3** are summarized in Table 1. The tendency in the thermal decoloration rate for the crowned spirobenzopyran polymers **1** (no metal ion > Na^+ > Li^+) is similar to that for the corresponding

Table 1. First-Order Rate Constant (*k*) for Thermal Decoloration of UV-Light-Induced Merocyanine Moiety

spirobenzopyran derivative	k (10^{-3} s^{-1})^a		
	without metal ion	Li^+	Na^+
1(x = 0.59)	5.0	3.5	4.2
1(x = 0.16)	5.2	2.3	3.5
1(x = 0.04)	4.6	2.4	3.3
2	7.0	3.5	6.1
3	17.3	8.6	9.1

[a] Values determined in THF at 40 °C after UV-light irradiation for 2 min.

monomeric analogue **2**. This means that the stable metal-ion complex formation by the crowned spirobenzopyran moiety as described above augments the thermal stability of its merocyanine form in crowned spirobenzopyran derivatives **1** and **2**. In general, the polymeric derivatives **1** are slightly smaller in the rate constant than the monomeric analogue **2**. Some polymer rheology change accompanied by the isomerization might somewhat affect the thermal decoloration of crowned spirobenzopyran polymers, but the difference in the copolymer composition (x) did not change their rate constants very much.

In contrast, the thermal decoloration proceeds very fast at the measurement temperature (40 °C) in the polymer carrying crown ether and spirobenzopyran moieties independently, **3**, even in the presence of Li^+ and Na^+, although one can find some thermal stabilization of the merocyanine moiety on the basis of the merocyanine aggregation.[13] This indicates strongly that there is little merocyanine stabilization derived from the interaction between its phenolate anion and a metal ion in the crown ether ring.

Photoinduced Switching of Ionic Conductivity. As already described, the crowned spirobenzopyran moiety in polymers **1** binds an alkali metal ion powerfully not only by the complexation with its crown ether ring but also by the additional ionic interaction of a phenolate anion of its merocyanine form. Also, visible-light irradiation forces the merocyanine form to isomerize back to the corresponding electrically neutral spiropyran form and thus eliminates the additional interaction. One can, therefore, expect photocontrol of metal-ion binding and thereby ionic conduction by using crowned spirobenzopyran polymer **1**, as has also been seen in crowned spirobenzopyran **2**. We fabricated photoresponsive ion-conducting composite films containing PVC, a plasticizer, crowned spirobenzopyran polymer **1**, and $LiClO_4$. Crown ether−spirobenzopyran polymer **3** was also tested as the photocontrol reagent for comparison. Figure 5 depicts typical profiles of photoinduced ionic conductivity changes for both systems of **1**(x = 0.59) and **3**. The ionic conductivity for the composite films containing crowned spirobenzopyran polymer **1**(x = 0.59) was decreased by UV-light irradiation and increased by visible-light irradiation. UV light enhanced the isomerization of the spirobenzopyran moiety to its corresponding merocyanine form and thus the metal-ion binding. This in turn diminished the concentration of uncomplexed Li^+ that can contribute to ionic conduction, thus decreasing the ionic conductivity. Subsequent visible-light irradiation induced reverse isomerization from the merocyanine to spiropyran forms, restoring the ionic conductivity.

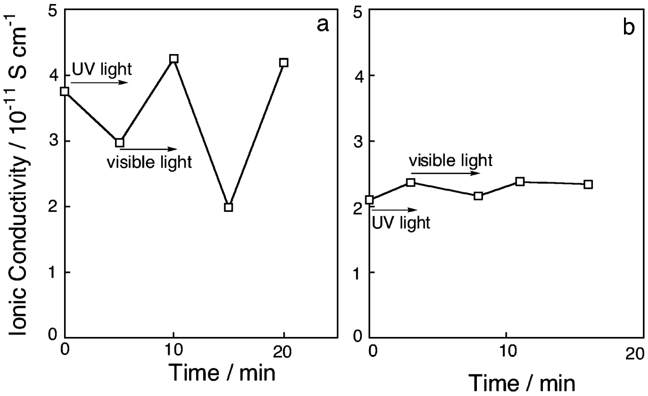


Figure 5. Photoinduced ionic conductivity changes in composite films containing crowned spirobenzopyran polymer **1**(x = 0.59) (a) and crown ether−spirobenzopyran polymer **3** (b).

