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Cation Complexation, Photochromism, and Aggregation of Copolymers Carrying Crown Ether and Spirobenzopyran Moieties at the Side Chains

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Methacrylate monomers containing monoaza-12-crown-4 and spirobenzopyran moieties were copolymerized to obtain polymers carrying their moieties at the side chains. The crown ether-spiropyran polymers can bind alkali metal ions with their crown ether moiety in the selectivity order of $Na^+ > K^+ > Li^+$. The spirobenzopyran moiety, on the other hand, undergoes UV-light-induced isomerization from its spiropyran to the merocyanine form, leading to merocyanine aggregate formation. The metal-ion complexation of the crown ether moiety enhanced interpolymer merocyanine aggregation by extending the polymer chain on the basis of the electrostatic repulsion between the complexed metal ions. Thus, tetrahydrofuran solutions of a crown ether-spiropyran copolymer with 1 : 1 composition of the moieties led to significant polymer precipitation on UV irradiation in the presence of an alkali metal ion, especially Li^+. The photochromism and aggregate formation were studied in detail by absorption and fluorescence spectrometry and by light scattering measurements.

Photochromic compounds are very convenient tools for the photocontrol of physical properties. Specifically, spirobenzopyran derivatives are useful for this purpose, since they isomerize photochemically from their electrically neutral spiropyran form to the zwitterionic merocyanine form.[1] Examples for the application include photocontrol of membrane transports,[2,3] membrane potentials,[4–6] polymer rheology,[7,8] and enzyme reactions.[9–11] We have also designed spirobenzopyran derivatives incorporating a monoazacrown ether moiety at the 8-position; these are referred to as crowned spirobenzopyran. Thus the combination of a spirobenzopyran moiety with a crown ether ring has led to a novel attractive functionality, i.e., photochemical control for metal ion complexation and ionic conduction.[12,13] Another easy way to combine a crown ether with a spirobenzopyran moiety is copolymerization of vinyl monomers carrying these moieties. Such crowned spirobenzopyran polymers are endowed with some advantages over their corresponding monomeric crowned spirobenzopyran for applications as materials, i.e., easy immobilization of the crowned spirobenzopyran moiety and high processibility.

The combination of spirobenzopyran and crown ether moieties on polymer chains may be expected to bring about new aspects besides the photocontrol of metal-ion manipulation. Spirobenzopyran derivatives, when isomerized to their zwitterionic merocyanine form, are likely to aggregate to form merocyanine pairs by electrostatic attraction.[14] The merocyanine aggregation seems to be enhanced in polymers carrying a spirobenzopyran moiety at the side chain.[15–17] On the other hand, the metal-ion complexation by the crown ether moiety in crown ether polymers brings about rheology changes due to the expansion and contraction of the polymer chains.

We have designed and synthesized copolymers carrying monoaza-12-crown-4 and spirobenzopyran moieties with different compositions of the moieties in the side chain, in order to obtain a polymeric photocontrol system of cation complexation and also to elucidate polymer effects on the interesting behaviors of crowned spirobenzopyrans. Recently, we communicated a photoregulated precipitation of a crown ether-spiropyran copolymer with 1 : 1 composition in the presence of an alkali metal ion due to the efficient interpolymer merocyanine aggregation.[18] This paper describes in detail the synthesis, metal-ion complexation, photochromism, and aggregation of the crown ether-spiropyran copolymers with different moiety compositions.

Experimental

Synthesis of Copolymers Carrying Crown Ether and Spirobenzopyran Moieties at the Side Chain (Crown Ether-Spiropyran Copolymers). 10-[2-(Methacryloyloxy)ethyl]-1,4,7-trioxa-10-azacyclododecane (Monoaza-12-crown-4 Methacrylate Monomer). 10-(2-Hydroxyethyl)-monoaza-12-crown-4 was prepared according a procedure given in the literature.[19] The condensation of the hydroxyethyl crown ether with methacryloyl chloride in the presence of triethylamine was carried out as follows. A mixture of 10-(2-hydroxyethyl)-monoaza-12-crown-4 (28 mmol) and triethylamine (56 mmol) dissolved in anhydrous benzene (180 cm^3) was cooled in an ice bath under an argon atmosphere. To the mixture was added dropwise methacryloyl chloride (42 mmol) while stirring. The mixture was stirred at room temperature for an additional 3 h. After the reaction, the triethylamine hydrochloride was filtered off. The filtrate was washed with water and then dried over $MgSO_4$. The solvent evaporation yielded a crude product of monoaza-12-crown-4 methacrylate monomer, which was purified by silica-gel column chromatography ($CHCl_3$/MeOH = 96/4, R_f = 033). Yield: 48%. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.93 (3H, s, CH_3CCH_2), 2.82 (4H, t, $CH_2OCH_2CH_2N$), 2.88 (2H, t, $CO_2CH_2CH_2N$), 3.6–3.7 (12H, m, CH_2OCH_2), 5.55 and 6.09 (1H each, s, $CH_3C{=}CH_2$); MS *m/z* 288 (M^+, 100%). Anal. Calcd for $C_{14}H_{25}NO_5$: C, 58.52; H, 8.77; N, 4.87; O, 27.84%. Found: C, 58.41; H, 8.67; N, 4.69%.

