Inorganica Chimica Acta, *207* (1993) 233–240

Fluorescence properties of europium(II) and other divalent metal ion doubly-doped poly(methacrylate containing 15-crown-5 structure) complexes

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(Received August 23, 1992; revised January 20, 1993)

Abstract

Eu^{2+} and an alkaline earth metal ion: Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, or a Group IIB metal ion: Zn^{2+} and Cd^{2+}, doubly-doped poly(methacrylate containing 15-crown-5 structure) complexes were prepared. Their fluorescence properties were investigated in the solid state and compared to those of an Eu^{2+} only-doped polymer complex. Under UV irradiation, blue emissions based on the electric transition of the Eu^{2+} ions in the Eu^{2+}–15C5 moiety complexes are observed for all the polymer complexes. The maximum fluorescence intensity obtained for the Eu^{2+}–Zn^{2+} doubly-doped polymer reaches *c.* 50% of that for $CaWO_4$:Pb (NSB1026), whereas the emission intensity of the polymer containing Eu^{2+} alone was at most *c.* 20% of that of NSB1026. The emission intensity for the Eu^{2+}–M^{2+} doubly-doped polymer (M = Mg, Ca, Sr) is almost the same value as that for the Eu^{2+} only-doped one. All the doubly-doped polymers as well as the Eu^{2+} only-doped one indicate concentration quenching. The concentration quenching is suppressed to some extent by the presence of the metal ions: Mg^{2+}, Ca^{2+} and Sr^{2+}, since the maximum of the emission intensity shifts to the higher $EuCl_2$ concentration side for these doubly-doped than for the Eu^{2+} only-doped samples. The Eu^{2+}–Ba^{2+} doubly-doped polymer gives the smallest emission intensity of all the alkaline earth codoped ones. The bulky Ba^{2+} ions would influence the surroundings of the Eu^{2+}–15C5 moiety complexes and/or interfere with the complexation. By codoping with Zn^{2+}, the luminescence lifetime of Eu^{2+} is apparently lengthened. This behavior is not observed in the case when using the alkaline earth ions as codopant ions. These results suggest that the way Zn^{2+} is present in the polymer, is different from the alkaline earth metal ions. The latter ions are present in the polymer as complexes with 15-crown-5. On the other hand, for the Eu^{2+}–Zn^{2+} doubly-doped one, $ZnCl_4^{2-}$ complex anions are formed in the polymer matrix, confirmed by Raman spectroscopy. Temperature dependent reciprocal magnetic susceptibilities for the Eu^{2+} only-doped and Eu^{2+}–Zn^{2+} doubly-doped polymers indicate antiferromagnetic interactions and the interatomic distances of the Eu^{2+} ions are discussed on their asymptotic Curie points. For the Eu^{2+}–Cd^{2+} codoped one, it also indicates a higher maximum emission intensity than for the Eu^{2+} only-doped one. An Eu^{2+}–Hg^{2+} doubly-doped polymer was not available. The formation of the halogeno complex anions significantly affects the fluorescence properties.

Introduction

The fluorescence properties of lanthanide ions in various polymer matrixes have been studied. They reflect the surroundings and concentration of the lanthanide ions and the nature of the polymer. Banks *et al.* [1], Ueba *et al.* [2, 3] and Okamoto *et al.* [4] have investigated the structures of lanthanide ion-containing polymers, using the trivalent lanthanide ions as fluorescence probes, and they interpreted their data in terms of ion aggregate formation in the polymer.

The divalent europium ion is known to emit on the $4f^65d$–$4f^7$ transition, which depends strongly on the crystal field [5]. The photophysical property of Eu^{2+} in the polymer is, therefore, greatly influenced by the coordination site of the polymer. It has been found that Eu^{2+} emits strong blue light under UV irradiation when complexed with monomeric crown ethers and cryptands [6–9]. We have prepared Eu^{2+} complexes with several kinds of polymer ligands containing crown ethers and have studied their fluorescence properties [10]. By studying a series of polymer ligands, a 15-crown-5 methyl methacrylate (MA15C5)–methyl methacrylate (MMA) copolymer: copoly(MA15C5–MMA), shown in Fig. 1, was found to be the most suitable for a strongly blue emitting phosphor. In order to suppress fluorescence concentration quenching, Eu^{2+}–Sr^{2+} doubly-doped polymer complexes were prepared and their fluorescence properties were studied [11]. The presence of Zn^{2+} with Eu^{2+} in copoly(MA15C5–MMA) greatly

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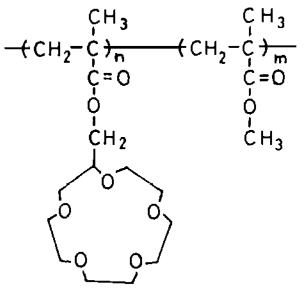

Fig. 1. Copoly(MA15C5–MMA).

enhanced the emission intensity [12]. In this paper, we report the effects of codopant divalent metal ions: Zn^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, on the Eu^{2+} luminescence and propose a mechanism for the enhancement of the emission intensity. This mechanism is characteristic of Zn^{2+} and Cd^{2+}. This may be attributed to their formation of halogeno complexes.

