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Fluorescence behavior of water-soluble copolymers with pendant (4-carboxylatophenoxy)cyclotriphosphazene/europium ion complexes

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Abstract

The water-soluble copolymers composed of styrene derivative with (4-carboxylatophenoxy)cyclotriphosphazene (CCP) and *N*-isopropylacrylamide (NIPAM) have been prepared as host polymers of Eu^{3+} ion. When CCP units were excited at 260 nm, the characteristic fluorescence of Eu^{3+} was remarkably enhanced compared to that of the excitation of Eu^{3+} at 396 nm, suggesting occurrence of efficient energy transfer from CCP units to Eu^{3+} ion. The content of CCP units in the polymer chains significantly affected the fluorescence behaviors; for the copolymer with 1.7 mol% CCP unit (**6a**) the intensity increased with increasing of Eu^{3+} ion and reached a limiting value at $[Eu^{3+}]/[\text{CCP unit}] = 1.0$, whereas the fluorescence intensity of the copolymer with 12.4 mol% CCP unit (**6d**) reached a maximum at $[Eu^{3+}]/[\text{CCP unit}] = 0.25$, decreased by the further addition of Eu^{3+}, and then has a constant value. In the **6d**–Eu^{3+} complexes, the number of water molecules coordinated with Eu^{3+} ions, which act as a quencher, varies from 2.8 at $[Eu^{3+}]/[\text{CCP unit}] = 0.25$ to 4.1 at $[Eu^{3+}]/[\text{CCP unit}] = 1.5$. The reduced viscosity of **6d** decreased with increasing the concentration of Eu^{3+} ions, indicating the contraction of polymer chains. The environment of Eu^{3+} bound to the copolymer is not affected by the coil–globule transition of the copolymer chain, although the **6a**–Eu^{3+} system showed a lower critical solution temperature at 38 °C. The fluorescence behaviors of Eu^{3+} trapped by new host polymers based on cyclotriphosphazene are described.

Keywords: Water-soluble polymer; Cyclotriphosphazene; Lanthanide ion complex

1. Introduction

In the last two decades, materials containing lanthanide ions such as Eu^{3+} and Tb^{3+} have been extensively investigated by the interest in their uses in photo- and electroluminescence materials [1–7]. While the fluorescence behavior of their complexes is intriguing, the polymers capable of exhibiting high luminescence intensity are rather limited. The fluorescence intensity of Eu^{3+} and Tb^{3+} is very weak in aqueous solution since the coordinated water molecules act as efficient quenchers of the emission [8]. The replacement of coordinated water molecules with ligands leads to the enhancement of the fluorescence intensity and lifetimes of the ions. Considerable effort is devoted to the design of ligands such as calixarene or cyclodextrin derivatives with carboxylic acid groups and bipyridine-type units to produce stable complexes with strong fluorescence [9–12].

We have focused on the synthesis and functionality of vinyl polymers carrying pendant cyclotriphosphazene, e.g. the ionically high conductive polymers [13] and Ag^{+}-selective polymers [14]. Recently, the polymers carrying pendant (dimethylaminopropyl)cyclotriphosphazene have been found to form fluorescent complexes with Eu^{3+} in methanol [15]. In addition, we have reported that hexakis(4-carboxylatophenoxy)-cyclotriphosphazene (CPN) binds Eu^{3+} through three carboxylatophenoxy groups at the both sides of nearly planar phosphazene ring to give a 1:2 CPN–Eu^{3+} complex [16]. Therefore, the polymers carrying CPN moiety in the side chain would be expected to act as host of Eu^{3+} ions, where carboxylatophenoxy groups could bind cooperatively Eu^{3+} ions, leading to the enhancement of fluorescence intensity.

