Cation Complexation and Photochromism of Copolymers Carrying Pendant Crowned Malachite Green Moiety

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ABSTRACT: Vinyl monomers containing a bis-crowned Malachite Green leuconitrile moiety were copolymerized with several vinyl monomers to afford polymers carrying the photochromic crown ether moiety at the side chain. The polymeric crowned Malachite Green derivatives were found to have the higher metal ion complexing ability toward K^+ and Cs^+ than Li^+ and Na^+, the ion selectivity being quite different from their corresponding monomeric analogues. The photochromism of their Malachite Green moiety was affected considerably by the metal ion complexation of their crown ether moiety. The decoloration reaction of the photoinduced cationic form was also governed by the polymer rheology in solution.

Introduction

Triphenylmethane dyes are well-known photochromic compounds.[1] Many triphenylmethane dyes undergo photoionization to triphenylmethyl cations and their counteranions, which thermally revert to the electrically neutral species. Malachite Green leuconitrile is a famous triphenylmethane, and photochromic Malachite Green dyes have been receiving attention as attractive tools for photocontrol of ionic environments.[2−5]

We had designed ion-conducting polymers containing a Malachite Green dye moiety whose ionic conductivities are photochemically switchable by a photoinduced carrier-generation mechanism. One-component-type ion-conducting polymers carrying a Malachite Green leuconitrile moiety, that is, copolymers of a Malachite Green leuconitrile vinyl monomer with a methacrylate-type monomer, were synthesized as a convenient material for photoresponsive ionic conduction.[6] A unique type of photochemical cation complexation control system can be also designed by providing Malachite Green dyes with a crown ether moiety. We already reported that in a Malachite Green leuconitrile carrying a crown ether moiety, so-called crowned Malachite Green, the metal ion complexation of its crown ether moiety can be controlled photochemically, based on electrostatic repulsion between the triphenylmethyl cation and a metal ion complexed by its crown moiety.[7] Specifically, bis-crowned Malachite Green derivative **1** (see Chart 1) realized all-or-none-type switching of metal ion complexation; i.e., the electrically neutral form binds a metal ion powerfully by cooperation of two adjacent crown ether rings, while the quinoid cationic form ejects a complexed metal ion by efficient electrostatic repulsion between a metal ion and its positive charge delocalized on the crown ring nitrogen atoms (Scheme 1).[8]

Expecting significant polymer effects, we have synthesized polymers carrying a bis-crowned Malachite Green moiety at the side chain, which were obtained by copolymerization of vinyl monomers bearing a bis-crowned Malachite Green moiety with several widely used vinyl monomers. This paper describes the polymerization, metal ion complexation, photochromism, and rheology of the bis-crowned Malachite Green polymers in detail.

Experimental Section

Syntheses of Vinyl Monomers of Bis-Crowned Malachite Green. Bis[4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)phenyl](4-vinylphenyl)methanenitrile or Vinyl Monomer of Bis-Crowned Malachite Green Leuconitrile 2. *N*-(4-Bromophenyl)monoaza-15-crown-5 (10.7 mmol), which was prepared by the reaction of *N*-phenyl-monoaza-15-crown-5 and *N*-bromosuccinimide (NBS) in refluxing CCl_4 for 3 h, was dissolved in anhydrous tetrahydrofuran (THF) (20 cm^3), and the solution was kept at −78 °C in a liquid nitrogen bath under an argon atmosphere.[9] A hexane solution of butyllithium (12.3 mmol) was injected gradually into the THF solution while stirring. To the mixture was added dropwise a THF (10 cm^3) solution of methyl 4-vinylbenzoate (4.6 mmol). The reaction mixture was allowed to warm slowly to room temperature and then stirred for an additional hour. After the reaction, the THF was evaporated off under vacuum without heating, and water (about 25 cm^3) was added to the residue. The aqueous phase was then neutralized by 0.1 mol dm^{-3} hydrochloric acid. Extraction with chloroform, followed by vacuum evaporation of the solvent, afforded a crude dark green oily product of vinyl monomer of bis-crowned Malachite Green hydroxide, which was used for the subsequent cyanization without further purification. The crude bis-crowned Malachite Green leuco-hydroxide (2.3 mmol) was dissolved in dimethyl sulfoxide (DMSO) (about 10 cm^3) and heated at 60 °C in a hood. Aqueous HCl (18.5 mmol) and KCN (69.3 mmol) were added to the solution, and the mixture was then stirred for 10 min. For complete dissolution of the added KCN, an appropriate amount (about 300 cm^3) of water was added. The color of the reaction mixture turned light yellow, and a crude product of vinyl monomer of bis-crowned Malachite Green leuconitrile **2** was then precipitated. Silica gel chromatography (eluent: $CHCl_3$/MeOH = 98/2), followed by gel permeation chromatography (eluent: $CHCl_3$), yielded a pale green solid of **2** (45%); mp 66 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.5−3.8 (m, 40H, CH_2O), 5.24 (d, J = 10.8 Hz, 1H, *trans*-H of PhCH=CH_2), 5.72 (d, J =

