Cation-Sensitive Fluorescence of Polymers Bearing Crowned Acetophenone Moieties

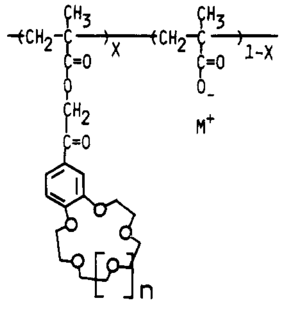
MASAMITSU SHIRAI,* SHINICHI ISHIMARU, AND MASAHIRO TSUNOOKA

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

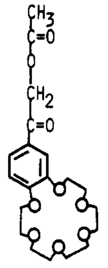
Received August 6, 1990

Introduction

The absorption spectrum of chromogenic crown ethers, which are molecules bearing chromophoric units and crown ether units, changes remarkably in response to alkali and alkaline earth metal cations.[1] Since fluorimetry can, in principle, be more sensitive than absorption photometry, it is of importance for chemical trace analysis.[2] Crown ethers, monoaza crown ethers, and cryptands having fluorescent moieties have been synthesized, and the effect of the binding of alkali and alkaline earth metal cations on the emission properties of the ionophores has been studied.[3-8] Recently, we reported that the emission of crowned acetophenones changes in response to alkali and alkaline earth metal cations.[9] In this paper we report the effect of alkali metal cations on the fluorescence properties of polyelectrolytes bearing crowned acetophenone moieties as fluoroionophores. Since the COO⁻ groups in the polymer chain increase the concentration of cations close to the polymer-bound crown ethers, the sensitivity of the change in the fluorescence intensities toward cations would be enhanced compared to that of the corresponding model compound.



P15: n=1, X=0.049
P18: n=2, X=0.049
P21: n=3, X=0.048



4

Experimental Section

4′-(Bromoacetyl)benzo-15-crown-5 (1). Bromine (1.03 g) in $CHCl_3$ (5 mL) was added stepwise to a solution of 4′-acetylbenzo-15-crown-5[10] (2.0 g) in $CHCl_3$ (15 mL) during 1 h with stirring at room temperature. The reaction was continued for 3 h. The reaction mixture was washed with 10% $NaHCO_3$ and water. After the mixture was dried with $MgSO_4$, the chloroform was removed, and the residual solid was recrystallized from a mixture of ethyl acetate and heptane (1:4 (v/v)): yield 11.0%; mp 80–84 °C. 1 has the following properties: ^1H NMR ($CDCl_3$) δ 6.8–7.7 (m, 3 H, aryl), 4.4 (s, 2 H, $BrCH_2$), 3.6–4.3 (m, 16 H, CH_2); IR ($CHCl_3$) ν 1670, 1600, 1180 cm^{-1}. Anal. Calcd for $C_{16}H_{21}BrO_6$: C, 49.36; H, 5.44. Found: C, 49.54; H, 5.58.

4′-(Bromoacetyl)benzo-18-crown-6 (2). 2 was prepared from the bromination of 4′-acetylbenzo-18-crown-6[10] by a procedure similar to that described for 1: yield 56.8%; mp 95–98 °C; ^1H NMR ($CDCl_3$) δ 6.9–7.6 (m, 3 H, aryl), 4.4 (s, 2 H, $BrCH_2$), 3.6–4.3 (m, 20 H, CH_2). Anal. Calcd for $C_{18}H_{25}BrO_7$: C, 49.90; H, 5.82. Found: C, 49.77; H, 5.91.

4′-(Bromoacetyl)benzo-21-crown-7 (3). 3 was prepared from the bromination of 4′-acetylbenzo-21-crown-7[9] by a procedure similar to that described for 1: yield 40.8%; mp 70–75 °C; ^1H NMR ($CDCl_3$) δ 6.9–7.6 (m, 3 H, aryl), 4.4 (s, 2 H, $BrCH_2$), 3.6–4.3 (m, 24 H, CH_2). Anal. Calcd for $C_{20}H_{29}BrO_8$: C, 50.33; H, 6.12. Found: C, 51.08; H, 6.32.

4′-(Acetoxyacetyl)benzo-18-crown-6 (4). Potassium acetate (0.76 g) in ethanol (5 mL) was added stepwise to a solution of 2 (3.3 g) in ethanol (20 mL) at 30 °C. The reaction was continued for 1.5 h at 70 °C. After the separation of salt by filtration, the ethanol was removed, and the residual solid was dissolved in $CHCl_3$ and washed with water. After the mixture was dried with $MgSO_4$, the chloroform was removed, and the residual solid was recrystallized from a mixed solvent of ethyl acetate and heptane (1:4 (v/v)): yield 23%; mp 91–93 °C. ^1H NMR ($CDCl_3$) δ 6.9–7.5 (m, 3 H, aryl), 5.3 (s, 2 H, $COCH_2O$), 3.7–4.2 (m, 20 H, CH_2). Anal. Calcd for $C_{20}H_{28}O_9$: C, 58.25; H, 6.84. Found: C, 57.79; H, 6.87.