In this study, new water-soluble host copolymers for

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Eu^{3+} ion utilizing styrene derivative with (4-carboxylatophenoxy)cyclotriphosphazene unit and *N*-isopropylacrylamide (NIPAM) were designed. Poly(NIPAM) segment provides the solubility and thermosensitivity in water, whereby aqueous solutions of this polymer exhibit a coil–globule transition at lower critical solution temperatures (31–32 °C) [17]. It is of interest whether the fluorescence intensity of the copolymer–Eu^{3+} complexes is affected by the coil–globule transition of the copolymer chain. We describe here the preparation of water-soluble copolymers carrying pendant (4-carboxylatophenoxy)cyclotriphosphazene and the fluorescence properties of the copolymer–Eu^{3+} complexes.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene was kindly supplied by Otsuka Chemical Co. and purified by recrystallization from *n*-hexane. *N*-Isopropylacrylamide was purified by recrystallization from hexane and dried in vacuo. Benzene and THF were distilled from appropriate drying reagents before use. $EuCl_3\cdot 6(H_2O)$ (Nacalai Tesqu, 99.9%) was used without further purification.

2.2. Synthesis of monomer

2,4,4,6,6,-(4-Ethoxycarbonylphenoxy)-2-(4-vinylphenoxy)cyclotriphosphazene (**4**) was synthesized as follows. A benzene solution of 2-(4-vinylphenoxy)pentachlorocyclotriphosphazene (**3**) [13] (5.0 g, 0.012 mol) was added slowly to a solution of 4-hydroxy-ethylbenzoate (19.3 g, 0.12 mol), triethylamine (23.5 g, 0.23 mol), and *N*,*N*-dimethylaminopyridine (0.7 g, 0.006 mol) in benzene. After stirring for 36 h at room temperature, the reaction mixture was filtered and the solvent was evaporated under reduced pressure. The residue was washed with water and chromatographed on silica gel (*n*-hexane-ethyl acetate, 5:1) to afford **4** as a white crystal. Yield, 85%. IR(nujol): 1720, 1600, 1500, 1210–1160, 955 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.7–8.0 (m, 24H, aroma. H), 5.0–7.0 (m, 3H, $-CH-CH_2-$), 4.1–4.6 (q, 10H, $-CH_2-$), 1.2–1.6 (t, 15H, $-CH_3$). Anal. Calcd. for $C_{53}H_{52}N_3O_{16}P_3$ C, 58.95; H, 4.85; N, 3.89 Found: C, 58.93; H, 4.80; N, 4.10%.

2.3. Synthesis of polymers

A typical synthetic procedure of the copolymers carrying pendant (4-carboxylatophenoxy)cyclotriphosphazene is as follows. The radical copolymerizations of **4** (2.7×10^{-2} g, 2.5×10^{-5} mol) and NIPAM (1.8 g, 1.6×10^{-2} mol) were carried out in THF (5 ml) at 70 °C for 48 h using azobis(isobutyronitrile) (AIBN) (2.5×10^{-3} g, 1.5×10^{-5} mol) as an initiator. The resulting copolymers were poured into a large excess amounts of *n*-hexane and then were purified by reprecipitation from chloroform into a large excess of *n*-hexane. Then, the copolymers were hydrolyzed with *t*-BuOK to give the desired copolymers with carboxylate moiety on the phosphazene, and dialyzed against deionized water. The content of CCP unit in the copolymers was determined by the integral ratio of phenylene (CCP) to methyl (NIPAM) protons in ^1H NMR spectra. IR (KBr): 2850, 1630, 1600, 1560, 1460, 1395, 1210–1160, 970 cm^{-1}. ^1H NMR (D_2O): δ 7.7–7.9 (br d, aroma. H), 6.8–7.0 (br d, aroma. H), 3.8 (br s, $-CH(CH_3)_2$), 2.1–1.2 (br m, $-CH_2-CH-$), 1.1 (br s, $-CH_3$).