Experimental

Materials

$EuCl_2$ was prepared from 99.99% Eu_2O_3 mixed with excess NH_4Cl, heated at 300 °C for 1 h, at 400 °C for 2 h, at 500 °C for 1 h, and at 700 °C for 2 h, under a 99.99% hydrogen atmosphere. $BaCl_2$ was prepared by dehydration of $BaCl_2 \cdot 2H_2O$ under vacuum at 130 °C for 2 h.

Anhydrous methanol was degassed by repeated freeze–pump–thaw cycles on a high vacuum line in order to minimize the oxidation of Eu^{2+} to Eu^{3+} during complexation.

Polymer ligand

The monomer containing the crown ether, 15-crown-5-methyl methacrylate (MA15C5) was synthesized as previously reported [13]. The copolymerization of MA15C5 and methyl methacrylate (MMA) initiated by AIBN was carried out at 60 °C for 15 h at an initial molar ratio of MA15C5:MMA = 1:10. The copolymer was purified and washed with chloroform using a Soxhlet extractor for *c.* 2 days. The purified polymer was swollen in acetone, ground to powder, dried, and used without further characterization because of its insolubility [10]. A copolymer or MA15C5 and MMA was also prepared by another method. It was synthesized by polymerization in benzene at 60 °C for 20 h, using 3.6×10^{-3} mol MA15C5, 1.8×10^{-2} mol MMA, 0.1 mol% AIBN and 21.7 ml benzene. This copolymer was purified by two reprecipitations. In this procedure, a benzene solution (50 ml) of the polymer was added to a large excess (1 l) of diethyl ether with vigorous stirring. The polymer obtained was soluble in benzene and THF, and its molecular weight and composition were determined by a gel permeation chromatograph (GPC) (Waters 600E, mobile phase THF) and ^1H NMR measurement using a JEOL JNM-GSX-400 (400 MHz NMR), respectively. Typical values for the polymer were $\overline{Mn} = 5.5 \times 10^4$, $\overline{Mw} = 8.3 \times 10^4$, and $\overline{Mw}/\overline{Mn} = 1.5$. In the NMR spectra (in $CDCl_3$), the multiplet lines around $\delta = 3.680$ ppm are ascribed to the protons in $-OCH_2-$ and $-OCH-$ in MA15C5. The singlet line at 3.597 ppm is due to the protons of $-OCH_3$ groups in MMA. The mole ratio of MA15C5:MMA was estimated as *c.* 1:5. It is reasonable to apply the result to bulk polymerization and the copolymer obtained by bulk polymerization was determined to have almost the same ratio (MA15C5:MMA = 1:10) as that of the initial mixed monomers.

Complexes doubly-doped with Eu^{2+} and other divalent cations

Various divalent metal ion codoped Eu^{2+} complexes were prepared as follows. 60–100 mg of the bulk-polymerized copolymer were soaked in methanol solutions containing both $EuCl_2$ and another divalent metal chloride (MCl_2). The $EuCl_2$ concentrations of solutions ranged from 5×10^{-3} to 1×10^{-1} M. The maximum concentration of MCl_2 was 5×10^{-2} M for $MgCl_2$, 5×10^{-2} M for $CaCl_2$, 9.5×10^{-2} M for $SrCl_2$, 5×10^{-3} M for $BaCl_2$, 2×10^{-1} M for $ZnCl_2$ and 5×10^{-2} M for $CdCl_2$. When $HgCl_2$ was mixed with $EuCl_2$ in methanol, a gray precipitate was obtained presumably due to the reduction of Hg^{2+} by Eu^{2+}. The solutions soaking the polymer ligand were allowed to stand under N_2 for *c.* 1 day. The doubly-doped polymer complexes (except the Eu^{2+}–Hg^{2+} doubly-doped polymer) were separated from the mother liquors by decantation and dried *in vacuo* at room temperature.

Measurements

Corrected excitation and emission spectra were determined on a Shimadzu absolute spectrofluorophotometer, model RF-502, using an automatic compensation and pre-calibration system for the instrumental factors [14] and a cell with a front face holder. All measurements were carried out on freshly prepared samples.

The emission intensity was expressed as the area of the recorded emission band. The relative emission intensity in this study was determined by comparison of the emission intensity for the sample under optimal UV excitation with that of the $CaWO_4$:Pb (NBS1026) standard phosphor excited at 254 nm. The quantum efficiency of the standard phosphor is *c.* 76% under 254 nm excitation [15, 16].

The fluorescence lifetime was measured using a Horiba time-resolved spectrofluorometer, NAES-1100, equipped with a high pressure hydrogen lamp (pressure: 1 MPa; half-width of the pulse: less than 2 ns). Fluorescence decays were analysed by deconvolution using a built-in-microcomputer.

The $EuCl_2$, $ZnCl_2$ and $CdCl_2$ concentrations in the polymer complexes were determined by both EDTA titration and atomic absorption spectrometry, after the metal ions were dissociated from the polymer complexes with 10% hydrochloric acid. The MCl_2 (M = Mg, Ca, Sr, Ba) concentrations were calculated from both the $EuCl_2$ concentration and the M/Eu mole ratio which was measured by X-ray fluorometry, using a Rigaku Ultra trace. Ratios of the 15-crown-5 ring to the metal ion (L/M) in the polymer complexes were determined from the above assumption that the copoly-(MA15C5–MMA) obtained by bulk polymerization had the same composition as that of the mixed monomers, i.e. MA15C5:MMA = 1:10.

