

Complexation and fluorescence behavior of a copolymer bearing azacrown ether and anthracene moieties

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ABSTRACT

Copolymers bearing azacrown ether and anthracene moieties were synthesized using methacrylates of *N*-2-ethyl-azacrown ether or 9-hydroxymethylanthracene. Their fluorescence behaviors in the presence of alkali metal ions were measured in THF:H₂O = 10:1 solution. Maximum fluorescence intensities for copolymers bearing aza-12-crown-4, 15-crown-5 and 18-crown-6 were observed for with Na⁺, K⁺ and K⁺, respectively. The largest change in fluorescence behavior was observed for the copolymer bearing aza-18-crown-6 in the presence of K⁺. The magnitude of the increase in the fluorescence intensity was related to the content of the crown ether moiety. The time-dependent changes in the fluorescence spectra under photo-irradiation were also investigated.

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1. Introduction

Many fluorescent ionophores based on crown ethers have been reported to date [1–5], most of which are small molecules consisting of crown and fluorophore moieties. These ionophores were investigated as ON/OFF switching devices and fluorescent reagents for the determination of metal ions in the field of analytical chemistry. In particular, fused aromatic moieties, such as anthryl and pyrenyl groups, have been widely used in many fluoroionophores because the fluorescence spectra of these derivatives are highly responsive to their surroundings, including the electronic conditions of the neighboring heteroatoms and media [6,7]. For example, the fluorescence of an azacrown ether derivative bearing the anthracene moiety is quenched by photo-induced electron transfer (PET) from the nitrogen atom of the azacrown ether to the anthracene moiety. However, an azacrown ether cannot form a stable complex with an alkali metal ion in aqueous solution due to competition with hydration of the metal ion. Thus, fluorescent ionophores bearing crown ethers are generally not useful in aqueous solution for detecting metal ions.

The complexation behaviors of crown ether-based polymers with metal ions in aqueous solution have been investigated by examining their fluorescence spectral changes. There are three categories of fluorescence that involve complexation between a polymer and metal ions: (1) The metal ion, such as a lanthanide ion, bound to the crown ether polymer is photoluminescent [8]. (2)

The fluorescent dye competes with the metal ion for complexation with the crown ether polymer [9]. (3) The crown ether polymer has fluorophores or fluorescent parts whose fluorescence spectra change upon complexation of the crown ether moiety and the metal ion [10–12]. These studies have shown that crown ether polymers can form relatively stable complexes with metal ions in aqueous solution. The crown ether polymer, which forms micelles, can form a stable complex with K⁺ even in aqueous solution [12].

In this study, water soluble polymers bearing crown ether and anthracene moieties were synthesized, and their fluorescence spectral changes were examined in aqueous solution in the absence and presence of alkali metal ions. The time-dependent changes in the fluorescence intensity of the polymers were investigated under photo-irradiation conditions.

2. Experimental

2.1. Materials and equipment

All reactions were carried out under an atmosphere of argon unless otherwise noted. Anhydrous THF was purchased from Kanto Chemicals and used without further purification. Perchlorates of lithium, sodium, potassium and cesium were of analytical grade. Infrared spectra were recorded on a FT-SP FT/IR spectrometer (JASCO). UV–vis spectra were measured with a UV–VIS V-530 spectrophotometer (JASCO). Fluorescence spectra were recorded on a FP-6200 (JASCO). Elemental analyses were performed using a JM10 MICRO CORDER (J-Science Laboratory). A 505T (JASCO) tem-

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perature controller was used. MALDI-TOF and ESI mass spectra were obtained using a AXIMA-TFR (SHIMADZU) and Finnigan LCQ™ Deca, respectively. NMR spectra were measured with a JNM-ECA 400 FT-NMR spectrometer (JEOL) using CDCl₃ or DMSO-*d*₆ solution containing tetramethylsilane as an internal standard. Gas chromatograms were recorded on a CR5A Chromatopac (SHIMADZU) and GC-14A gas chromatograph (SHIMADZU). Silica gel (100 mesh) was used for column chromatography.