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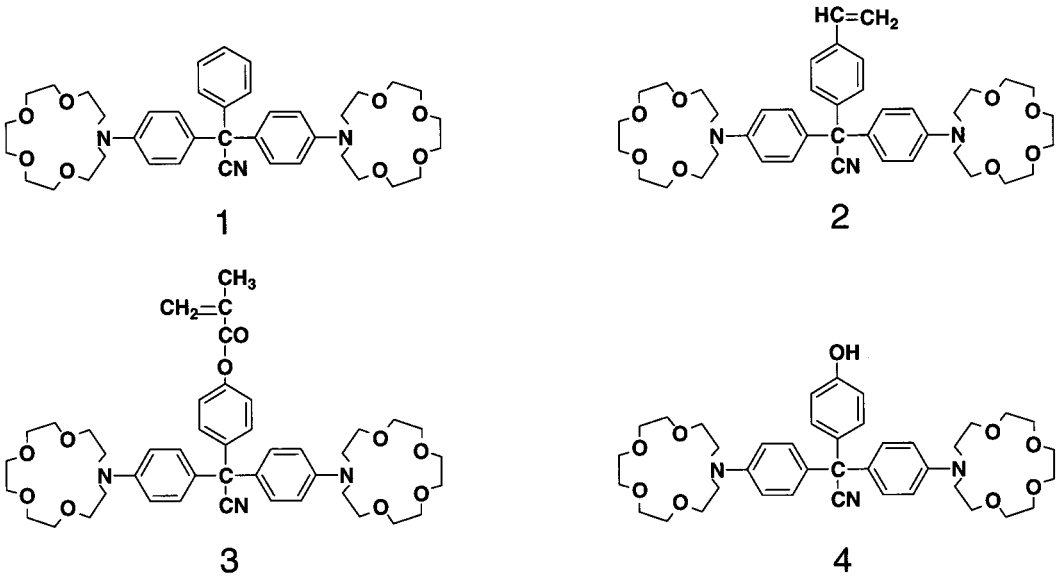
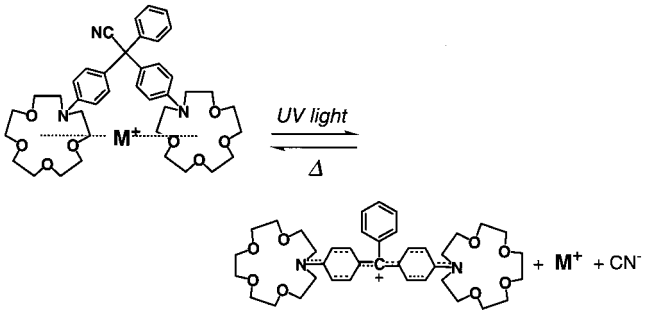
Chart 1



Scheme 1



17.6 Hz, 1H, *cis*-H of PhCH=CH_2), 6.56 (d, J = 9.2 Hz, 4H, *m*-H of NPh), 6.65 (d, J = 10.8 Hz, 1H, PhCH=C), 6.99 (d, J = 8.9 Hz, 4H, *o*-H of NPh), 7.20 (d, J = 8.4 Hz, 2H, *o*-H of PhC=C), 7.35 (d, J = 8.6 Hz, 2H, *m*-H of PhC=C). MS: *m/e* 730 (M^+, 66), 307 (100). Anal. Calcd for $C_{42}H_{55}N_3O_8 \cdot H_2O$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.37; H, 7.47; N, 5.59.