Raman spectra were obtained on a JASCO R-800 spectrometer using 180 mW of the 514.5 nm line from an NEC-GLG 3200 argon ion laser as the exciting source.

Magnetic susceptibilities were measured for the Eu^{2+} only-doped and Eu^{2+}–Zn^{2+} doubly-doped polymers from liquid nitrogen temperature to *c.* 150 or 300 K. The metal chloride concentration for the former was $[EuCl_2] = 4.9$ wt.%, and those for the latter were $[EuCl_2] = 1.4$ wt.%, $[ZnCl_2] = 1.3$ wt.%. The magnetic field employed in the measurements was 5.96 kOe. Effective magnetic moment was calculated by the equation, $P_{eff} = 2.83\sqrt{C}\,\mu_B$; C is Curie constant. Diamagnetic correction was done using the value of -1.689×10^{-6} emu/g for copoly(MA15C5–MMA).

Specific gravity of a sample of Eu^{2+} only-doped copoly(MA15C5–MMA); $[EuCl_2] = 4.6$ wt.%, was determined by means of a small pycnometer and then the nearest-neighboring Eu^{2+}–Eu^{2+} distance is estimated to be *c.* 18 Å on the assumption that the Eu^{2+} ions individually disperse in the polymer.

Results and discussion

The luminescence properties of the Eu^{2+} and metal ion doubly-doped polymer complexes are summarized in Table 1.

Excitation and emission properties of the complexes

The excitation and emission spectra for both the Eu^{2+} only-doped and the Eu^{2+}–Zn^{2+} doubly-doped polymers, and those for the Eu^{2+}–M^{2+} (M = Mg, Ca, Sr, Ba) doubly-doped ones are shown in Figs. 2 and 3 at their optimal $EuCl_2$ concentrations for the maximum emission intensities, respectively. These band emissions located in the blue–violet region are attributed to the $4f^65d$–$4f^7$ transition of Eu^{2+}. No apparent change was observed in the shapes of the emission spectra, although the emission which originated from the $4f^65d$ configuration is strongly influenced by the crystal field. Hence, such a behavior confirms that good-emitting, i.e. high efficient luminescent Eu^{2+} species are the Eu^{2+} ions coordinated by the crown ethers in the polymer matrix [10], even when the other metal ions are codoped.

The dependence of emission peak wavelength on the $EuCl_2$ concentration has been illustrated for several polymer complexes in Fig. 4. While the emission peak wavelengths for both Eu^{2+} only-doped and alkaline earth ion doubly-doped polymers apparently shift from 420 to 442 nm as the $EuCl_2$ concentration increases, those for the Eu^{2+}–Zn^{2+} doubly-doped polymers are constant at about 420 nm. All the latter polymer complexes emitted at almost the same wavelength as that of the lowest $EuCl_2$ concentrated Eu^{2+} only-doped one prepared.

Figure 5 shows the excitation spectra for the Eu^{2+} only-doped copoly(MA15C5–MMA) complexes of several $EuCl_2$ concentrations. In the excited spectrum for the Eu^{2+} only-doped polymer of the lowest $EuCl_2$ concentration (< 0.05 wt.%), there are two peaks which locate at *c.* 260 and 330 nm. This profile is very similar to that of the absorption spectrum for $EuCl_2$ in methanol [9]. The excitation spectra for the Eu^{2+} only-doped polymers changed dramatically as its concentration increased. The profiles of the higher $EuCl_2$ concentrated (> 1.1 wt.%) polymers became quite different and the two peaks at *c.* 260 and 330 nm disappeared and a new peak appeared at *c.* 400 nm. Similar results were obtained for the alkaline earth ion codoped polymers. Variations in the profiles of the excitation spectra for the Eu^{2+}–Zn^{2+} doubly-doped ones with $EuCl_2$ concentration are shown in Fig. 6. These profiles are similar for all the $EuCl_2$ concentrated polymers and resemble that of the Eu^{2+} only-doped one containing the smallest amount of Eu^{2+}. These results suggest that the presence of Zn^{2+} causes the local environments of the Eu^{2+} ions to be similar to those in the polymer of the very lowest $EuCl_2$ concentration, even if the Eu^{2+}–Zn^{2+} doubly-doped complexes have relatively high $EuCl_2$ concentration.

The dopant ion contents of the polymers are illustrated in Fig. 7. It can be seen that the alkaline earth metal contents increase with decreasing the Eu^{2+} content. However, for the Eu^{2+}–Zn^{2+} doubly-doped polymers, the Zn^{2+} content generally increased with Eu^{2+}. Such a different behavior suggests that Zn^{2+} is quite different from the alkaline earth ions in the way it is present in the polymer.