2.4. Measurements

Gel permeation chromatography (GPC) was performed on a Shimadzu LC-6A instrument, equipped with Shimadzu HSG-30 and HSG-60 columns, and UV detector, using THF as the eluent. The molecular weights of the copolymers were determined by GPC using polystyrene standards. Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence and excitation spectra were recorded on a Shimadzu RF-5000 spectrofluorometer. Excitation spectra were corrected precisely with the same instrument. Lifetime measurements were carried out using a modified UNISOKU FSS-400 spectrometer equipped with a Hamamatsu R2949 photo tube and a transient memory (KAWASAKI TMR-80). The samples were excited by the UV light of 260 nm selected through Toshiba interference filter from a pulsed lamp. The resulting emission was detected at 620 nm for Eu^{3+}. Viscosity was measured with a modified Ubbelhode capillary viscometer at 30 °C. The LCSTs of the polymer solutions (2.00×10^{-3} g/ml) were measured by UV spectrophotometer to determine the turbidity of the polymer solutions as a function of temperatures at a fixed wavelength (500 nm). The temperature at 50% light transmittance was defined as the LCST.

3. Results and discussion

The water-soluble copolymers carrying pendant (4-carboxylatophenoxy)cyclotriphosphazene (CCP) were prepared by the copolymerization of **4** and NIPAM in THF, followed by hydrolysis with *t*-BuOK. The copolymerization of **4** and NIPAM with AIBN initiator in THF gave copolymers with moderate molecular weights ($M_n = 2.8$–5.9×10^4), where the contents of **4** units were somewhat lower than that of monomer feed. The hydrolysis of the copolymers with *t*-BuOK afforded water-soluble copolymers carrying five carboxyl groups on the pendant phosphazene ring. The average number of CCP unit per a polymer chain with 1.7 mol% (**6a**) and 12.4 mol% (**6d**) of CCP units are estimated to be 7.7 and 16.6, respectively (Chart 1).

The fluorescence intensity of Eu^{3+} in water is extremely

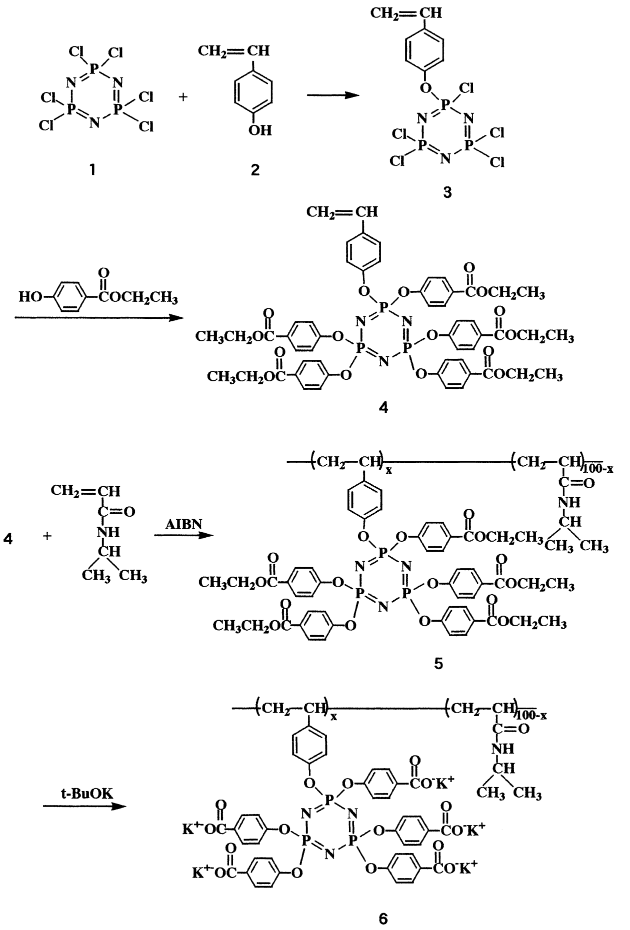


Chart 1. Preparation of water-soluble host copolymers.