Bis[4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)phenyl](4-methacryloyloxyphenyl)methanenitrile or Vinyl Monomer of Bis-Crowned Malachite Green Leuconitrile (3). A similar reaction to the vinyl monomer of bis-crowned Malachite Green leuconitrile (**2**) using methyl 4-hydroxybenzoate instead of methyl 4-vinylbenzoate afforded bis[4-(1,4,7,-10-tetraoxa-13-azacyclopentadec-13-yl)phenyl](4-hydroxyphenyl)methanenitrile (**4**). The hydroxy derivative **4** (1.85 mmol) and triethylamine (3.69 mmol) were dissolved in THF (20 cm^3). Methacrylic chloride (2.77 mmol) was added dropwise to the mixture while stirring in an iced bath. The mixture was then continued to stir at room temperature overnight. After filtering off the resulting triethylamine hydrochloride, the solvent was replaced with chloroform. The chloroform solution was washed successively with water, 5% $NaHCO_3$ aqueous solution, and water. After drying the organic layer over $MgSO_4$, the solvent was evaporated off to yield a crude product of **3**. Purification by gel permeation chromatography afforded a pale green solid of **3** (36%); mp 72 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.06 (s, 3H, CH_3), 3.5−3.8 (m, 40H, CH_2O), 5.76 (s, 1H, *trans*-H of CH_2=CCO), 6.35 (s, 1H, *cis*-H of CH_2=CCO), 6.57 (d, J = 9.2 Hz, 4H, *o*-H of NPh), 6.99 (d, J = 8.9 Hz, 1H, *m*-H of NPh), 7.07 (d, J = 8.6 Hz, 2H, *m*-H of PhOCO), 7.27 (d, J = 8.6 Hz, 2H, *o*-H of PhOCO). MS: *m/e* 788 (M^+, 97), 307 (100). Anal. Calcd for $C_{44}H_{57}N_3O_{10} \cdot H_2O$: C, 65.57; H, 7.38; N, 5.21. Found: C, 64.92; H, 7.05; N, 5.09.

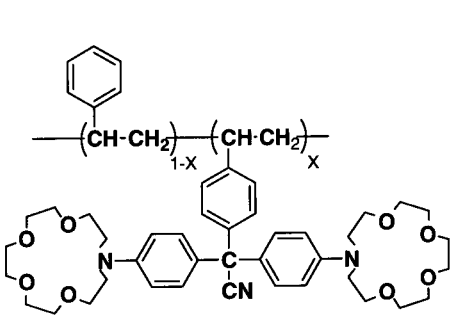
Polymerization. Radical polymerization of a vinyl monomer of bis-crowned Malachite Green leuconitrile (**2** or **3**) with a widely used vinyl monomer was carried out in benzene at 60 °C for 24 h, using a glass tube sealed after several freeze−pump−thaw cycles under vacuum. The total monomer concentration ranged from 0.69 to 0.91 mol dm^{-3}, and α,α′-azobis(isobutyronitrile) (AIBN) was used as the initiator (0.5 mol % to the total monomer). After the polymerization, the solvent and the other volatile material were vacuum-evaporated to dryness. The crude polymers were purified by fractionation to appropriate portions by gel-permeation chromatography (GPC, JAIGEL-1H and 2H, $CHCl_3$). The molecular weight and mole fraction of bis-crowned Malachite Green unit for the copolymers were determined by GPC (Shodex KF-2003, THF) and elemental analysis, respectively.

Other Materials. Alkali metal salts (perchlorate and hydroxide) and picric acid were of analytical grade. The solvents for the measurements were spectro-grade ones from Dojindo Laboratories (Kumamoto, Japan), and water was deionized.

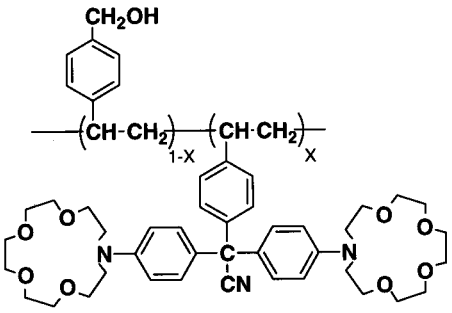
Metal Ion Extraction. Equal volumes (3 cm^3) of 2.1×10^{-3} mol dm^{-3} (for bis-crowned Malachite Green unit) crown ether−1,2-dichloroethane solution and an aqueous solution containing a mixture of 0.1 mol dm^{-3} alkali metal hydroxide and 7.0×10^{-5} mol dm^{-3} picric acid were introduced into a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

Spectrophotometric Measurements. THF/acetonitrile (50/50 vol %) solutions containing a copolymer of bis-crowned Malachite Green (4×10^{-4} mol dm^{-3} for bis-crowned Malachite Green unit) and an appropriate concentration of an alkali metal perchlorate were prepared, and their absorption spectra were then taken under dark conditions. UV irradiation was made by using a light (200−400 nm) that was obtained by passing a light from a 500 W Xe lamp through a Toshiba UV-D33S color filter. For thermal decoloration measurements, bis-crowned Malachite Green polymer THF/acetonitrile (1:1) solution (2×10^{-5} mol dm^{-3} for bis-crowned Malachite Green unit) with and without an appropriate concentration of alkali metal perchlorate was irradiated in a 1 mm quartz cell by UV light for 1 min. The absorbance for the corresponding open colored form at 625 nm was followed with time at 30 °C, immediately after UV irradiation. For the kinetic analysis of decoloration reaction, a second-order reaction rate was applied, which is defined as follows: $1/A_t - 1/A_0 = kT$ (k = rate constant; T = time; A_t and A_0 = absorbance at 625 nm, at $T = t$ and $T = 0$, respectively). The second-order rate constants of thermal