2.2. Preparation of methacrylates of azacrown ethers

2.2.1. General procedure

To the CH₂Cl₂ solution of *N*-(2-hydroxyethyl)azacrown ether [13], 4-(*N,N*-dimethylamino)pyridine and triethylamine in a 50 mL two-necked flask equipped with a dropping funnel, methacryloyl chloride in a dry CH₂Cl₂ solution was added dropwise at 0 °C over 30 min, and the mixture was stirred for 4 h maintained at the same temperature. After the reaction, the solvent was evaporated *in vacuo* at ca. 30 °C. The methacrylate of the azacrown ether was isolated with silica gel column chromatography using a mixed solvent of chloroform and methanol (10/1) as the eluent.

2.2.2. 10-(2-Methacryloyloxyethyl)-1,4,7-trioxa-10-azacyclododecane or aza-12-crown-4- methacrylate

N-(2-Hydroxyethyl)aza-12-crown-4 (1.1 g, 5 mmol), 4-(*N,N*-dimethylamino)pyridine (0.06 g, 0.5 mmol), triethylamine (0.76 g, 7.5 mmol) and methacryloyl chloride (0.52 g, 5 mmol) were used, and 0.263 g of the desired compound was obtained (yield: 24%). ¹H NMR (400 MHz, CDCl₃): δ 6.10 (s, 1H), 5.56 (s, 1H), 4.26 (t, *J* = 6.0 Hz, 2H), 2.87 (t, *J* = 6.0 Hz, 2H), 3.63–3.68 (m, 12H), 2.81 (t, *J* = 4.8 Hz, 4H), 1.94 (s, 3H) ppm.

2.2.3. 13-(2-Methacryloyloxyethyl)-1,4,7,10-tetraoxa-13-azacyclotetradecane or aza-15-crown-5-methacrylate

N-(2-Hydroxyethyl)aza-15-crown-5 (2.63 g, 10 mmol), 4-(*N,N*-dimethylamino)pyridine (0.12 g, 1.0 mmol), triethylamine 2.02 g, 20 mmol) and methacryloyl chloride (2.08 g, 20 mmol) were used, and 0.66 g of the desired compound was obtained (yield: 20%). ¹H NMR (400 MHz, CDCl₃): δ 6.09 (s, 1H), 5.55 (s, 1H), 3.64 (m, 18H), 2.89–2.76 (m, 6H), 1.94 (s, 3H) ppm.

2.2.4. 16-(2-Methacryloyloxyethyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane or aza-18-crown-6-methacrylate

N-(2-Hydroxyethyl)aza-18-crown-6 (0.46 g, 2.5 mmol), 4-(*N,N*-dimethylamino)pyridine (0.03 g, 0.25 mmol), triethylamine (0.252 g, 2.5 mmol) and methacryloyl chloride (0.395 g, 3.8 mmol) were used, and 0.19 g of the desired compound was obtained (yield: 20%). ¹H NMR (400 MHz, CDCl₃): δ 6.10 (s, 1H), 5.55 (s, 1H), 4.28 (t, *J* = 12.0 Hz, 2H), 3.75–3.57 (m, 20H), 2.88–2.80 (m, 6H), 1.96 (t, *J* = 8.0 Hz, 3H) ppm.

2.3. Preparation of 9-anthrylmethyl methacrylate

To the CH₂Cl₂ solution of 9-hydroxymethylanthracene (0.416 g, 2 mmol), 4-(*N,N*-dimethylamino)pyridine (0.024 g, 0.2 mmol) and triethylamine (0.404 g, 4 mmol) in a 100 mL two-necked flask equipped with a dropping funnel, methacryloyl chloride (0.416 g, 4 mmol) in 5 mL of dry CH₂Cl₂ solution was added dropwise at 0 °C for 30 min, and the mixture was stirred for 4 h and maintained at the same temperature. After the reaction, the solvent was evaporated *in vacuo* at ca. 30 °C. The 9-anthrylmethyl methacrylate was isolated with silica gel column chromatography using chloroform as the eluent (0.441 g, yield: 80%). ¹H NMR (400 MHz, CDCl₃): δ 8.50 (s, 1H), 8.36 (d, 2H), 7.98 (d, 2H), 7.57 (t, 2H), 7.49 (t, 2H), 6.22 (t, *J* = 6.0 Hz, 2H), 6.05 (s, 1H), 5.50 (s, 1H), 1.91 (s, 3H) ppm.