P15 was prepared by the reaction of poly(methacrylic acid) (PMAA) with 1. The viscosity-average molecular weight of PMAA was 3.1×10^5. 1,8-Diazabicyclo[5.4.0]undec-7-ene (44.1 mg) was added stepwise to a dimethyl sulfoxide (DMSO) solution (12 mL) containing PMAA (0.50 g) and 1 (0.11 g) at room temperature. The reaction was continued for 3 h at room temperature. The reaction mixture was poured into a large excess of ether. The precipitated polymer was purified by dissolving in DMSO and precipitating with ether. The polymer neutralized with LiOH was dialyzed against water. The dialyzed solution was acidified with dilute HCl and dialyzed for 3 days. After removal of the water, P15 was obtained. P18 and P21 were prepared by the same procedure. The fractions of crown ether units in the polymers were determined from their absorbance at 277 nm ($\epsilon = 1.14 \times 10^3$ L/(mol cm)) in a mixture of methanol and water (1:1 (v/v)) at room temperature. The polymers neutralized with LiOH were used for the measurements of the emission spectrum. The emission spectra were measured in a mixture of methanol and water at 30 °C with a Shimadzu RF-500 spectrofluorophotometer. The excitation and emission slit widths were 3 and 10 nm, respectively. The wavelength of the excitation light was 330 nm. The quantum yields of fluorescence (Φ) were determined by comparison of the intensities of the fluorescence spectra of the polymers with that of quinine sulfate ($\Phi = 0.55$).[11]

Results and Discussion

The polymers showed an absorption maximum at 230 nm and shoulder peaks at 277 and 306 nm in a mixed solvent of methanol and water (9:1 (v/v)). The ring size of the crown ether moieties did not significantly affect the absorption spectra. On addition of alkali metal chlorides, the absorption peaks of the polymers shifted slightly to shorter wavelength (2–3 nm). The magnitude of the peak shifts was consistent with the order of the cation-binding ability of benzocrown ethers of corresponding ring size.[12] The absorption peaks of benzocrown ethers are known to shift to shorter wavelength when alkali metal cations are bound to the crown ether cavities.[13] However, the shift of the absorption peak is too small to use as a means of detecting cations.

On excitation with 330-nm light, the polymers showed fluorescence at 410 nm in a mixed solvent of methanol and water (9:1 (v/v)) at 30 °C. The wavelength of the fluorescence peak did not depend upon the ring size of the crown ether moieties. When the emission at 410 nm was monitored, λ_{max} of the excitation spectrum was observed at 330 nm for all polymers. When the water content of the mixed solvent of methanol and water increased, λ_{max} of the excitation spectrum shifted to shorter wavelength, suggesting that the fluorescence at 410 nm arose from an n–π^* excitation of the chromophore. The fluorescence quantum yields (Φ_0) of P15, P18, and P21 were 0.0045, 0.0058, and 0.0058, respectively, in a mixed solvent of methanol and water (9:1 (v/v)) at 30 °C. The Φ_0 values were smaller than those of crowned fluorophores such as dibenzo-18-crown-6[5] or anthraceno cryptands.[6] When the

0024-9297/91/2224-1690$02.50/0

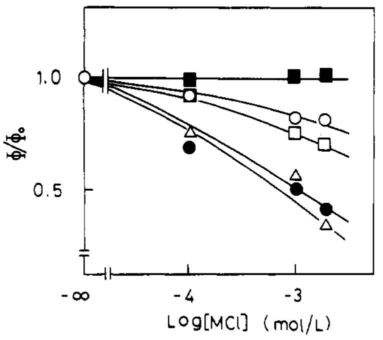


Figure 1. Relationship between Φ/Φ_0 and alkali metal chlorides added. [Crown unit] = 1.0×10^{-4} mol/L. Salt: (■) LiCl; (○) NaCl; (●) KCl; (△) RbCl; (□) CsCl.

volume fraction of water of the mixed solvent increased from 5% to 100%, the Φ_0 values decreased by a factor of 0.44. Figure 1 shows the Φ/Φ_0 ratio for P15 on addition of alkali metal chlorides in the mixed solvent at 30 °C, where Φ and Φ_0 are the fluorescence quantum yields in the presence and absence of alkali metal chlorides, respectively. The Φ/Φ_0 values decreased with increasing alkali metal chlorides in the order LiCl > NaCl > CsCl > RbCl ≈ KCl, which was consistent with the reverse order of the cation-binding ability of polymers bearing benzo-15-crown-5 units in their side chain.[10]