Chart 2



5 (a, b, and c)



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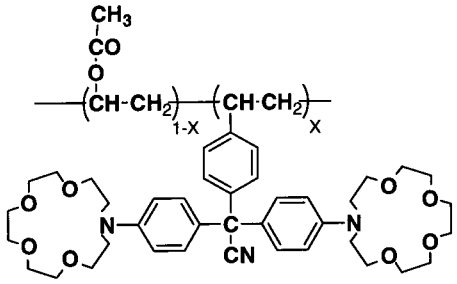

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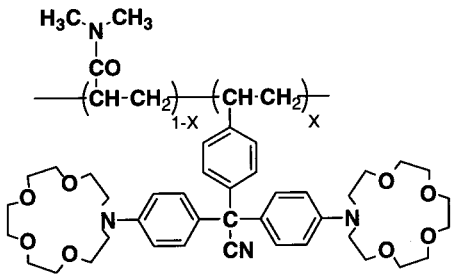

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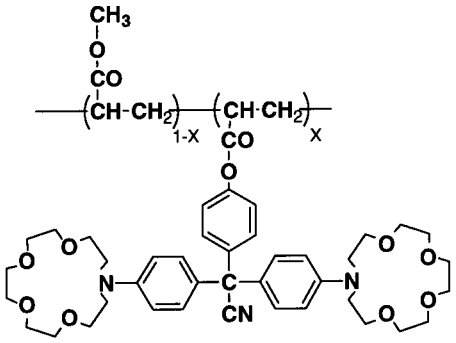

9 (a and b)

decoloration (k) were therefore determined from the slope in the plots of $1/A_t$ vs time (T).

Reduced Viscosity Measurements. Viscosity of the polymer solutions was measured in THF/acetonitrile (50/50 vol %) solution at 30 °C, by using a Ubbelohde viscometer. The concentrations of the polymer solutions were 0.02, 0.04, 0.06, 0.08, and 0.10 g dL^{-1} (1 g dL^{-1} = 10 g dm^{-3}). The polymer solutions were filtered by membrane filters (TOYO, PTFE, pore size 0.50 μm) prior to the measurements. The UV irradiation was carried out for 1 min.

Results and Discussion

Syntheses of Copolymers Carrying Bis-Crowned Malachite Green Leuconitrile Moiety at the Side Chain. Two types of vinyl monomers of bis-crowned Malachite Green were designed which are styrene- and methyl methacrylate-type monomers **2** and **3**. Both of the vinyl monomers were synthesized by the reaction of lithiated phenyl-monoaza-15-crown-5 with the corresponding methyl benzoates, followed by cyanization. Homopolymerization of the vinyl monomers of bis-crowned Malachite Green was attempted, but it failed probably due to the steric hindrance of a bulky pendant group (bis-crowned Malachite Green unit). We, therefore, decided to copolymerize the bis-crowned Malachite Green vinyl monomers with a widely used vinyl monomer. Methyl methacrylate, styrene, and vinyl acetate were selected as lipophilic comonomers and *N*,*N*-dimethylacrylamide and 4-hydroxymethylstyrene as hydrophilic comonomers. Thus, copolymers carrying a bis-crowned Malachite Green moiety with its content of 20−40 mol %, polymers **5**−**9** (see Chart 2), were obtained, and their data for the composition and molecular weight are summarized in Table 1. All of the bis-crowned Malachite Green polymers are soluble in halogenated alkanes such as 1,2-dichloroethane, but they are quite different in the solubility in THF and dimethyl sulfoxide (DMSO). Polymers **5**−**7** are soluble in THF, but polymers **8** and **9** are very hard to dissolve in it. Polymers **7** and **9** have only modest solubility in DMSO, and the others are insoluble in it.

Metal Ion Complexation. The metal ion complexing ability of the resulting polymers carrying a bis-crowned Malachite Green moiety toward alkali metal ions (Li^+, Na^+, K^+, and Cs^+) was evaluated by cation extraction

Table 1. Characteristics of Bis-Crowned Malachite Green Polymers with Various Comonomers

copolymer	x[a]	M_w	M_w/M_n
polymer **5a**	0.41	6.1×10^4	1.24
polymer **5b**	0.34	6.7×10^4	1.29
polymer **5c**	0.26	5.8×10^4	1.34
polymer **6**	0.41	1.2×10^5	2.67
polymer **7**	0.36	8.0×10^4	2.30
polymer **8**	0.30	5.2×10^4	1.68
polymer **9a**	0.30	8.0×10^4	1.27
polymer **9b**	0.17	9.7×10^4	1.24

[a] x: mole fraction of bis-crowned Malachite Green unit in copolymer.