Copolymerization of Crown Ether and Spirobenzopyran Methacrylate Monomers. 1′-[2-(Methacryloyloxy)ethyl]-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (spirobenzopyran methacrylate monomer) was obtained by a previously reported procedure.[20] Radical polymerization of vinyl monomers possessing monoaza-12-crown-4 and spirobenzopyran moieties was carried out in benzene at 60 °C for 36 h, using a glass tube sealed after several freeze-pump-thaw cycles under vacuum. The total monomer concentration was 0.8 mol dm^3. α,α'-Azobisisobutyronitrile (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, $CHCl_3$). The molecular weight for the polymer was determined by GPC (Shodex KF-2003) using tetrahydrofuran (THF) as the eluent and polystyrenes as the molecular weight standard.

Other Materials. Alkali metal salts (perchlorate and hydroxide) and picric acid were of analytical grade. The solvents for the measurements were spectro-grade from Dojindo. 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. The mixture was shaken vigorously by a reciprocating shaker under dark conditions for 15 min.[21] After phase separation, the organic and aqueous phases were subjected to absorption-spectral measurements. The percent 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 crown ether-spiropyran copolymer (4×10^{-4} mol dm^{-3} of spirobenzopyran units) and an appropriate concentration of an alkali metal perchlorate were prepared and their absorption spectra were then taken under dark conditions. UV light (300–400 nm) and visible light (> 500 nm) for photoirradiation 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, a crown ether-spiropyran copolymer THF solution (4×10^{-4} mol dm^{-3} of spirobenzopyran units) with and without an appropriate concentration of alkali metal perchlorate was irradiated in a 1-cm quartz cell by UV light for 5 min. The absorbance for the corresponding merocyanine form at 580 nm was followed with time at 20 °C, immediately after the 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 the absorbance at 580 nm at $T = t$, $T = 0$, and $T =$ infinity, respectively.

Fluorescence spectra for THF solutions containing a crown ether-spiropyran copolymer (4×10^{-4} mol dm^{-3} of spirobenzopyran units) with and without an alkali metal perchlorate (4×10^{-4} mol dm^{-3}) were measured by 590-nm excitation at room temperature.

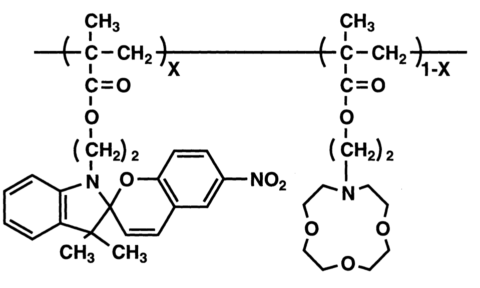
Static Light Scattering. Static light scattering intensity was measured with THF solutions of crown ether-spiropyran copolymer solutions (1×10^{-3} – 4×10^{-4} mol dm^3 of spirobenzopyran units) in the absence and presence of an equimolar amount of an alkali metal perchlorate. A dissymmetry method was applied for the analysis.