In order to obtain further information about the chemical state of Zn^{2+} in the polymer, Raman spectra were measured for the Eu^{2+} only-doped and Eu^{2+}–Zn^{2+}

TABLE 1. Luminescence properties of Eu^{2+}–M^{2+} doubly-doped complexes

M	$[EuCl_2]$ in MeOH (M)	$[MCl_2]$ in MeOH (M)	$[EuCl_2]$ in polymer (wt.%)	$[MCl_2]$ in polymer (wt.%)	L/Eu[a]	L/M[a]	Eu[b] content (μ mol g^{-1})	M[b] content (μ mol g^{-1})	I[c] (%)	τ[d] (ns)	λ[e] (nm)
Mg	0.1	0.05	2.2	0.73	7.5	9.6	99	77	18.4		440
Ca	0.07	0.03	5.8	0.23	2.7	34	260	21	19.6	423	440
Sr	0.07	0.03	1.9	0.25	8.7	47	85	16	20.6	431	435
Ba	0.05	0.005	1.2	0.30	14	52	54	14	15.3	457	434
Zn	0.1	0.2	0.68	3.7	24	2.7	31	270	50.5	639	421
	0.1	0.1	0.48	2.5	34	4.0	22	180	49.5	640	420
Cd	0.005	0.05		0.30		46		16	26.3	571	422
	0.05	0.05	0.38	0.68	45	20	17	37	21.2	520	422

[a] Mole ratio of 15-crown-5 to metal ions in the polymer. [b] Content of metal ions per 1 g of the polymer. [c] The emission intensity determined by comparison with that (=100%) of $CaWO_4$:Pb(NBS1026). [d] The longest luminescence lifetime with an error of at most 10%. [e] Emission peak wavelength.

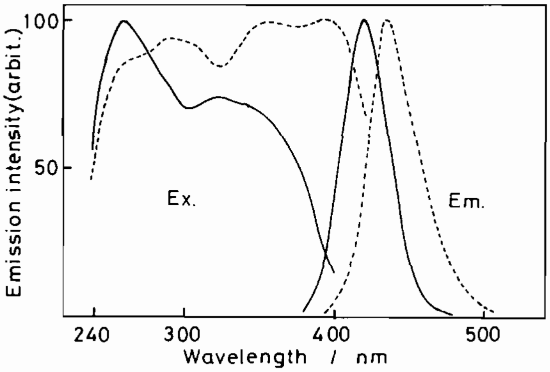

Fig. 2. Emission (Em.) and excitation (Ex.) spectra: (– – –) Eu^{2+}–copoly(MA15C5–MMA), $[EuCl_2]=1.07$ wt.%; (——) Eu^{2+}–Zn^{2+}–copoly(MA15C5–MMA), $[EuCl_2]=0.68$ wt.%; $[ZnCl_2]=3.7$ wt.%.

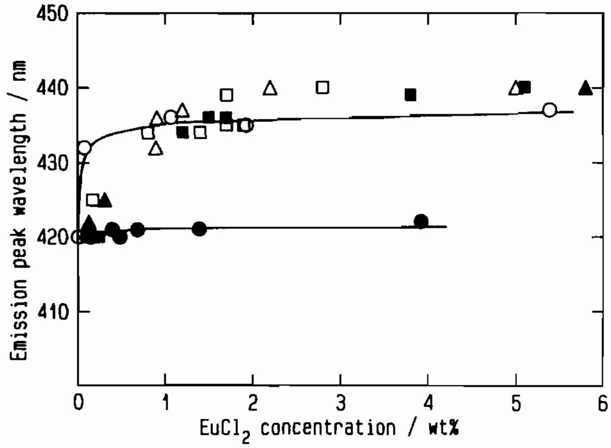

Fig. 4. Dependence of emission peak wavelength of Eu^{2+}–copoly(MA15C5–MMA) (○) and Eu^{2+}–M^{2+}–copoly-(MA15C5–MMA): M = Mg (△), M = Ca (▲), M = Sr (□), M = Ba (■), M = Zn (●), on $EuCl_2$ concentration.

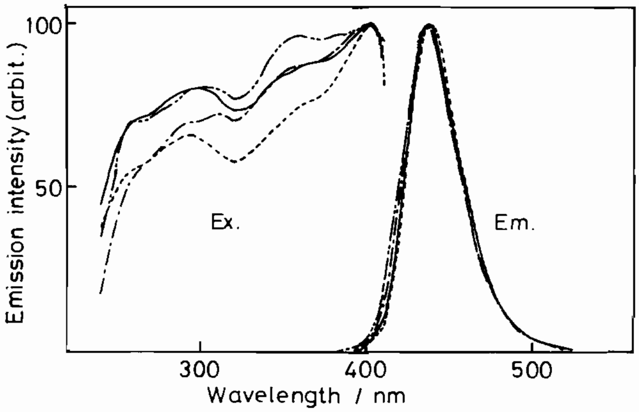

Fig. 3. Emission (Em.) and excitation (Ex.) spectra for Eu^{2+}–M^{2+}–copoly(MA15C5–MMA) complexes: (——) M = Mg, $[EuCl_2]=2.2$ wt.%, $[MgCl_2]=0.73$ wt.%; (– – –) M = Ca, $[EuCl_2]=5.8$ wt.%, $[CaCl_2]=0.23$ wt.%; (–·–) M = Sr, $[EuCl_2]=1.9$ wt.%, $[SrCl_2]=0.25$ wt.%; (–···–) M = Ba, $[EuCl_2]=1.2$ wt.%, $[BaCl_2]=0.30$ wt.%.