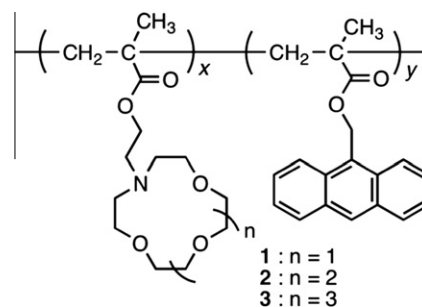


Fig. 1. Copolymers employed in this study.

2.4. Polymerization of the azacrown ether methacrylate and 9-anthrylmethyl methacrylate

2.4.1. General procedure

Copolymerization of the azacrown ether methacrylate and 9-anthrylmethyl methacrylate, using AIBN as a radical initiator, was carried out in THF in a sealed glass tube at 60 °C under vacuum conditions for 24 h in a shaking incubator. The polymerization was monitored by ¹H NMR. After the reaction, the mixture became a yellowish gel, and this gel was poured into diethyl ether to purify the polymer by reprecipitation. The composition of the obtained copolymer was estimated by ¹H NMR and elemental analysis. The viscosity of the copolymer dissolved in THF was measured using Ostwald's viscometer at 25 °C.

2.4.2. Copolymer of aza-12-crown-4-methacrylate and 9-anthrylmethyl methacrylate (1:1)*

Aza-12-crown-4-methacrylate (0.64 g, 2.2 mmol), 9-anthrylmethyl methacrylate (0.61 g, 2.2 mmol), AIBN (3.5 mg, 0.021 mmol) and 2.0 mL of THF were used, and conversion to the polymer yielded 0.152 g (12%). ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m), 4.04 (brs), 3.65 (brs), 1.85 (brs), 1.02–0.84 (m) ppm. [η] = 1.011. Elemental analysis data for the copolymer (1.3:1): Calc'd.: C, 60.63; H, 6.55; N, 2.37. Found: C, 60.69; H, 6.80; N, 2.38.

((1:1)* means that the initial mixing ratio of azacrown-methacrylate and anthrylmethyl methacrylate is 1:1).

2.4.3. Copolymer of aza-12-crown-4-methacrylate and 9-anthrylmethyl methacrylate (5:1)*

Aza-12-crown-4-methacrylate (0.64 g, 2.2 mmol), 9-anthrylmethyl methacrylate (0.12 g, 0.4 mmol), AIBN (2.1 mg, 0.013 mmol)

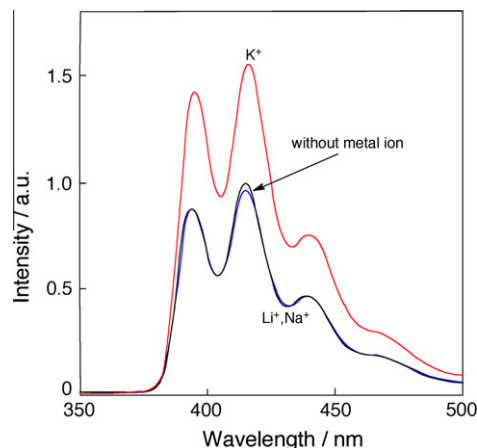


Fig. 2. Fluorescence spectral changes of copolymer 3 bearing an aza-18-crown-6 moiety. The vertical axis units are normalized against the maximum fluorescence intensity in the absence of metal ions. [MClO₄] = 1.0 × 10⁻³ mol dm⁻³ (M = Li, Na, K) and [Anthracene unit] = 1.0 × 10⁻⁵ mol dm⁻³ in THF:H₂O = 10:1; λ_{ex} = 266 nm.

and 2.0 mL of THF were used, and conversion to the polymer yielded 0.308 g (40%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.02–7.51 (m), 3.69 (brs), 1.82 (brs), 1.54 (brs), 0.89 (m) ppm. $[\eta] = 0.401$. Elemental analysis data for the copolymer (4:1): Calc'd.: C, 55.31; H, 7.15; N, 3.41. Found: C, 55.33; H, 6.99; N, 3.41.

2.4.4. Copolymer of aza-12-crown-4-methacrylate and 9-anthrylmethyl methacrylate (10:1)*

Aza-12-crown-4-methacrylate (0.64 g, 2.2 mmol), 9-anthrylmethyl methacrylate (0.06 g, 0.2 mmol), AIBN (1.9 mg, 0.011 mmol) and 3.0 mL of THF were used, and conversion to the polymer yielded 0.264 g (38%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.02–7.51 (m), 3.81–3.64 (brs), 2.85 (brs), 1.82 (brs), 0.89 (m) ppm. $[\eta] = 0.348$. Elemental analysis data for the copolymer (5.9:1): Calc'd.: C, 53.93; H, 7.25; N, 3.62. Found: C, 53.97; H, 7.26; N, 3.62.