Results and Discussion

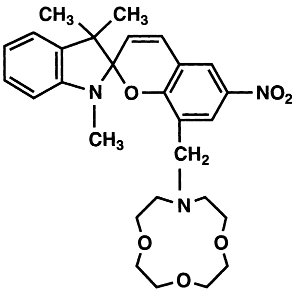
Copolymerization of Methacrylate Monomers Possessing Crown Ether and Spirobenzopyran Moieties. Radical copolymerization of the monoaza-12-crown-4 and spirobenzopyran methacrylate monomers was carried out with different initial monomer molar ratios, in order to obtain copolymers carrying monoaza-12-crown-4 and spirobenzopyran moieties **1**. Three crown ether-spiropyran copolymers with moiety compositions of 1 : 1 ($x = 0.48$), 3 : 7 ($x = 0.71$), and 17 : 3 ($x = 0.15$) were obtained after purification by gel-permeation chromatography. These have number-average molecular weights of about 1×10^4 with M_w/M_n ratios of about 1.3. The polymers were highly soluble in halogenated hydrocarbons such as chloroform and 1,2-dichloroethane, and were moderately soluble in THF. They are, however, not very soluble in acetonitrile.

Metal Ion Complex Formation. Metal ion complexation of the crown ether-spiropyran copolymer with about 1 : 1 composition of crown ether and spirobenzopyran moieties, **1** ($x = 0.48$), was evaluated by cation extraction with a 1,2-dichloroethane solution of the polymer from an alkali metal picrate aqueous solution. The results were summarized in Fig. 1, together with those for crowned spirobenzopyran **2** and *N*-benzyl-monoaza-12-crown-4 **3** for comparison. The complexation of alkali metal ions by **1** ($x = 0.48$) decreases in the order of $Na^+ > K^+ > Li^+$. This order is very different from that for its corresponding monomeric analogs, crowned spirobenzopyran **2** and *N*-benzyl-monoaza-12-crown-4 **3**. The *N*-benzyl crown ether exhibited only low extractability of alkali metal ions and also poor ion selectivity. The higher complexation of Na^+ and K^+ than of Li^+ by the crown ether-spiropyran copolymers is probably due to the facile formation of intrapolymer 2 : 1 (crown ether ring/metal ion) complexes with Na^+ and K^+ by cooperative action of two neighboring crown ether rings, as was the case with poly(12-crown-4) derivatives.[22] The intramolecular sandwich-type complex formation enhances the metal ion binding and thereby the extraction.

The difference in the metal-ion selectivity between the crown ether-spiropyran copolymer **1** ($x = 0.48$) and crowned spirobenzopyran **2** may be understood by the consideration of absorption-spectral changes in the organic phase after the cation extraction (Fig. 2). Remarkable spectral changes were observed in the organic phase of the **2** system after metal-ion extraction.[12] The remarkable absorption around 550 nm after ex-



1 (x = 0.48, 0.71, 0.15)



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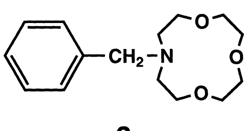

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Chart 1.

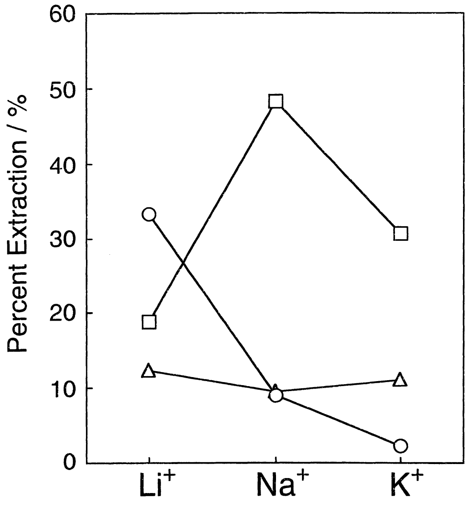

Fig. 1. Alkali-metal ion extraction with crown ether derivatives under dark conditions. (□): **1** (x = 0.48), (○): **2**, (△): **3**.

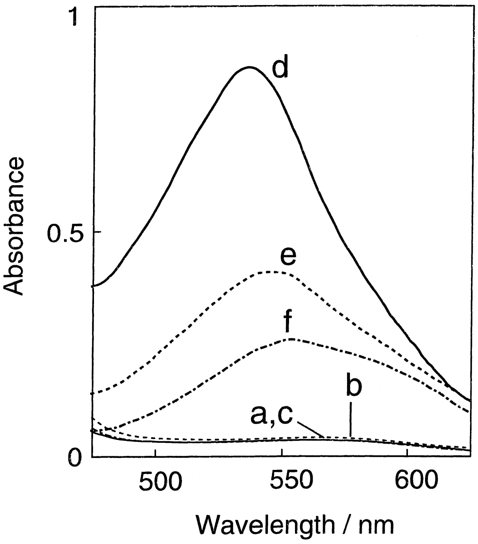

Fig. 2. Absorption spectra for organic phase after alkali-metal ion extraction without photoirradiation. (a): **1** (x = 0.48) – Li^+; (b): **1** (x = 0.48) – Na^+; (c): **1** (x = 0.48) – K^+; (d): **2** – Li^+; (e): **2** – Na^+; (f): **2** – K^+.