week, since the coordinated water molecules efficiently quench the luminescence. Fig. 1 shows typical absorption, excitation, and emission spectra of the **6a**–Eu^{3+} system in an aqueous solution. The absorption spectrum of **6a** exhibited a red shift by the addition of Eu^{3+} ions. The characteristic fluorescence of Eu^{3+} complexed with **6a** was observed under the metal-center excitation at 396 nm. Such an enhancement of fluorescence was not observed for the poly(NIPAM)–Eu^{3+} system, showing that Eu^{3+} ions are trapped by carboxylates on the phosphazene units. In a previous paper [16], we showed that the quantum yield (ϕ) of the hexakis(4-carboxylatophenoxy)cyclotriphosphazene (CPN)–Eu^{3+} system was very high ($\phi = 0.01$) due to the occurrence of efficient energy transfer from ligands to Eu^{3+} ions. As expected, when CCP units were excited at 260 nm, the fluorescence of the **6a**–Eu^{3+} complex of $[Eu^{3+}]/[\text{CCP units}] = 1$ was remarkably enhanced compared to that excited at 396 nm. The excitation spectrum of the **6a**–Eu^{3+} complex was nearly identical with its absorption spectrum. These results indicate that the excited CCP group can transfer its energy to Eu^{3+} without any influence of NIPAM groups.

The metal to ligand ratio for the copolymer–Eu^{3+} complexes was determined by means of the molar ratio method (Fig. 2). In the **6a**–Eu^{3+} system ($[\text{CCP}] = 1.00 \times 10^{-5}$ M), the fluorescence intensity increased with increasing the concentration of Eu^{3+} and reached a constant value at $[Eu^{3+}]/[\text{CCP}] \geq 1$, suggesting that CCP unit interacts with Eu^{3+} to form a 1:1 complex. In the CPN–Eu^{3+} complex, Eu^{3+} was coordinated to three carboxylatophenoxy groups at both sides of nearly planar phosphazene ring to form a 1:2 CPN–Eu^{3+} complex [16]. Thus, it is reasonable to suppose that the 1:1 complex forms only at one side of the phosphazene ring in the **6a**–Eu^{3+} complex. For the **6a**–Eu^{3+} system, it seems likely that the complex might be formed on one side located three carboxylatophenoxy groups, where the complex formation is scarcely subject to steric hindrance caused by the polymer backbone (Scheme 1(a)). On the other hand, the **6b**–, **6c**–, and **6d**–Eu^{3+} system showed different behaviors. For the **6d**–Eu^{3+} complexes, the fluorescence intensity abruptly increased by the addition of Eu^{3+} ion, reached a maximum around $[Eu^{3+}]/[\text{CCP}] = 0.25$, decreased, and then had leveled off. The constant value at high concentrations of Eu^{3+} suggests that 'concentration quenching' is not

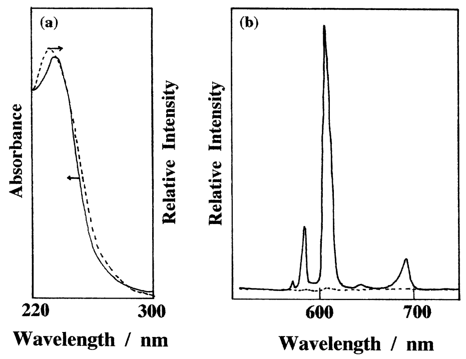


Fig. 1. (a) Absorption (—) and corrected excitation spectra (--) of the **6a**–Eu^{3+} system in water. $\lambda_{em} = 615$ nm. (b) Fluorescence spectra of the **6a**–Eu^{3+} system under the direct excitation of Eu^{3+} at 396 nm (--) and the excitation of carboxylatophenoxy unit at 260 nm (—). [CCP] (the CCP unit concentration of **6a**) $= 1.00 \times 10^{-5}$ M, $[Eu^{3+}] = 1.00 \times 10^{-5}$ M.