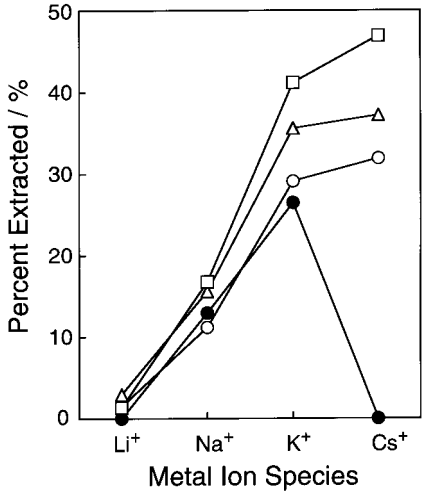

Figure 1. Alkali metal ion extraction by polymers carrying bis-crowned Malachite Green moiety (polymers **5a**, **5b**, and **5c**) and comparison with monomeric model **1**: (□) **5**a, (△) **5**b, (○) **5c**, (●) **1**.

with a 1,2-dichloroethane solution of the polymers from an alkali metal picrate aqueous solution. The results for bis-crowned Malachite Green copolymer with styrene, **5**, are summarized in Figure 1, together with those for the monomeric model of bis-crowned Malachite Green **1** for comparison. The metal ion complexing ability for polymers **5** is in the order $Cs^+ > K^+ > Na^+ > Li^+$ and that for the monomeric model **1** in the order $K^+ > Na^+ > Cs^+, Li^+$. The polymers are generally higher than the monomeric model **1** in the metal ion complexing ability, especially toward Cs^+. In general, 15-crown-5 derivatives tend to form 2:1 (crown ether ring/metal ion) sandwich-type complexes with metal ions that are slightly greater in size than the crown ether cavity. So, the bis(15-crown-5) derivative, bis-crowned Malachite Green **1**, is very easy to form sandwich-type K^+ complexes by cooperative action of two adjacent crown ether rings, that is, by a bis(crown ether) effect. This is the reason for the high affinity of **1** on the K^+ extraction. The higher affinity of bis-crowned Malachite Green polymers toward Cs^+ than K^+ is probably attributed to a kind of polymer effect, that is, a more sophisticated cooperative action of two or more crown ether rings at the polymer side chain on the metal ion complexation. In addition to the bis- and poly(crown ether) effects on metal ion complexation, the higher lipophilicity of bis-crowned Malachite Green polymers than that of the monomeric model **1** may augment the metal ion complexing ability of the polymers, which was evaluated by metal ion extraction from aqueous to organic phases. It is also of much interest to compare the metal ion complexing ability among the polymers of bis-crowned

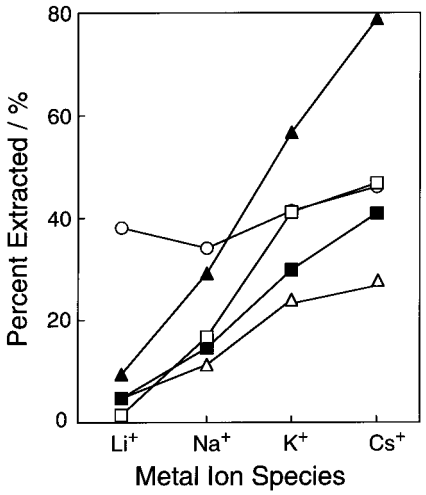

Figure 2. Comparison of polymers carrying bis-crowned Malachite Green with different comonomers (polymer **5a**, **6**, **7**, **8**, and **9a**) in alkali metal ion extraction: (□) **5a**, (■) **6**, (▲) **7**, (○) **8**, (△) **9a**.

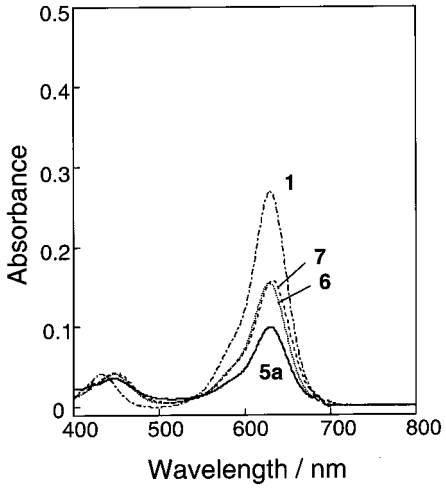

Figure 3. Absorption-spectral changes of bis-crowned Malachite Green polymers (**5a**, **6**, and **7**) and monomeric model **1** in THF/acetonitrile after UV irradiation for 1 min.