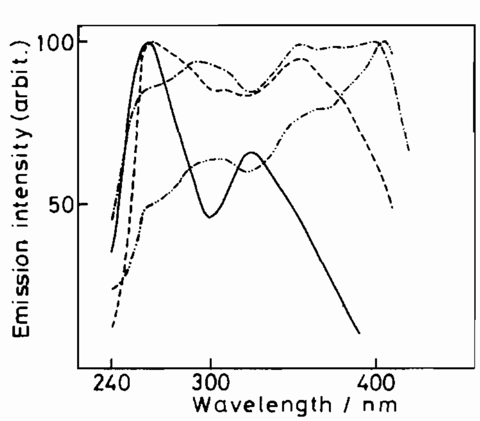

Fig. 5. Excitation spectra for the Eu^{2+}–copoly(MA15C5–MMA) complexes. (——) $[EuCl_2]<0.05$ wt.%; (– – –) $[EuCl_2]=0.07$ wt.%, L/Eu = 230; (–·–) $[EuCl_2]=1.1$ wt.%, L/Eu = 16; (–···–) $[EuCl_2]=5.4$ wt.%, L/Eu = 3.0.

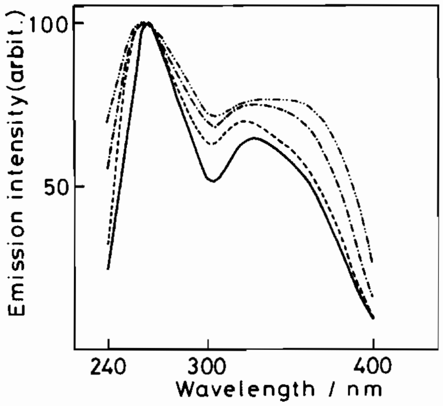

Fig. 6. Excitation spectra for the Eu^{2+}–Zn^{2+}–copoly(MA15C5–MMA) complexes. (——) $[EuCl_2] = 0.15$ wt.%, L/Eu = 110; (– – –) $[EuCl_2] = 0.39$ wt.%, L/Eu = 42; (– · –) $[EuCl_2] = 1.4$ wt.%, L/Eu = 12; (– · · · –) $[EuCl_2] = 3.9$ wt.%, L/Eu = 4.0.

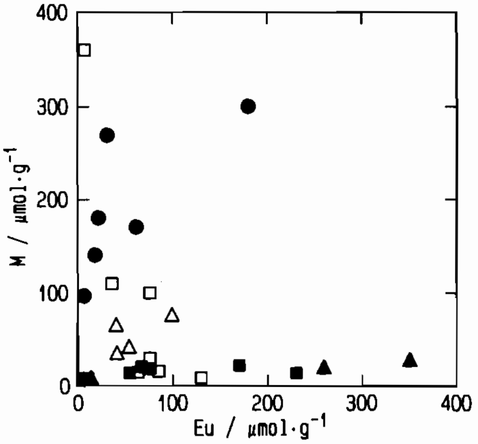

Fig. 7. Relationship between M^{2+} and Eu^{2+} contents per 1 g of copoly(MA15C5–MMA): M = Mg (△), M = Ca (▲), M = Sr (□), M = Ba (■), M = Zn (●).

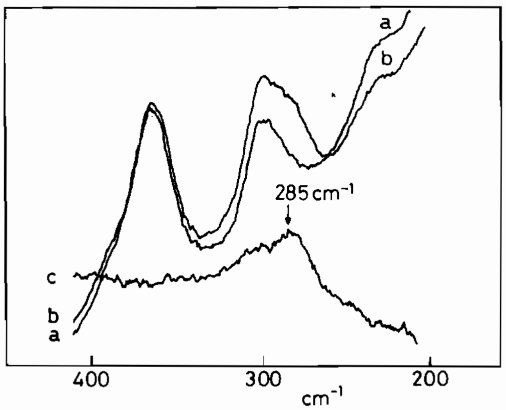

Fig. 8. Raman spectra for: (a) copoly(MA15C5–MMA); (b) Eu^{2+}–Zn^{2+}–copoly(MA15C5–MMA), $[EuCl_2] = 2.2$ wt.%, $[ZnCl_2] = 3.7$ wt.%; (c) spectrum (a) subtracted from (b).

doubly-doped polymers; they are shown in Fig. 8. The Raman line, which was not found in the spectrum obtained for the Eu^{2+} only-doped polymer, appeared at *c.* 285 cm^{-1}, when Eu^{2+} and Zn^{2+} were doubly doped in the polymer. This line is assigned to a tetrahedral $ZnCl_4^{2-}$ ion, as the frequency of a totally symmetric vibration of $ZnCl_4^{2-}$ is 283 cm^{-1} [17]. The Zn^{2+} ions were found to be present in the form of $ZnCl_4^{2-}$ as the counter ions of Eu^{2+}. The high Zn^{2+} content of the polymer complexes and its tendency to increase with the Eu^{2+} content (Fig. 7) could be explained by this fact. On the other hand, the alkaline earth metal ions appear to be directly coordinated to the crown ether ring. This supports the fact that the alkaline earth metal content decreased with increasing Eu^{2+} since they compete with Eu^{2+} for coordination to the crown ethers.