2.4.5. Copolymer of aza-15-crown-5-methacrylate and 9-anthrylmethyl methacrylate (1:1)*

Aza-15-crown-5-methacrylate (0.27 g, 0.81 mmol), 9-anthrylmethyl methacrylate (0.225 g, 0.81 mmol), AIBN (1.6 mg, 0.0095 mmol) and 3.0 mL of THF were used, and conversion to the polymer yielded 0.045 g (9%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.38–7.26 (m), 3.65 (brs), 2.86 (brs), 1.85 (brs) ppm. Elemental analysis data for the copolymer (1.1:1): Calc'd.: C, 32.27; H, 3.28; N, 0.90. Found: C, 32.33; H, 3.78; N, 0.90.

2.4.6. Copolymer of aza-15-crown-5-methacrylate and 9-anthrylmethyl methacrylate (5:1)*

Aza-15-crown-5-methacrylate (0.27 g, 0.81 mmol), 9-anthrylmethyl methacrylate (0.045 g, 0.16 mmol), AIBN (1.6 mg, 0.0095 mmol) and 3.0 mL of THF were used, and conversion to the polymer yielded 0.030 g (10%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.10 (m), 3.65 (brs), 2.83 (brs), 1.88 (brs) ppm. Elemental analysis data for the copolymer (1.8:1): Calc'd.: C, 53.28; H, 6.19; N, 2.17. Found: C, 53.08; H, 8.10; N, 2.17.

2.4.7. Copolymer of aza-15-crown-5-methacrylate and 9-anthrylmethyl methacrylate (10:1)*

Aza-15-crown-5-methacrylate (0.27 g, 0.81 mmol), 9-anthrylmethyl methacrylate (0.023 g, 0.01 mmol), AIBN (1.6 mg, 0.0095 mmol) and 3.0 mL of THF were used, and conversion to the polymer yielded 0.030 g (10%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.10 (m), 3.65 (brs), 2.83 (brs), 1.88 (brs) ppm. Elemental analysis data for the copolymer (5.2:1): Calc'd.: C, 57.77; H, 7.79; N, 3.32. Found: C, 57.76; H, 8.45; N, 3.32.

2.4.8. Copolymer of aza-18-crown-6-methacrylate and 9-anthrylmethyl methacrylate (1:1)*

Aza-18-crown-6-methacrylate (1.18 g, 3.56 mmol), 9-anthrylmethyl methacrylate (0.98 g, 3.56 mmol), AIBN (5.7 mg, 0.035 mmol) and 4.0 mL of THF were used, and conversion to the polymer yielded 0.246 g (11%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.50–7.50 (m), 3.64 (brs), 2.83 (brs), 1.80 (brs), 1.00–0.83 (m) ppm. $[\eta] = 0.599$. Elemental analysis data for the copolymer (1.3:1): Calc'd.: C, 65.67; H, 7.26; N, 2.04. Found: C, 65.68; H, 7.14; N, 2.04.

2.4.9. Copolymer of aza-18-crown-6-methacrylate and 9-anthrylmethyl methacrylate (5:1)*

Aza-18-crown-6-methacrylate (1.18 g, 3.56 mmol), 9-anthrylmethyl methacrylate (0.20 g, 0.71 mmol), AIBN (3.4 mg, 0.021 mmol) and 2.0 mL of THF were used, and conversion to the polymer yielded 0.419 g (30%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.52 (m), 3.73 (brs), 2.84 (brs), 1.01 (brs) ppm. $[\eta] = 0.384$. Elemental analysis data for the copolymer (7.2:1): Calc'd.: C, 55.34; H, 7.75; N, 2.99. Found: C, 55.35; H, 8.16; N, 2.99.