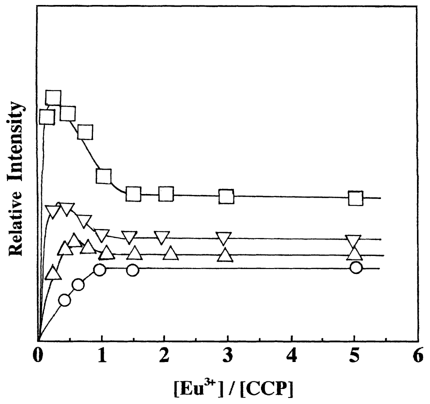
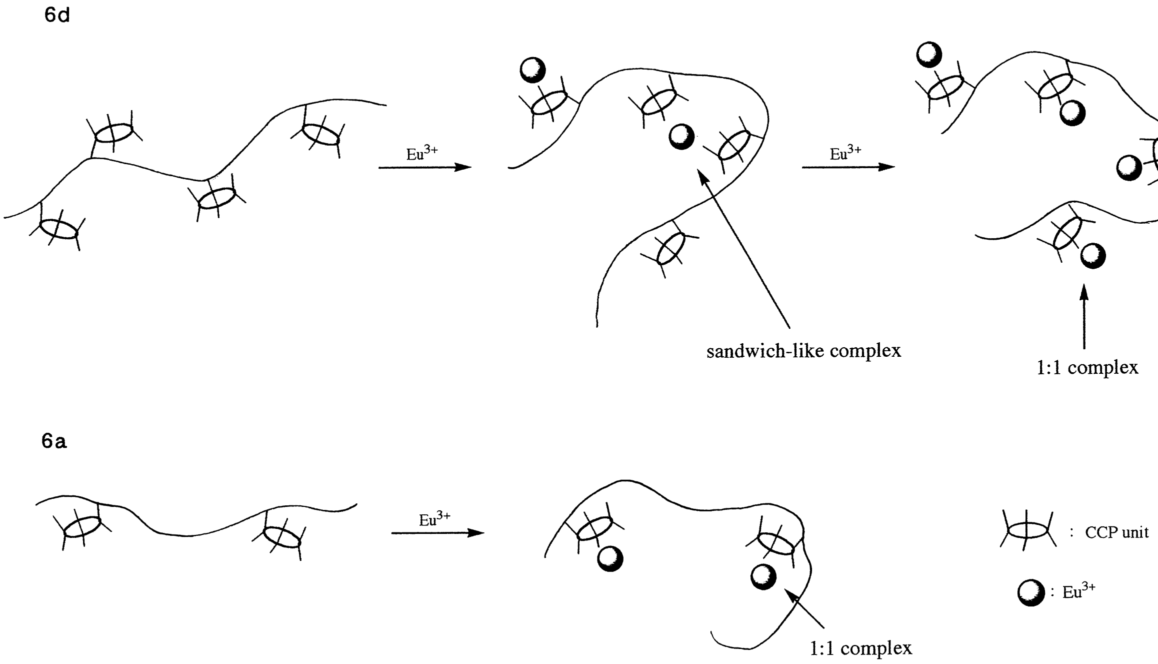


Fig. 2. Dependence of the fluorescence intensity of Eu^{3+} on the Eu^{3+} concentration in an aqueous **6a** (○), **6b** (△), **6c** (▽) and **6d** (□) solution. $[\text{CCP}] = 1.00 \times 10^{-5}$ M. $\lambda_{ex} = 396$ nm.



Scheme 1. Schematic representation of the copolymer–Eu^{3+} complexes.

responsible for the decrease of fluorescence intensity (Table 1).