traction of an alkali metal ion, especially of Li^+, can be assigned to the corresponding merocyanine form of **2**. This means that the metal-ion complexation of crowned spirobenzopyran **2** induces isomerization of the spirobenzopyran moiety to its corresponding merocyanine form even in the dark. The efficient intramolecular interaction between a phenolate anion and a metal ion complexed by the crown ether moiety in the metal-ion complex of the **2** merocyanine form reflects the selectivity order of $Li^+ > Na^+ > K^+$, as already discussed.[12] On the contrary, there are only slight spectral changes in the extraction system of crown ether-spiropyran copolymer **1** (x = 0.48) in spite of the fact that the polymer also carries crown ether and spirobenzopyran moieties intramolecularly. This suggests that such intramolecular interaction as seen in crowned spirobenzopyran **2** is quite difficult in the polymer, **1** (x = 0.48), probably due to the much longer distance between its crown ether and spirobenzopyran moieties than in crowned spirobenzopyran **2**. This is the main reason for the ion selectivity difference between crown ether-spiropyran copolymer **1** (x = 0.48) and crowned spirobenzopyran **2**.

Photoisomerization Followed by Merocyanine Aggregation. UV irradiation on a THF solution of crown ether-spiropyran copolymer **1** (x = 0.48) led to a new absorption peak between 500 and 600 nm, as shown in Fig. 3. This indicates that the photoinduced isomerization of the spiropyran moiety can proceed in the present polymer. The presence of alkali metal ions such as Li^+ and Na^+, which can be complexed by crown ether rings in the polymer, affects its photochromism (spirobenzopyran moiety) and rheology significantly.

A THF solution of crown ether-spiropyran copolymer **1** (x = 0.48) showed a different behavior for the photoinduced spectral changes in the absence and presence of an alkali metal ion (Li^+ and Na^+) (Fig. 3). On photoirradiation of the polymer

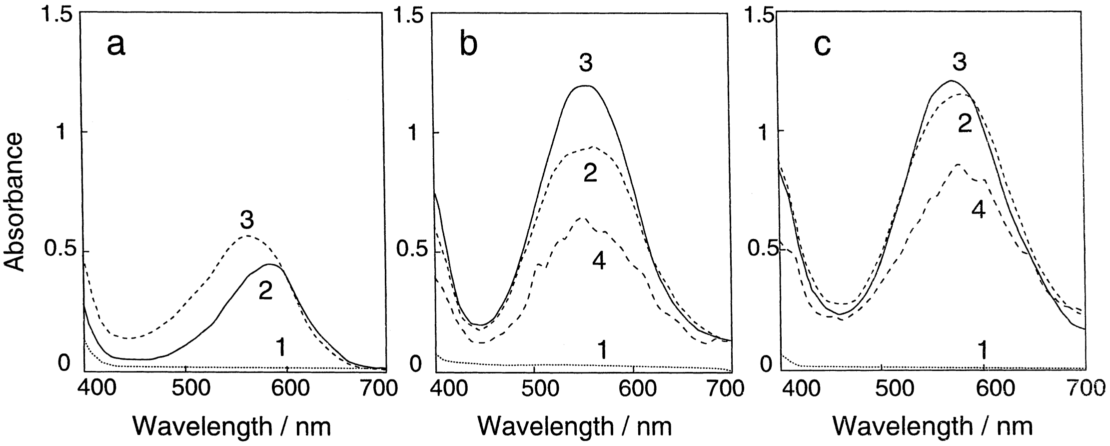

Fig. 3. UV-light-induced absorption-spectral changes for THF solutions of crown ether-spiropyran copolymer **1** ($x = 0.48$) without metal ion (a), with Li^+ (b), and with Na^+ (c). Photoirradiation time: (1), 0 min; (2), 5 min; (3), 15 min; (4), 20 min.