Malachite Green with different vinyl comonomers (Figure 2). The bis-crowned Malachite Green polymers resemble one another in the metal ion complexing ability. This means that there is hardly any significant difference in the metal ion complexing behavior among the bis-crowned Malachite Green polymers except polymer **8**. The polymer containing 4-hydroxymethylstyrene as the comonomer, **6**, possesses a little smaller metal ion complexing ability than polymers **5a** and **7**, probably due to some hydrophilicity of the hydroxymethyl moiety, which in turn suppresses the metal ion extraction from aqueous to organic phases. The polymer having methyl methacrylate as the comonomer, **9a**, also showed a comparatively low metal ion complexing ability. This is attributable to the poor solubility of **9a** in the solvent, which in turn decreases the number of the crown ether group contributing to the metal ion extraction. A significant difference was observed in the metal ion complexing ability between the polymer containing *N*,*N*-dimethylacrylamide as the comonomer, **8**, and the other polymers. For polymer **8**, the metal ion complexing ability toward Li^+ and Na^+ is greater than those for the other polymers, probably due to some contribution of the amide groups in the polymer side chain to the

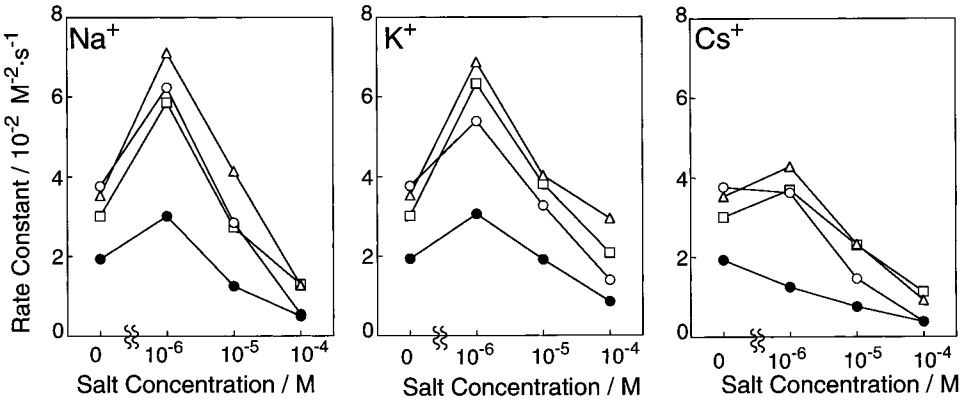

Figure 4. Dependence of metal ion concentrations upon thermal decoloration rate in systems of polymers **5a**, **5b**, and **5c** and monomeric model **1**: (□) **5a**, (△) **5b**, (○) **5c**, (●) **1** (1 M = 1 mol dm^{-3}).

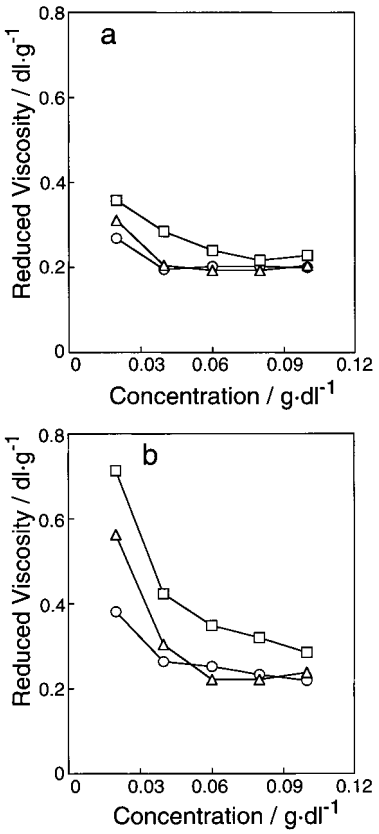

Figure 5. Viscosity measurements for THF/acetonitrile (50/50 vol %) solutions of bis-crowned Malachite Green polymers **5a**, **5b**, and **5c**: (a) under dark conditions, (b) after UV irradiation for 1 min. (□) **5a**, (△) **5b**, (○) **5c**.

complexation, especially of the higher charge density alkali metal ions, Li^+ and Na^+.

Photoisomerization Followed by Decoloration. In any of the polymers of bis-crowned Malachite Green, the photochromic moiety ionizes to its triphenylmethyl (or quinoid) cation and a cyanide anion by UV irradiation. The photoionization is apt to proceed in polar solvents, as anticipated. Since most of the polymers are soluble in THF, the photochromism of Malachite Green in the polymers was first studied in the solvent. It was, however, found that the photoionization is still hard to occur in THF. We, therefore, decided to use THF/acetonitrile (50/50 vol %) as a more polar solvent for the photochromism study, although this solvent system could not be applied in the polymers **8** and **9** due to their poor solubility.