Emission intensities

The emission intensity versus the $EuCl_2$ concentration is illustrated in Figs. 9 and 10 for several complexes. In all cases, concentration quenching was observed. The self-quenching mechanism of Eu^{2+} is briefly explained as follows. If the concentration of the activator, such as Eu^{2+}, becomes so high that the probability of energy transfer exceeds that of radiative emission, the excited activator starts transferring its excitation energy to another activator ion. Now the excitation energy may be non-radiatively lost, such as at dislocations, impurities, etc. and then the emission intensity decreases.

The emission intensity for the Eu^{2+} only-doped complexes reached a peak at *c.* 1 wt.% of the $EuCl_2$ concentration and then decreased with further increasing concentration. For the Eu^{2+}–M^{2+} doubly-doped ones (M = Mg, Ca, Sr), the concentration quenching

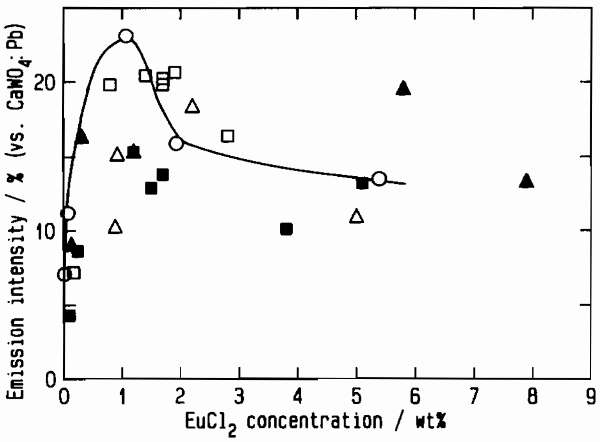

Fig. 9. Dependence of emission intensity of Eu^{2+}–copoly(MA15C5–MMA) (○) and Eu^{2+}–M^{2+}–copoly(MA15C5–MMA): M = Mg (△), M = Ca (▲), M = Sr (□), M = Ba (■), on $EuCl_2$ concentration.

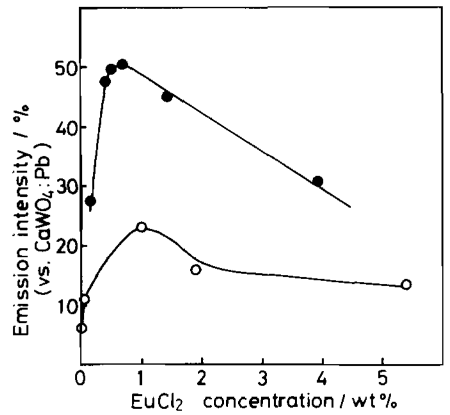

Fig. 10. Dependence of emission intensity of Eu^{2+}–copoly(MA15C5–MMA) (○) and Eu^{2+}–Zn^{2+}–copoly(MA15C5–MMA) (●) on $EuCl_2$ concentration.

appeared to be suppressed, as the position of the maximum emission intensity located at the higher $EuCl_2$ concentration side (Fig. 9). Nevertheless, this did not cause enhancement of the emission intensity. For the Eu^{2+}–Ba^{2+} codoped complexes, the maximum emission intensity decreased. The maximum intensity for the Eu^{2+}–Zn^{2+} codoped polymer became *c.* 2.5 times as large as that for the Eu^{2+} only-doped one and reached *c.* 50% of that for $CaWO_4$:Pb (NBS1026), as shown in Fig. 10. This emission intensity was the highest one ever obtained for Eu^{2+} polymer systems. For the Eu^{2+}–Cd^{2+} doubly-doped polymer, the emission intensity was also enhanced and its maximum value was *c.* 26% (versus $CaWO_4$:Pb), see Table 1.

It is widely known that the probability of an Eu^{2+}–Eu^{2+} energy transfer which frequently takes place as a non-radiative deactivation process significantly depends on the distance between the Eu^{2+} ions [5, 18–20]. A decrease of the distance in general raises this probability and decreases the emission efficiency. This accounts for concentration quenching. The Eu^{2+} ions are considered to have a tendency to aggregate in the polymer matrix even at low $EuCl_2$ concentration, as mentioned later. A binuclear complex of Eu^{2+} by forming bridges with Cl^- may be considered as one possible model for the Eu^{2+} aggregates or clusters proposed to exist in the polymer. Otherwise the species which are somehow in close proximity each other would be forming. Such species have a high probability of energy transfer so that their emission efficiency becomes low. Even if the $EuCl_2$ concentration increases gradually from zero, the number of such species should increase rapidly. This interpretation is supported by the way of changes of both the excitation spectra and emission peak wavelength for the Eu^{2+} only-doped and Eu^{2+}–alkaline earth metal doubly-doped complexes. In the case of the Eu^{2+}–Zn^{2+} doubly-doped polymer, it is suggested that $ZnCl_4^{2-}$ breaks such Cl^- bridges or at least is inserted between the Eu^{2+} ions as a bigger anion than Cl^-, resulting in a separation of the Eu^{2+} ions from each other in the polymer matrix. The separation leads Eu^{2+} to have a better luminescence efficiency by reducing the concentration quenching.