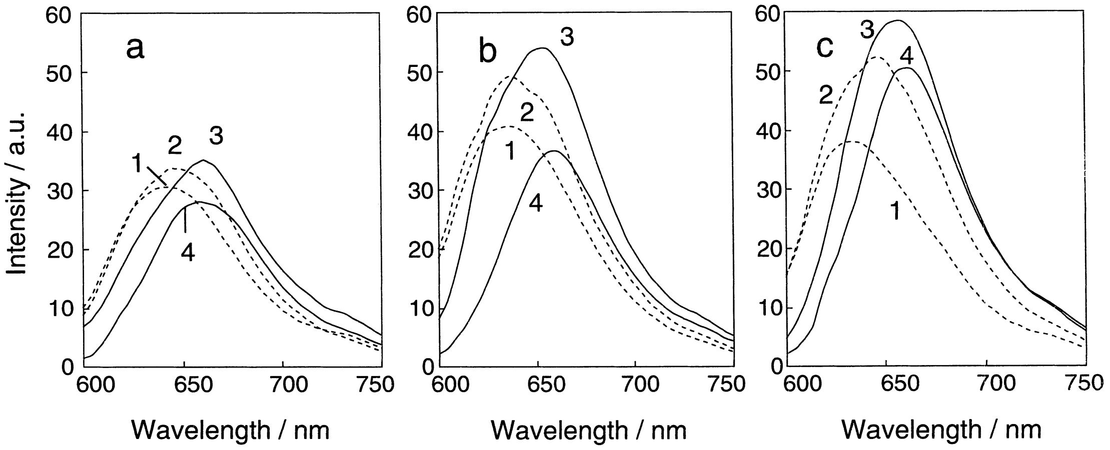

Fig. 4. UV-light-induced fluorescence-spectral changes for THF solutions of crown ether-spiropyran copolymer **1** ($x = 0.48$) without metal ion (a), with Li^+ (b), and with Na^+ (c). Photoirradiation time: (1), 0.5 min; (2), 1 min; (3), 3 min; (4), 10 min.

solution without any metal ion, a merocyanine peak first appeared at 590 nm and then shifted to 580 nm. This blue shift of the merocyanine peak indicates some aggregation of the resulted merocyanine moiety, as is the case with the copolymers of spiropyran methacrylate monomer and methyl methacrylate reported by Krongauz et al.[16] Addition of an equimolar amount of $LiClO_4$ to the THF solution of **1** ($x = 0.48$) enhanced the photoisomerization of its spirobenzopyran moiety to its merocyanine form and thereby the merocyanine aggregation. In the early stage of photoirradiation, a strong absorption was found at 560 nm, accompanied by a more intense blue shift than for the system without any metal ion. Further UV irradiation resulted in an absorbance decrease and finally in a distorted spectrum, which can be attributed to some polymer precipitation, as described later. Similar spectral changes were seen in the presence of $NaClO_4$, although the Na^+ system was not as remarkable as the Li^+ system in the photoinduced blue shift and absorbance decrease of the merocyanine peak.

Fluorescence spectra gave further information about the photoinduced merocyanine aggregation of the crown ether-spiropyran copolymer **1** ($x = 0.48$). The fluorescence spectra for THF solutions of **1** ($x = 0.48$) after UV irradiation for a given time are shown in Fig. 4. In any systems with or without an alkali metal perchlorate, a fluorescence peak appeared at 630–640 nm and shifted to a longer wavelength with an intensity increase in the early stage of photoirradiation. Further photoirradiation induced a significant fluorescence quenching. Presumably, this is ascribable to the intersystem crossing, which is in turn due to the H-type aggregate formation of the merocyanine moiety in the crown ether-spiropyran copolymer.[14,23] Qualitatively, the fluorescence quenching is more remarkable in the crown ether-spiropyran copolymer solution with Li^+ than in that with Na^+ or in the absence of any metal ion. This fluorescence-spectral change also indicates that the photoinduced merocyanine aggregation of the crown ether-spiropyran copolymer **1** ($x = 0.48$) is enhanced in the presence of a metal ion, especially Li^+.