The fluorescence intensity is strongly affected by the number of coordinated water molecules to Eu^{3+} ion, which can be determined from the emission lifetimes of Eu^{3+} in the copolymer–Eu^{3+} complexes measured in water and deuterated water [18]. As shown in Fig. 3, monoexponential fluorescence decay curves were observed. Table 2 shows the fluorescence lifetimes and the number of the coordinated water molecules (NH_2O) to Eu^{3+} ion in the copolymer–Eu^{3+} complexes, which was calculated by Horrocks and Sudnick's equation [18], $NH_2O = 1.05(1/\tau_H - 1/\tau_D)$, where τ_H and τ_D are life time of the complex in H_2O and D_2O, respectively. The lifetimes in H_2O and D_2O are much longer than that of the monomeric 2,4,4,6,6-(4-carboxylatophenoxy)-2-(4-vinylphenoxy)-cyclotriphosphazene–Eu^{3+} complex, suggesting that the microenvironment of Eu^{3+} in the polymer complexes is different from that in the monomeric phosphazene–Eu^{3+} complex. In the polymer systems, the fluorescence behaviors of Eu^{3+} may be affected by the proximity of CCP units.

Table 1
Physical properties and composition of the copolymers

Monomer feed (mol/l)		Composition[a] (mol%)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	
4×10^2	NIPAM	CCP unit			
4.9	3.2	1.7	5.9	1.5	**6a**
7.1	3.0	2.7	4.4	1.8	**6b**
12.0	2.2	6.6	2.8	2.1	**6c**
19.0	1.8	12.4	3.2	2.0	**6d**

[a] From ^1H NMR spectrum (solvent: D_2O).
[b] From GPC data.

The NH_2O value for the **6a**–Eu^{3+} complex with $[Eu^{3+}]/[CCP] = 1.5$ was 4.1. Assuming that the Eu^{3+} aquo ion is hydrated with 9 water molecules [18], ca 5 water molecules are estimated to be expelled due to the 1:1 complexation. In the **6d**–Eu^{3+} system, somewhat small value ($NH_2O = 3.9$) was obtained at $[Eu^{3+}]/[CCP] = 1.5$, suggesting that the microenvironment of Eu^{3+} is different from that of the **6a**–Eu^{3+} system. Under the condition of $[Eu^{3+}] = 2.50 \times 10^{-6}$ M and $[\text{CCP unit}] = 1.00 \times 10^{-5}$ M, where the fluorescence intensity reached a maximum, NH_2O was found to be 2.8. Thus, the fluorescence behavior observed for the **6d**–Eu^{3+} system could be interpreted in terms of the number of coordinated water molecules. The **6d** contains 16.6 CCP units per a polymer chain on the average, where the unoccupied CCP units in the vicinity of CCP unit already complexed with Eu^{3+} ion are considered to

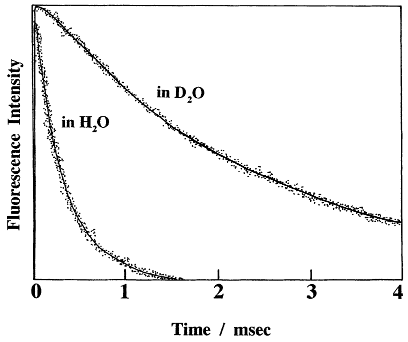


Fig. 3. Fluorescence decays of Eu^{3+} at 620 nm for the **6a**–Eu^{3+} system ($[CCP] = 1.00 \times 10^{-5}$ M, $[Eu^{3+}] = 1.50 \times 10^{-5}$ M) in H_2O and D_2O. $\lambda_{ex} = 260$ nm.

Table 2
Fluorescence lifetimes and number of coordinated water molecules (NH_2O) to Eu^{3+} in the copolymer–Eu^{3+} complexes

Complex	$[Eu^{3+}]$/M	Lifetimes (ms)[a]		Number of coordinated water molecules, NH_2O
		τ (H_2O)	τ (D_2O)	
Hydrolyzed derivative of **4**–Eu^{3+}	1.50×10^{-5}	0.18	1.4	5.1
6a–Eu^{3+}	1.50×10^{-5}	0.23	2.2	4.1
6d–Eu^{3+}	1.50×10^{-5}	0.24	2.1	3.9
6d–Eu^{3+}	2.50×10^{-6}	0.33	2.6	2.8

[CCP unit] = 1.00×10^{-5} M.