Figure 3 shows typical UV-light-induced absorption-spectral changes of bis-crowned Malachite Green polymers and their monomeric model **1** in THF/acetonitrile solutions. After UV irradiation for 1 min, the spectra had a strong absorption at 625 nm that can be assigned to a quinoid cation. Obviously, the Malachite Green leuconitrile moiety undergoes photoionization in the solvent. Some a difference in the absorption-spectral changes suggests that photoionization in the polymers is suppressed more or less as compared with the corresponding monomeric model. Heating a solution of bis-crowned Malachite Green derivatives after UV irradiation decreased the absorption in the visible region. The thermal decoloration indicates that the quinoid cation and cyanide anion carry out recombination to yield an electrically neutral bis-crowned Malachite Green moiety in the polymers of bis-crowned Malachite Green.

The thermal decoloration was, therefore, followed for the quantitative photochromism comparison of bis-crowned Malachite Green derivatives in the absence and presence of metal ions. Figure 4 summarizes the rate constants for the second-order reaction of thermal decoloration for a THF/acetonitrile solution of bis-crowned Malachite Green polymers **5a**−**5c** and monomeric analogue **1**, in the presence of various concentrations of Na^+, K^+, and Cs^+. In both of the polymeric and monomeric systems, the presence of a small quantity of Na^+ accelerated the thermal decoloration reaction. That is to say, the metal ion complexation of the crown ether ring in the bis-crowned Malachite Green moiety promotes the thermal reaction back to the electrically neutral Malachite Green leuconitrile form owing to the electrostatic repulsion between the quinoid cation and a metal cation complexed by the crown ether rings. By contrast, further Na^+ addition to the solutions decreased the thermal decoloration rates. A large excess of Na^+ led to the increased polarity of a solvent employed, which in turn lowered the thermal reversion reaction to the electrically neutral form by stabilization of the ionic form, quinoid cation. The tendency for the metal ion addition effect on the thermal decoloration is quite similar in all of the bis-crowned Malachite Green derivatives. This is the case with the K^+ addition systems. A significant difference in the tendency for the metal ion addition effect was found between the bis-crowned Malachite Green polymers and the monomeric analogue in the system of Cs^+. In the tendency for the metal ion addition system of the polymers, the Cs^+ system still resembles the Na^+ and K^+ systems. It is

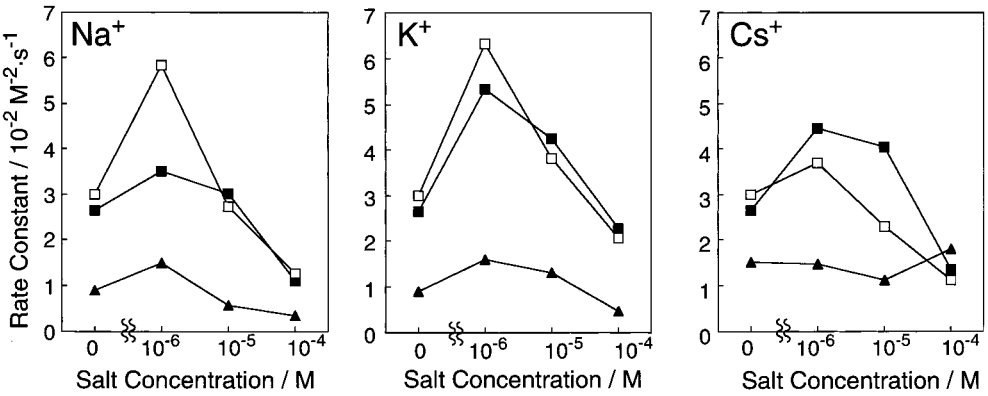

Figure 6. Comonomer effect on thermal decoloration rate for systems of polymers **5a**, **6**, and **7**: (□) **5a**, (■) **6**, (▲) **7**.