Photoinduced Precipitate Formation. UV irradiation of a THF solution of crown ether-spiropyran copolymer **1** ($x = 0.48$) in the early stage induced isomerization of its spirobenzopyran moiety to the corresponding merocyanine form, the solution thus turning purple. A most interesting thing for the photochromism is polymer precipitation, i.e., prolonged UV irradiation led to marked precipitation of the purple-colored

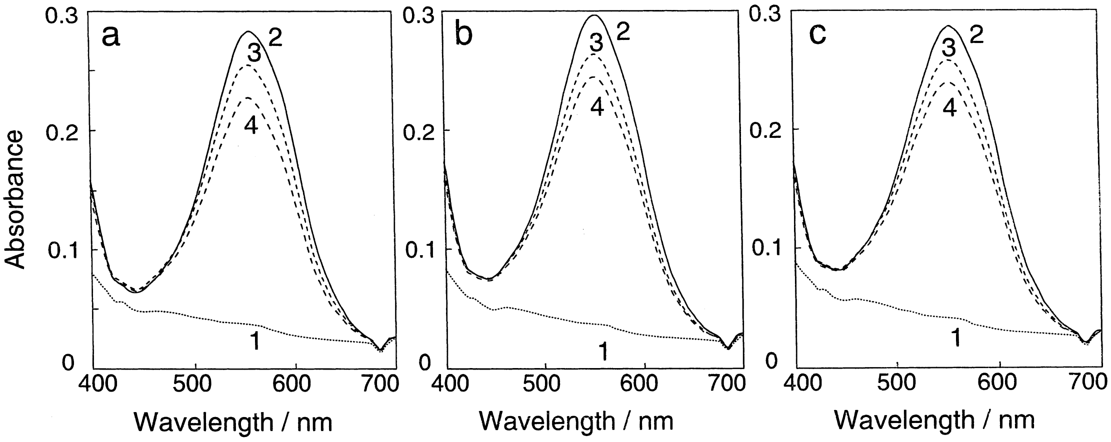

Fig. 5. UV-light-induced absorption-spectral changes for THF solutions of crown ether-spiropyran copolymer **1** ($x = 0.71$) without metal ion (a), with Li^+ (b), and with Na^+ (c). Photoirradiation time: (1), 0 min; (2), 5 min; (3), 15 min; (4), 20 min.

polymer.

Polymer chains of **1** ($x = 0.48$) should contract without any metal ion in a modestly good solvent such as THF, so the photoinduced merocyanine moieties tend to form H-type aggregates intramolecularly in a polymer chain. The polymer can, however, complex metal ions by its crown ether moiety. In the presence of a crown-ether-complexed metal ion, the polymer chains hold positive electric charges and expand due to the intramolecular electrostatic repulsion between the cationic charges. Results for static light scattering (under dark conditions) showed that the sizes of the polymer particle in the crown ether-spiropyran copolymer **1** ($x = 0.48$) solutions with and without Li^+ were 127 nm and 96 nm, respectively, indicating the enhanced interpolymer aggregation in the presence of Li^+. This may also imply the polymer chain expansion in the crown ether-spiropyran copolymer in the presence of Li^+, which in turn promotes the interpolymer formation of merocyanine aggregates. The interpolymer merocyanine aggregation results in crosslinking of **1** ($x = 0.48$) polymer chains, finally bringing about the polymer precipitation. X-ray diffraction patterns suggested that the crown ether-spiropyran copolymer precipitates resulting from by UV irradiation have little crystallinity, resembling the patterns of the original polymer as obtained just after polymerization. The crown ether-spiropyran copolymer is very different from the crystallized spiropyran polymers reported previously.[15]

More notably, the polymer precipitate induced by UV irradiation in the presence of a metal ion was again dissolved in the solution by subsequent visible-light irradiation, the **1** ($x = 0.48$) solution turning out to be almost transparent. In other words, the photoinduced precipitation of polymer **1** ($x = 0.48$) and dissolution in the presence of Li^+ is quite reversible. This phenomenon was also observed in the presence of Na^+, even though the UV-light-induced precipitation was not as remarkable as in the presence of Li^+. Since polymers carrying a 12-crown-4 moiety at the side chains tend to form intramolecular 2:1 (crown ether ring/metal ion) complexes with Na^+,[22] such intramolecular sandwich-type complex formation in the crown ether-spiropyran copolymer **1** ($x = 0.48$) may alleviate the polymer chain expansion which in turn promotes the interpolymer merocyanine aggregation.

Comparison among Copolymers with Different Moiety Compositions. It is of interest to compare the crown ether-spiropyran copolymers **1** ($x = 0.48$) with **1** ($x = 0.71$ and 0.15) in their photochromism and aggregation. The photoinduced absorption-spectral changes for copolymer **1** ($x = 0.71$) are almost the same in the absence and in the presence of a metal ion, as demonstrated in Fig. 5. The negligible metal ion effect can definitely be ascribed to the low content of the crown ether moiety (only 30%) in the polymer. Since the absorbance for merocyanine peak was decreased by prolonged UV irradiation, some aggregation of the resulting merocyanine moiety may occur. However, no significant polymer precipitation was found by long-term photoirradiation (even longer than 30 min) even in the presence of Li^+ or Na^+, unlike in the above-mentioned systems for copolymer **1** ($x = 0.48$).