In order to examine the effects of Zn^{2+} on the distance between Eu^{2+} and Eu^{2+}, magnetic susceptibilities were measured for the Eu^{2+} only-doped and Eu^{2+}–Zn^{2+} doubly-doped polymers at various temperatures. In Fig. 11, inverse magnetic susceptibilities are plotted against temperature. For both samples, the $1/\chi$ curves approach a Curie–Weiss term of $P_{\rm eff} = \approx 7.94\ \mu_B\ (Eu^{2+})$ at higher temperature. The asymptotic Curie points (θ) are negative so that they exhibit antiferromagnetism. Some antiferromagnetic interactions occur in both complexes. If Eu^{2+} individually disperses in an Eu^{2+} only-doped polymer of $EuCl_2$ concentration 4.6 wt.%, the nearest-neighbor interatomic distance of Eu^{2+} is estimated to be *c.* 18 Å so that such interactions cannot be observed. The Eu^{2+} ions, therefore, must form aggregates or clusters in the polymer matrixes. Figure 11 shows a departure from the Curie–Weiss relationship to the lower $1/\chi$ side with decreasing temperature. The following may give a reasonable explanation of the result. Components of several asymptotic Curie points (θ) are spatially distributed in the polymer matrixes. In this case

$$\chi = \frac{\mu_B^2}{3k_B}\left(\frac{N_1 P_{\rm eff}^2}{T-\theta_1} + \frac{N_2 P_{\rm eff}^2}{T-\theta_2} + \frac{N_3 P_{\rm eff}^2}{T-\theta_3} + \ldots\right)$$

where the parameters have their usual meanings. Now if $\theta_1 = 0$ and only two terms are considered,

$$\chi = \frac{\mu_B^2}{3k_B}\left(\frac{N_1 P_{\rm eff}^2}{T} + \frac{N_2 P_{\rm eff}^2}{T-\theta_2}\right)$$

and then at $T \gg 0$

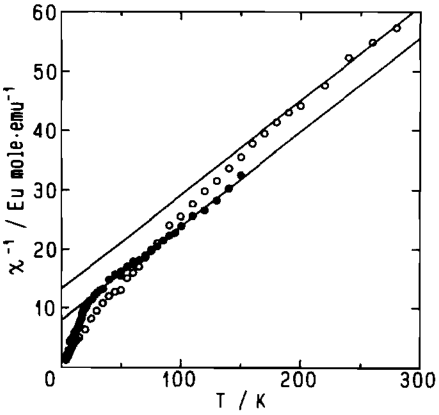

Fig. 11. Inverse susceptibility–temperature data for Eu^{2+}–copoly (MA15C5–MMA) (○) and Eu^{2+}–Zn^{2+}copoly(MA15C5–MMA) (●).

$$1/\chi \longrightarrow \frac{3k_B(T-\theta_2)}{\mu_B{}^2 P_{\text{eff}}{}^2(N_1+N_2)}$$

This means that it is antiferromagnetism and follows the Curie–Weiss relationship. As the temperature approaches 0, the $1/\chi$ curve indicates the deviation from the Curie–Weiss relationship and $1/\chi$ approaches 0. Although a more exact explanation may have to take into account the distribution of the components of more various asymptotic Curie points, this simple equation is enough to reproduce the experimental data roughly.

In Fig. 11, $1/\chi$ at higher temperature approaches the Curie–Weiss term of $P_{\text{eff}}=7.94$ μ_B due to Eu^{2+} and takes almost the same value for both samples because of the similarity in the surroundings of the 15-crown-5 complex. By the least-squares method for the data in the higher temperature parts, $P_{\text{eff}}=c.$ 7.10 μ_B was obtained for both samples from the Curie constants. In this case, the asymptotic Curie point ($\theta=c.$ -83 K) for the Eu^{2+} only-doped polymer is larger in absolute value than that ($c.$ -50 K) for the Eu^{2+}–Zn^{2+} doubly-doped one. This finding suggests that some parts in the former have greater antiferromagnetic exchange interaction and that in other words the interatomic distance of the Eu^{2+} ions for the former is smaller than in the latter. The presence of Zn^{2+}, therefore, is considered to lead the nearest-neighbor Eu^{2+}–Eu^{2+} distance to become larger.

This gradual deviation from the Curie–Weiss law is better seen at a higher temperature for the Eu^{2+} only-doped polymer than for the Eu^{2+}–Zn^{2+} doubly-doped one. This behavior may be explained by the fact that the former is composed of a greater variety of asymptotic Curie points.

These results are summarized as follows. Some Eu^{2+} ions apparently exist in close proximity, since the antiferromagnetic interactions were observed for both samples, although it is not clear about whether they indicate the magnetic ordering. This is evidence of the formation of aggregates or clusters in the polymer. In addition, several Eu^{2+} ions are certainly far away from each other and these species are thought to be paramagnetic ($\theta=0$). Since the absolute value of θ was decreased by codoping with Zn^{2+} and namely antiferromagnetic interaction was weakened, it is concluded that Zn^{2+} efficiently separates the nearest Eu^{2+} ions from each other.