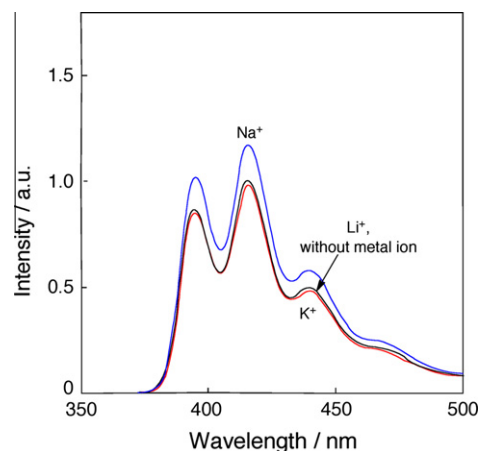


Fig. 3. Fluorescence spectral changes of copolymer **1** bearing an aza-12-crown-4 moiety. $[\text{MClO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ($M = \text{Li, Na, K}$) and $[\text{Anthracene unit}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ in $\text{THF:H}_2\text{O} = 10:1$; $\lambda_{\text{ex}} = 266 \text{ nm}$.

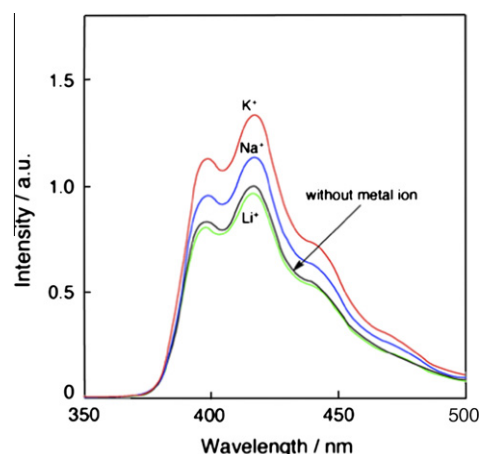


Fig. 4. Fluorescence spectral changes of copolymer **2** bearing an aza-15-crown-5 moiety. $[\text{MClO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ($M = \text{Li, Na, K}$) and $[\text{Anthracene unit}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ in $\text{THF:H}_2\text{O} = 10:1$; $\lambda_{\text{ex}} = 266 \text{ nm}$.

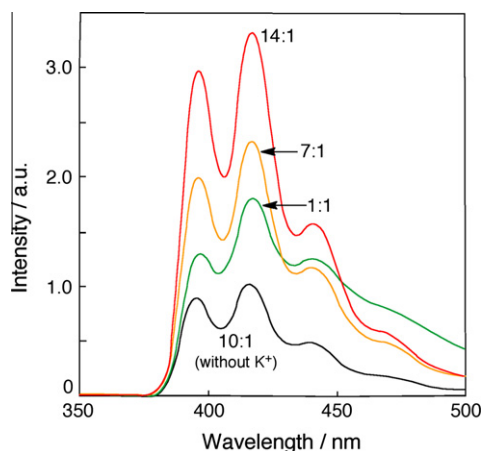


Fig. 5. Fluorescence spectral changes for aza-18-crown-6 copolymer **3** with different compositions of crown ether unit. The vertical axis units are normalized against the maximum fluorescence intensity of the copolymer in which the composition is crown ether:anthracene = 10:1 in the absence of K^+ . $[\text{KClO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{Anthracene unit}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ in $\text{THF:H}_2\text{O} = 10:1$; $\lambda_{\text{ex}} = 266 \text{ nm}$.

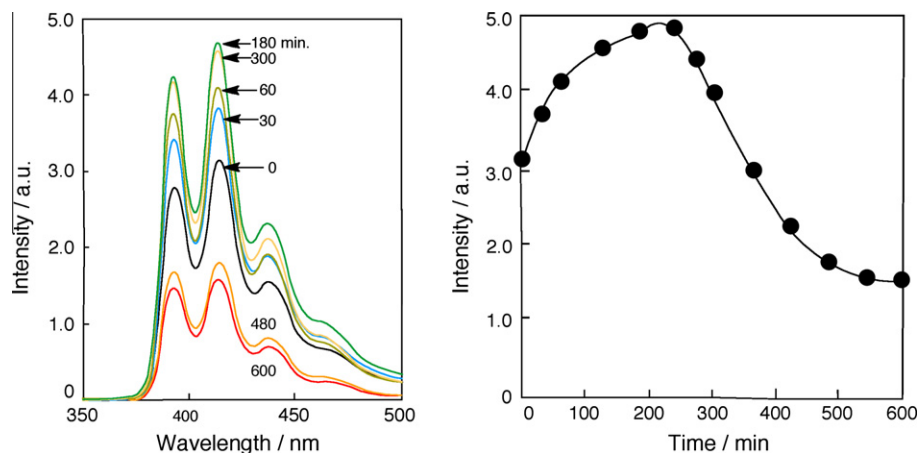


Fig. 6. Time-dependent changes in the fluorescence spectra of monoaza-12-crown-4 copolymer **1** under photo-irradiation conditions at 266 nm. Copolymer of aza-12-crown-4:anthracene (5:1); [Anthracene unit] = 1.0×10^{-5} M; $\lambda_{\text{ex}} = 266$ nm.