For copolymer **1** ($x = 0.15$), on the other hand, the presence of a metal ion enhanced photoinduced isomerization of its spiropyran moiety to merocyanine form (Fig. 6). This is because the high crown-ether content in the copolymer promotes its metal-ion binding. This provides the polymer with a polar atmosphere, which, in turn, stabilizes its ionic merocyanine moiety. There seems, however, to be only weak merocyanine aggregation in copolymer **1** ($x = 0.15$) in the absence and presence of a metal ion, since no significant peak shift and absorbance decrease were found in its photoinduced absorption-spectral changes. Therefore, in the **1** ($x = 0.15$) systems, such photoinduced precipitate formation as seen in the systems for copolymer **1** ($x = 0.48$) was not attained even in the presence of a metal ion, even though the isomerization was enhanced by the efficient metal-ion binding.

In order to obtain further information about the stability of the photoinduced merocyanine moiety and its aggregate in three of the crown ether-spiropyran copolymers **1** ($x = 0.48$, 0.71, and 0.15), their thermal decoloration on the back isomerization of merocyanine to spiropyran forms was followed after UV irradiation. Figure 7 shows the kinetic plots of $\log [(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time for the THF solutions of copolymer **1** ($x = 0.48$) with and without a metal ion. Each of the plots gave a straight line in the early stage, yielding a first-order rate constant for the thermal decoloration. The thermal decoloration for **1** ($x = 0.48$) THF solution proceeds quite rapidly in

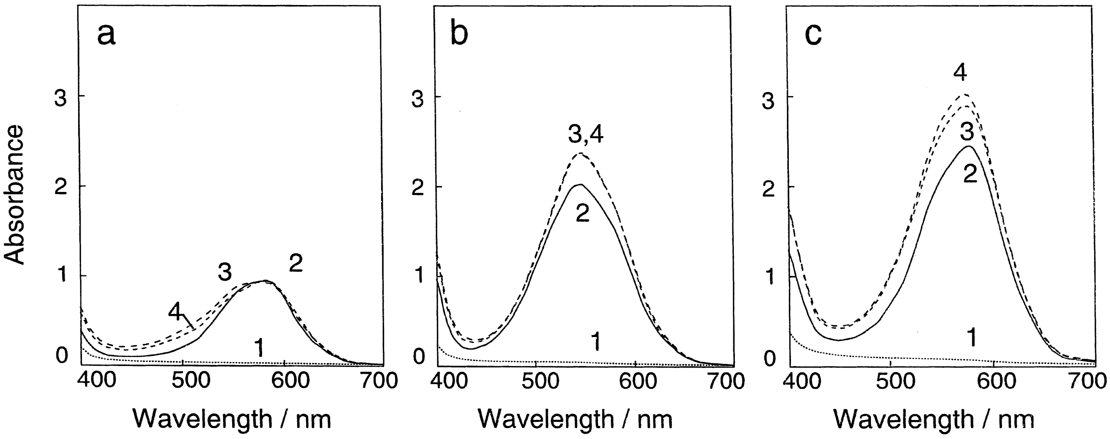

Fig. 6. UV-light-induced absorption-spectral changes for THF solutions of crown ether-spiropyran copolymer **1** (x = 0.15) without metal ion (a), with Li^+ (b), and with Na^+ (c). Photoirradiation time: (1), 0 min; (2), 5 min; (3), 15 min; (4), 20 min.