For the Cd^{2+} codoped complexes, Cd^{2+} appears to act like Zn^{2+}, judging from the unchanged profiles of the excitation and fluorescence spectra. The quantity of both Eu^{2+} and Cd^{2+} was found to be quite small. The Eu^{2+} content was relatively small for the Eu^{2+}–Cd^{2+} doubly-doped complexes, compared with the Eu^{2+} only-doped ones, so that the Cd^{2+} ions prevent Eu^{2+} from forming complexes with 15-crown-5. The larger ionic radius of Cd^{2+} (0.95 Å) than of Zn^{2+} (0.74 Å) [21] may account for the difference between Zn^{2+} and Cd^{2+}. The presence of Cd^{2+} is considered to disturb the formation of the Eu^{2+} complex or it would be more difficult for Cd^{2+} than for Zn^{2+} to form the halogeno complex anions.

The alkaline earth metal ions are present in the polymer, forming complexes with 15-crown-5. Their effects on the separation of Eu^{2+} may be much smaller than those of the halogeno complex anions. The presence of a bulky Ba^{2+} ion influences the surroundings of the Eu^{2+} complexes and reduces the fluorescence.

Luminescence lifetimes

We have performed multiexponential decay analysis, and succeeded in obtaining in best fit between the decay curves observed for the samples and calculated with one, two or three exponentials. This analysis has determined one, two or three luminescence lifetime values and an error in the longest lifetime for each sample has been at most of the order of 10%. The following discussion has been focused on the longest lifetime, in order to obtain information of the Eu^{2+}–Eu^{2+} distance in the species which have the best emission efficiency within each polymer.

Figure 12 indicates the dependence of luminescence lifetime of the polymer complexes on the $EuCl_2$ concentration. The luminescence lifetimes were apparently much longer for the Eu^{2+}–Zn^{2+} doubly-doped complexes than for the Eu^{2+} only-doped ones. The value of emission lifetime was 639 ns for the former and 477 ns for the latter, at each optimal $EuCl_2$ concentration (when they exhibit the maximum emission intensity). The curve in Fig. 12 was located in whole at the upper side for the Eu^{2+}–Zn^{2+} doubly-doped than for the Eu^{2+} only-doped complex. It indicates that the lu-

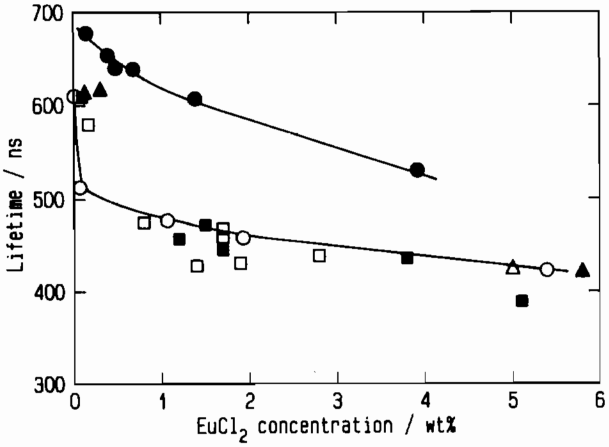

Fig. 12. Dependence of luminescence lifetime of Eu^{2+}–copoly-(MA15C5–MMA) (○) and Eu^{2+}–M^{2+}–copoly(MA15C5–MMA): M = Mg (△), M = Ca (▲), M = Sr (□), M = Ba (■), M = Zn (●), on $EuCl_2$ concentration.

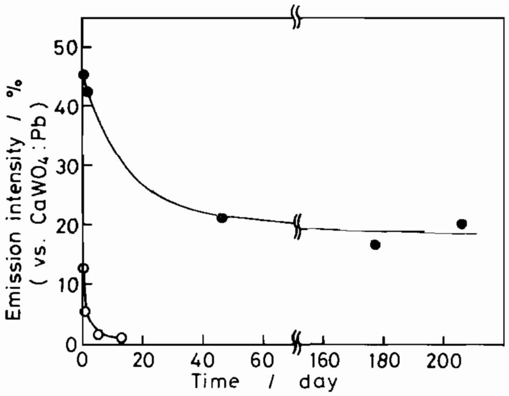

Fig. 13. Change on standing of the emission intensity of Eu^{2+}–copoly(MA15C5–MMA) (○) and Eu^{2+}–Zn^{2+}–copoly(MA15C5–MMA) (●).

minescence lifetimes which generally correspond to the emission efficiencies were elongated by virtue of the presence of Zn^{2+} inhibiting Eu^{2+} from concentration quenching. These results support the interpretation already given.

Stability against oxidation

The Eu^{2+} ions in the polymer were gradually oxidized to Eu^{3+} in the air. The changes in the emission intensity of the Eu^{2+} only-doped and Eu^{2+}–Zn^{2+} doubly-doped complexes with the passage of time are illustrated in Fig. 13. The resistivity of the Eu^{2+} ions in Eu^{2+}–Zn^{2+} doubly-doped complex against oxidation in the air was extremely enhanced compared with that for the Eu^{2+} only-doped complex. Although the reason is not known, the emission intensity for the former was maintained larger than the maximum intensity (*c.* 20% versus CaWO$_4$:Pb) for the Eu^{2+} only-doped complex over a period of 200 days.

Acknowledgements

The authors are very grateful to Dr K. Yoshimura, Kyoto University, for obtaining the data of the magnetic susceptibilities and many helpful discussions. We also thank Professor Y. Shirota, Osaka University, for his hospitality which allowed us to measure the gel permeation chromatograph (GPC) in his laboratory.

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