2.4.10. Copolymer of aza-18-crown-6-methacrylate and 9-anthrylmethyl methacrylate (10:1)*

Aza-18-crown-6-methacrylate (1.18 g, 3.56 mmol), 9-anthrylmethyl methacrylate (0.098 g, 0.35 mmol), AIBN (3.1 mg, 0.02 mmol) and 2.0 mL of THF were used, and conversion to the polymer yielded 0.180 g (14%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.52 (m), 3.67 (brs), 2.84 (brs), 2.16 (brs) ppm. $[\eta] = 0.573$. Elemental analysis data for the copolymer (13.7:1): Calc'd.: C, 59.28; H, 8.65; N, 3.48. Found: C, 58.76; H, 8.18; N, 3.75.

2.5. Absorption and fluorescence spectral measurements

The solvent employed in this study was a solution of THF and H_2O (10:1 v/v). The copolymer solution concentration was prepared against the concentration of the anthracene unit of the copolymer. Unless otherwise stated, the concentration of copolymer, i.e., anthracene unit, in solution was 1.0×10^{-5} mol dm^{-3} . The absorption and fluorescence spectra were measured at 25 ± 0.1 °C immediately after the copolymer solutions were prepared under dark conditions. For determination of the time-dependent fluorescence spectral changes, the fluorescence spectra were measured at 30 min intervals under photo-irradiation conditions at 266 nm.

3. Results and discussion

3.1. Synthesis

N-(2-Hydroxyethyl)azacrown ethers, e.g., aza-12-crown-4, 15-crown-5 and 18-crown-6 derivatives, were synthesized via the reaction of 2-aminoethanol and the corresponding oligoethylene-glycol diiodides in the presence of Na_2CO_3 as a base in CH_3CN [13]. The reaction of *N*-(2-hydroxyethyl)azacrown ether and methacryloyl chloride using triethylamine as a base in CH_2Cl_2 yielded the methacrylate of the *N*-2-ethylazacrown ether, which is referred to as the azacrown-methacrylate. 9-Anthrylmethyl methacrylate was synthesized in a similar manner. Copolymers **1–3** bearing azacrown ether and anthracene moieties were obtained via the radical reaction of the azacrown-methacrylate and anthrylmethyl methacrylate, usually in a ratio of 10:1; AIBN was used as the initiator, and the reaction was carried out at 60 °C for 24 h in a small amount of THF (Fig. 1). Compositions of the crown ether:anthracene in the obtained copolymers were determined by elemental analysis to be 7:1, 6:1, and 14:1 for the copolymers obtained with aza-12-crown-4, 15-crown-5, and 18-crown-6, respectively. These results indicate that the composition of the copolymer obtained from the copolymerization of azacrown-methacrylates and 9-anthrylmethyl methacrylate was independent of the size of the crown ether.