[a] Measured in correspondence with the most intense emission band (620 nm).

approach to form a sandwich-like complex, leading to the additional replacement of water. Such an interaction should bring about the conformational change from expanded **6d** chains due to electrostatic repulsion of carboxylates on the phosphazene to a coiled structure. As shown in Fig. 4, the reduced viscosity of an aqueous **6d** solution decreased with increasing the Eu^{3+} concentration, indicating the contraction of the **6d** chains. The further addition of Eu^{3+} ions effects the decrease in the opportunity to form the sandwich-like complex, and in other words, the predominant formation of the complex with 1:1 Eu^{3+}–CCP unit, leading to the constant fluorescence intensity. Thus, it seems likely that the further removal of water molecules by the formation of a sandwich-like complex is responsible for the appearance of maximum fluorescence for the **6d**–Eu^{3+} system (Fig. 2). This is also true for the **6c**–Eu^{3+} and **6b**–Eu^{3+} systems.

In the **6d**–Eu^{3+} system, when the formation of 1:1 complex is complete, the fluorescence intensity become constant, indicating that the further added Eu^{3+} ions do not take part in the complexation. However, the reduced viscosity keeps decreasing by the addition of further Eu^{3+} ions. On the other hand, the reduced viscosity of **6a**–Eu^{3+} system which do not form sandwich-like complex also decreases with increasing the Eu^{3+} concentration. These suggest that the decrease in the viscosity of copolymer–Eu^{3+} systems with increasing the Eu^{3+} concentration is caused by not only the sandwich-like complexation but also added salt effect of Eu^{3+}.

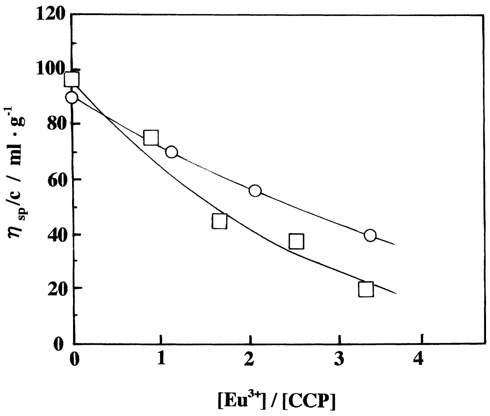


Fig. 4. Effect of the Eu^{3+} concentration of the reduced viscosity of aqueous **6a** (○) (2.11×10^{-3} g/ml) and **6d** (□) (5.31×10^{-4} g/ml) solution. [CCP] = 2.75×10^{-4} M.

If the same 1:1 complex is formed in all copolymer–Eu^{3+} systems at high concentrations of Eu^{3+}, the fluorescence intensities of all systems should be equal. However, the fluorescence intensity of the **6d**–Eu^{3+} complex was 2.1 times stronger than that of the **6a**–Eu^{3+} complex at $[Eu^{3+}]/[CCP] = 1.5$ as shown in Fig. 2. Although this detailed reasons are unclear, **6d** seems to be easy to interact with Eu^{3+} ions in comparison with **6a** due to more CCP units on the polymer chain.

Poly(NIPAM) is known to show a lower critical solution temperature (LCST) of 31–32 °C [17]. The LCST observed in aqueous solutions of the polymer results from a balance of hydrogen-bonding and hydrophobic effects [19,20]. Since the CCP unit is more hydrophilic than NIPAM, the LCST of **6a** is higher (38 °C) than that of poly(NIPAM) (31 °C). Moreover, the LCST of **6a** changed from 38 °C to 36 °C when **6a** was complexed with Eu^{3+}. On the other hand, the LCST was not observed in aqueous solutions of **6d**.