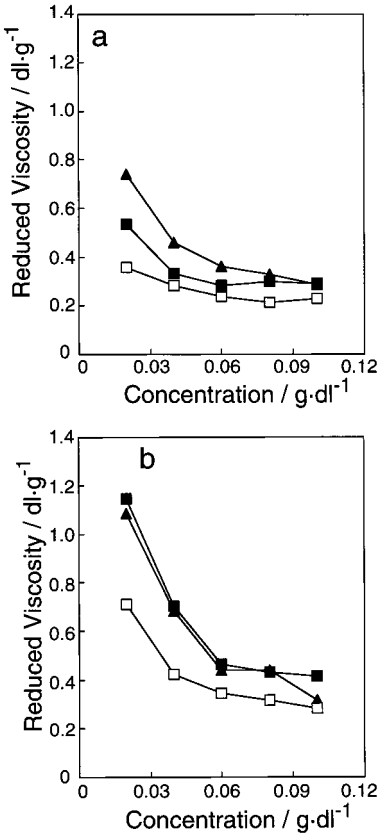

Figure 7. Comonomer effect on viscosity for THF/acetonitrile (50/50 vol %) solutions of bis-crowned Malachite Green polymers **5a**, **6**, and **7**: (a) under dark conditions; (b) after UV irradiation for 1 min. (□) **5a**, (■) **6**, (▲) **7**.

because the bis-crowned Malachite Green polymers can bind Cs^+ by the polymer effect as already mentioned above. On the contrary, the monomeric model **1** possesses such a poor complexing ability toward Cs^+ as seen in Figure 1. So, the Cs^+ addition to the solution of **1** augments the solvent polarity without any significant metal ion complexation, simply depressing the thermal reversion reaction due to the monotonic solvent polarity increase.

Another remarkable thing is a great difference in the thermal decoloration rate between the bis-crowned Malachite Green polymers and its monomeric model **1**. In any metal ion addition system, the bis-crowned Malachite Green systems are always greater in the thermal decoloration rate than the monomeric model. The high reaction rates in the thermal reversion reaction from the ionic form to electrically neutral one in the bis-crowned Malachite Green moiety must be related to the polymer rheology changes induced by intrapolymer electrostatic interaction among the ionic species, quinoid cation.[3] The polymers of bis-crowned Malachite Green **5a**, 5**b**, and **5c** are modestly soluble in THF/acetonitrile (50/50 vol %), and therefore the polymer chains are probably contracted in solution. The photoinduced ionization in the bis-crowned Malachite Green moiety of the polymers results in the cationic site formation in the polymer side chain. The resulting contracted polymer chain is apt to expand due to the intrapolymer electrostatic repulsion among the cationic sites. The photoinduced expansion of the polymer chain is evidenced by the measurements of reduced viscosity of the polymer solutions. Figure 5 shows that photoionization of polymer **5a**, **5b**, and **5c** solutions increases the viscosity of their solutions, based on the polymer chain expansion. Also, the higher content of bis-crowned Malachite Green moiety (a potential cationic site) brings about the more significant photoinduced viscosity change, that is, the more intense polymer chain expansion.

The kind of comonomers in the bis-crowned Malachite Green polymers affects their polymer rheology and thereby thermal decoloration of their Malachite Green moiety in solution. For instance, a comparison between polymers **5**a and **7** is of much interest (Figures 6 and 7). The bis-crowned Malachite Green polymer with styrene comonomer **5a** is not very different from the polymer with vinyl acetate comonomer **7** in the mole fraction of bis-crowned Malachite Green moiety and the molecular weight. Nevertheless, polymers **5a** and **7** are quite different in the thermal decoloration rate and reduced viscosity. The thermal reaction of the latter polymer is much slower than that for the former polymer, the rate constant of which is close to that for the monomeric model **1**. Polymer **5a** has a lower reduced viscosity than the polymer **7** under either dark or UV-irradiated conditions. Definitely, the polymer chain is more expanded in polymer **7** than in polymer **5a**, owing to the higher solubility of the former polymer than the latter one in THF/acetonitrile under dark conditions. Upon UV irradiation, the high solubility of polymer **7**, therefore, leads to the more intense expansion of its polymer chain than that for the less soluble polymer, **5a**, due to the intramolecular polymer chain repulsion induced by photoionization of its bis-crowned Malachite Green moiety. It is considered from the comparison in the reaction rate and viscosity that the less soluble polymer **5**a, the polymer chain of which is more contracted, experiences a higher polymer strain than the more soluble polymer **7** does on the polymer chain

expansion by photoionization of Malachite Green moiety. This polymer chain strain accelerates the thermal reversion reaction due to its alleviation. This is the reason the bis-crowned Malachite Green polymers, especially modestly soluble one such as polymers **5a, 5b**, and **5c** exhibit the enhanced thermal decoloration reaction as compared with the corresponding monomeric analogue.

In conclusion, the polymers carrying a bis-crowned Malachite Green moiety are very different from the corresponding monomeric analogue in the metal ion complexation and photochromism. The polymers undergo sophisticated metal ion complexation by a kind of polymer effect, that is, a cooperative action of their adjacent crown ether rings. The photochromism of the Malachite Green moiety can be affected dramatically by their polymer rheology under dark and UV-irradiated conditions.

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