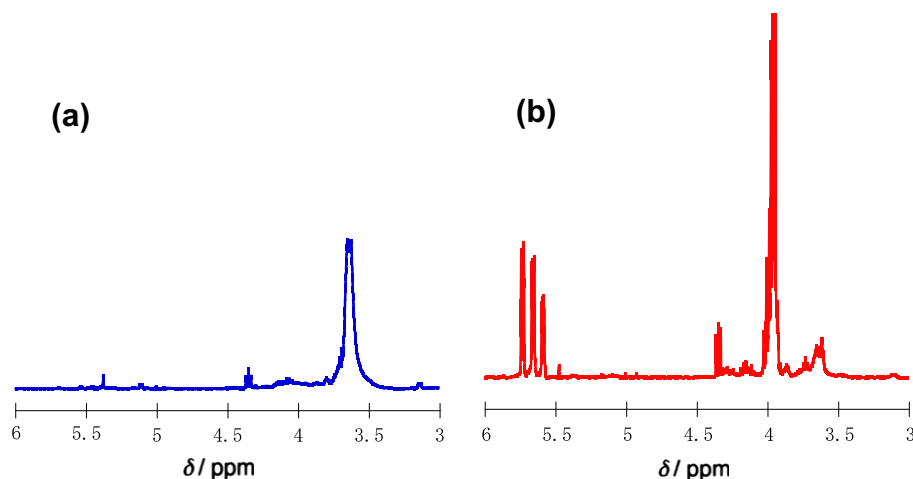


Fig. 7. $^1\text{H NMR}$ spectra of aza-12-crown-4 copolymer **1** (a) before and (b) after photo-irradiation for 24 h.

3.2. Fluorescence spectra in the presence of metal ions

The fluorescence spectra of the copolymers were measured in THF:H₂O = 10:1 solutions at 25 °C. In the presence of alkali metal ions, copolymer **3** bearing an aza-18-crown-6 moiety exhibited typical metal ion-selective spectral changes for K⁺ ions, which is expected because aza-18-crown-6 is known to form highly stable complexes with K⁺ (Fig. 2) [14]. When the aza-18-crown-6 moiety of the copolymer forms a stable 1:1 complex with K⁺, the nitrogen atom of the azacrown ether strongly interacts with the metal ion even in THF solution containing ca. 10% H₂O, and photo-induced electron transfer (PET) from the nitrogen atom to the anthracene moiety is suppressed, which increases the fluorescence spectral intensity [1–3].

Conversely, aza-12-crown-4 copolymer **1** and aza-15-crown-5 copolymer **2** showed the greatest increase in fluorescence intensity for Na⁺ and K⁺, respectively (Figs. 3 and 4). The composition of the complexes should be azacrown ether:metal ion = 2:1, i.e., a sandwich type complex because the radii of Na⁺ and K⁺ metal ions are larger in size than the cavities of aza-12-crown-4 and 15-crown-5, respectively. As shown in Fig. 5, the magnitude of the fluorescence spectral change of copolymer **3** in the presence of K⁺ was dependent on the number of azacrown ether moieties. As the number of azacrown ether moieties in the copolymer increases, PET occurrence also increases. Thus, if the number of azacrown ether moieties in the copolymer increases, PET from the nitrogen atom on the azacrown ether unit to the anthracene unit is more strongly interrupted when most of the azacrown ether units are complexed to metal ions.

3.3. Time-dependent fluorescence spectral changes

In the absence of metal ions, the fluorescence intensity of the copolymers under UV light irradiation at $\lambda = 266$ nm, which is an excitation wavelength for anthracene, initially increased up to ~200 min, but the intensity then decreased gradually (Fig. 6); in addition, the solution gelled slightly. ¹H NMR spectra of the copolymers were acquired before and after photo-irradiation (Fig. 7). Peaks between 5.5 and 6.0 ppm appeared in the ¹H NMR spectra after photo-irradiation, indicating that two neighboring anthracene units at the 9 and 10 positions formed an anthracene dimer. The time-dependent changes in fluorescence intensity showed that a structural change of the copolymer, such as expansion, would initially occur as soon as the copolymer was immersed in solution. The anthracene unit would subsequently form a dimer under photo-irradiation due to the orientation of neighboring anthracene units that promotes hydrophobic and π - π interactions

in solution. Anthracene is known to be dimerized by photo-irradiation at ca. 350 nm, and the dimer is decomposed by photo-irradiation at 254 nm [15,16]. In this study, however, light at 266 nm was used for irradiation of the copolymer, and the dimerization of anthracene was achieved immediately. This different behavior may occur under conditions in which the polymers have different structures and/or are in different media [17,18]. In the presence of metal ions, the dimerization rate of the copolymers was dependent on the kind of metal ion added. However, the behavior was not reproducible, so further studies are in progress.

4. Conclusion

Copolymers bearing anthracene and aza-12-crown-4, 15-crown-5 and 18-crown-6 moieties complex most favorably with Na⁺, K⁺ and K⁺ ions, respectively, in THF:H₂O (10:1) solution. In particular, the aza-18-crown-6 copolymer **3** recognized K⁺ selectively, exhibiting a large change in fluorescence in the presence of this metal ion. These results show that crown ether polymers are candidates for fluorescent dyes to detect alkali metal ions in aqueous solution.

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