The profile in the photoinduced ionic conductivity switching for the system of crown ether−spirobenzopyran polymer **3** is the opposite of that for crowned spirobenzopyran polymer **1**(x = 0.59). Accordingly, the ionic conductivity was increased by UV light and decreased by visible light. This profile in the photoinduced ionic conductivity switching is certainly not based on the mechanism for metal-ion complexation photocontrol for the crowned spirobenzopyran derivatives **1**. Also, the polymer **3** system was smaller in its magnitude of photoinduced ionic conductivity changes than the polymer **1**(x = 0.59) system. A plausible explanation for the photoinduced ionic conductivity changes is that UV-light-induced formation of the ionic merocyanine may bring about some polarity increase in the bulk of the composite film, which results in the ionic conductivity enhancement by promoting the migration of ion-conducting carriers.

A great advantage of the crowned spirobenzopyran polymers **1** over the corresponding monomeric derivative **2** as the photocontrol reagents for photoresponsive ion-conducting materials is that the polymers have the capability to form films by themselves. Since polymer **1**(x = 0.04) is able to form transparent self-supporting films thanks to its relatively high molecular weight (about 5×10^4), we fabricated ion-conducting films consisting of polymer **1**(x = 0.04), a plasticizer, and $LiClO_4$ without using PVC. The self-supporting films of crowned spirobenzopyran polymer contained more crown ether unit and less plasticizer than the corresponding PVC-based composite films, so a greater amount of lithium salt can be dissolved in the former films with a help of the cation binding ability of the crown ether moiety. This has in turn realized photochemical switching in the higher order of ionic conductivity (Figure 6). In the self-supporting films as cast, a considerable amount of spirobenzopyran moiety was isomerized to its merocyanine form due to the high electric constant in the bulk film. Visible-light irradiation allowed the merocyanine moiety to isomerize back to the spiropyran form, thus increasing the ionic conductivity. The subsequent UV-light irradiation again promotes the ionic conduction, as was the case with the corresponding PVC-based composite films.[4]

In conclusion, the present polymers carrying a crowned spirobenzopyran moiety at the side chain, **1**, showed similar behaviors to their corresponding monomeric analogue, **2**, in terms of metal-ion complexation, photochromism, and photoresponsive ionic conduction, although some polymer effect was observed in the polymeric analogues. Crowned spirobenzopyran vinyl polymers **1** are quite different from polymer **3** carrying crown ether and spirobenzopyran moieties indepen-

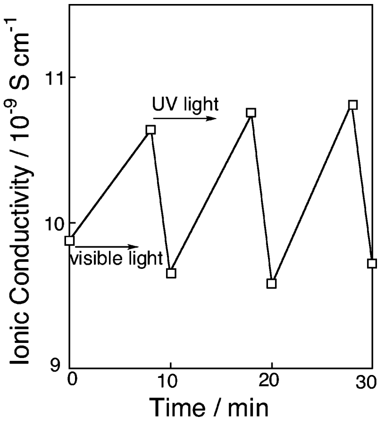


Figure 6. Photoinduced ionic conductivity changes in self-supporting composite films of crowned spirobenzopyran polymer **1**($x = 0.04$).

dently, despite the fact that the two types of polymers carry crown ether and spirobenzopyran moieties at the polymer side chain. In particular, crowned spirobenzopyran polymer **1**($x = 0.04$), which is able to form self-supporting films, is a promising photocontrol material for ionic conduction.

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