It is of interest whether the fluorescence intensity of the **6a**–Eu^{3+} complex is affected by the phase transition of the copolymer at the LCST. Hemmila et al. have reported that the enhancement of the fluorescence intensity of β-diketone ligand–Eu^{3+} complex was observed by the incorporation of the complex into micelle of Triton X 100 [21]. If **6a** forms a hydrophobic microdomain by the coil–globule transition at the LCST of 36 °C, the enhancement of the fluorescence intensity of Eu^{3+} would be expected due to the incorporation of Eu^{3+} complexed with CCP units into the hydrophobic microdomain. As for the formation of hydrophobic microdomain for poly(NIPAM), Winnik [22] reported that the ratio (I_1/I_3) of the fluorescence intensity of the first and third vibrational bands of the pyrene molecule, which is known to be a monitor of environment polarity, changed from 1.74 to 1.38 by the coil–globule transition and that the polarity of the polymer matrix in globule state correspond to solvents such as tetrahydrofuran or ethyl acetate. In an aqueous solution of **6a** (3.60×10^{-4} g/ml), the I_1/I_3 ratio changed from 1.80 at 15 °C to 1.56 at 50 °C, suggesting that the polymer matrix in globule state afford a

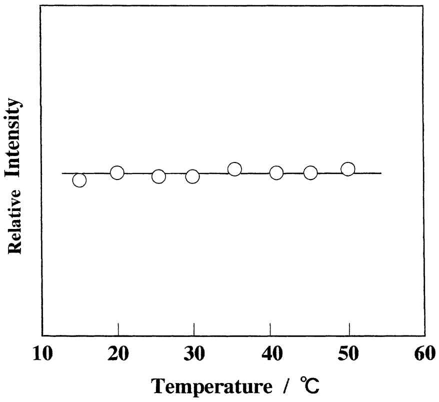


Fig. 5. Effect of temperature on the fluorescence intensity of Eu^{3+} for the **6a**–Eu^{3+} system. [**6a**] = 3.60×10^{-4} g/ml ([CCP] = 4.69×10^{-5} M), [Eu^{3+}] = 5.00×10^{-5} M. $\lambda_{ex} = 260$ nm.

hydrophobic microdomain with polarity such as DMF [23]. However, contrary to our expectation, the fluorescence intensity of Eu^{3+} of the **6a**–Eu^{3+} complex was independent of temperature (Fig. 5). This result suggests that the environment of Eu^{3+} in the copolymer complex is not affected by the coil–globule transition of the copolymer chain. It seems that Eu^{3+} ion complexed with CCP unit on the polymer chain, without incorporating in the hydrophobic polymer matrix in globule state, is exposed to bulk water phase.

In conclusion, the water-soluble copolymers composed of styrene derivative with (4-carboxylatophenoxy)cyclotriphosphazene (CCP) and *N*-isopropylacrylamide were prepared as host polymers to Eu^{3+} ions. The copolymer–Eu^{3+} complexes showed a strong fluorescence due to the energy transfer from the absorbing carboxylatophenoxy groups to the bound Eu^{3+}. The complexation of the copolymers with Eu^{3+} ions was influenced by the content of the CCP unit in the copolymer. From the relationship between the fluorescence intensity and [Eu^{3+}]/[CCP], the number of water molecules coordinated with Eu^{3+} ions, and the viscosity behavior of the complexed copolymer, it was found that **6a** (1.7 mol% CCP) interact with Eu^{3+} to form a 1:1 complex, whereas the **6d** (12.4 mol% CCP) forms a sandwiched complex when [Eu^{3+}]/[CCP] ≤ 0.25. The fluorescence intensity of the **6a**–Eu^{3+} complex was not influenced by the coil–globule transition, suggesting that Eu^{3+} complexed the CCP units on the copolymer chain is located outside of the hydrophobic polymer matrix in globule state.

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