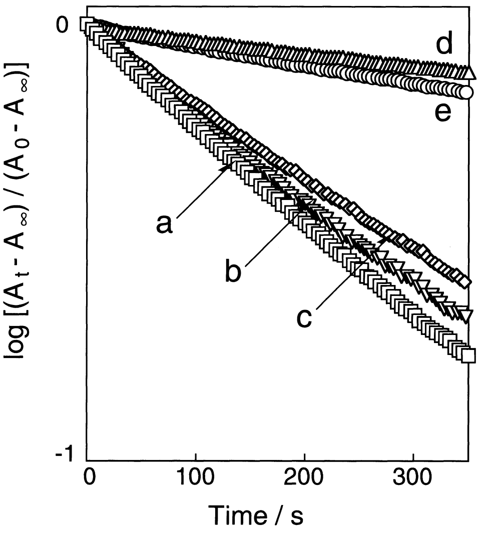

Fig. 7. Plots of $\log[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs time for thermal decoloration **1** (x = 0.48) without metal ion (a), with 4×10^{-6} mol dm^{-3} Li^+ (b), with 4×10^{-5} mol dm^{-3} Li^+ (c), with 4×10^{-4} mol dm^{-3} Li^+ (d), and with 4×10^{-4} mol dm^{-3} Na^+ (e). Spiropyran concentration of **1** (x = 0.48): 4×10^{-4} mol dm^{-3} (for the unit).

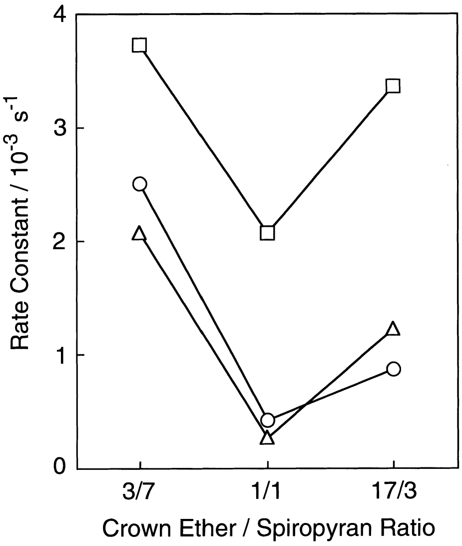

Fig. 8. Comparison of first-order rate constants for thermal decoloration among THF solutions crown ether-spiropyran copolymers **1** (x = 0.48, 0.71, and 0.15). (□): without any metal ion, (△): with 4×10^{-4} mol dm^{-3} Li^+, (○): with 4×10^{-4} mol dm^{-3} Na^+. The crown ether spiropyran ratios are 1/1, 3/7, and 17/3 for copolymers **1** (x = 0.48, 0.71, and 0.15), respectively.

the absence of a metal ion ($k = 2.1 \times 10^{-3}$ s^{-1}), whereas Li^+ addition depresses the decoloration. The reaction rate was decreased with increasing Li^+ concentration. The rate constant was decreased to 2.7×10^{-4} s^{-1} on addition of Li^+ in equimolar amount to the spiropyran unit. The merocyanine stabilization can be attributed to the metal-ion complexation and its aggregation followed by the precipitation, as already described. The decoloration for the **1** (x = 0.48) system is slightly faster on addition of equimolar Na^+ than in the case of Li^+, probably due to the difference in the electrostatic polymer expansion between the two metal-ion addition systems. The rate constants for thermal decoloration were also measured for the other copolymers **1** (x = 0.71 and 0.15). The results for the copolymer systems with and without an equimolar amount of Li^+ or Na^+ are summarized in Fig. 8, together with those for copolymer **1** (x = 0.48) for comparison. In both copolymer systems, the coexistence of a metal ion (Li^+ or Na^+) stabilizes their merocyanine moiety, either by the merocyanine aggregation or by the metal-ion-complexation induced polarity. It should be noted that copolymer **1** (x = 0.48) possesses the smallest thermal decoloration rate constants among all the copolymers under identical metal-ion conditions. Only copolymer **1** (x = 0.48) allowed the photoinduced precipitation of polymer aggregate in the presence of Li^+ or Na^+. The plausible reason for the relationship between the copolymer composition and the ease of the aggregate precipitation is as follows. Conceivably, the copolymer with 1 : 1 composition of crown ether and spiropyran moieties favors merocyanine aggregation more than the other copolymers due to steric hindrance and/or polymer conformation. In addition, the metal-ion-complexation induced polymer chain expansion, followed by the interpolymer merocyanine aggregation, proceeds most efficiently and cooperatively with 1:1 composition of crown ether and spiropyran moieties.

In conclusion, the aggregate precipitation happens specifically in copolymer **1** ($x = 0.48$) on addition of a metal ion (Li^+ or Na^+). The other attractive aspect for the crown ether-spiropyran copolymer **1** ($x = 0.48$) is the reversible photoinduced aggregate precipitation, which may be a promising phenomenon for photoinduced mechanochemical materials.

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