The decrease in the fluorescence intensity of the polymers with cation-binding ability can be explained as follows: Acetophenone is known to be nonfluorescent because of the high efficiency of the intersystem crossing from the $n-\pi^*$ singlet to the $\pi-\pi^*$ triplet.[14] However, introduction of an electron-donating substituent such as an alkoxy group in the phenyl ring of acetophenone reduces the $n-\pi^*$ character of the singlet state of the acetophenone derivatives and it diminishes the rate of the intersystem crossing efficiency from the $n-\pi^*$ singlet to the $\pi-\pi^*$ triplet.[14] Therefore a fluorescence appears. Since the positive charge in the crown ether cavity by the cation binding can reduce the electron-donating ability of the crown ether moieties as a substituent of the acetophenone moieties, the intersystem crossing efficiency can be enhanced by the increase in the $n-\pi^*$ nature of the singlet state of the crowned acetophenone, and hence the fluorescence decreases. For the binding of Cs^+ and perhaps Rb^+, the increase in the efficiency of the intersystem crossing by the heavy-atom effect may decrease the fluorescence of the polymers as suggested by Sousa et al.[3] The contraction of the polymer coil with increasing ionic strength of the solutions on addition of alkali metal salts does not change the Φ/Φ_0 values as shown by the fact that LiCl, which cannot be bound to the crown ether units, does not change the Φ/Φ_0 values.

Figure 2 shows the Φ/Φ_0 values of P15, P18, P21, and 4 in the presence of alkali metal chlorides ([crown unit]/[MCl] = 20). The Φ/Φ_0 values for P15, P18, and P21 decreased in the orders LiCl > NaCl > CsCl > KCl > RbCl, LiCl > NaCl > RbCl ≈ CsCl > KCl, and LiCl ≈ NaCl > KCl > RbCl ≈ CsCl, respectively. The orders were roughly consistent with the reverse order of the cation-binding ability of polymers bearing benzocrown ether units with corresponding ring size.[10,15] Similar results on the cation-controlled fluorescence were obtained for poly(acrylic acid) bearing crowned acetophenone moieties. The Φ/Φ_0 values for 4 decreased in the order LiCl ≈ NaCl ≈ CsCl > KCl > RbCl, which is different from that for P18. The Φ_0 value for 4 was one-third that for P18. The Φ/Φ_0 values are determined by the total number of the cation–crown complexes formed in the system. The degree of the complex formation depends on both the cation concentration in the neighborhood of the polymer-bound crown ether units and the cation-binding ability of the crown ether units. The neighboring COO^- groups in the polymer chain play an important role in increasing the concentration of cations close to the polymer chain. This concentration effect for cations seems to be more effective for less solvated cations such as Rb^+ and Cs^+. Higher Φ/Φ_0 values for compound 4 than those for P18 are due to the absence of the concentration effect for cations.

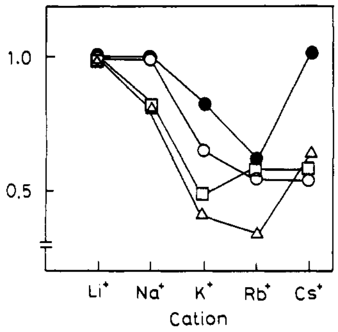


Figure 2. Φ/Φ_0 values of (△) P15, (□) P18, (○) P21, and (●) 4 in the presence of alkali metal cations. [Crown unit] = 1.0×10^{-4} mol/L; [MCl] = 2.0×10^{-3} mol/L.

References and Notes

(1) Vögtle, F. *Host–Guest Complex Chemistry III*; Springer-Verlag: Berlin, 1984.
(2) Löhr, H. G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65.
(3) Sousa, L. R.; Larson, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 307.
(4) Larson, J. M.; Sousa, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 1943.
(5) Shizuka, H.; Takada, K.; Morita, T. *J. Phys. Chem.* **1980**, *84*, 994.
(6) Konopelski, J. P.; Hibert, F. K.; Lehn, J. M.; Desvergne, J. P.; Fages, F.; Castellan, A.; Laurent, H. B. *J. Chem. Soc., Chem. Commun.* **1985**, 433.
(7) Silva, A. P.; Silva, S. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1709.
(8) Forgues, S. F.; Bris, M. T.; Guette, J. P.; Valeur, B. *J. Chem. Soc., Chem. Commun.* **1988**, 384.
(9) Shirai, M.; Morimoto, S.; Tanaka, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1187.
(10) Kopolow, S.; Hogen-Esch, T. E.; Smid, J. *Macromolecules* **1973**, *6*, 133.
(11) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.
(12) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271.
(13) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.
(14) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing: Menlo Park, CA, 1978.
(15) Shirai, M.; Kuwahara, M.; Tanaka, M. *Eur. Polym. J.* **1988**, *24*, 403.