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Performance

Complexation of Europium Ion with Poly(Methacrylic Acid)s and Fluorescent Property of the Complexes

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Dedicated to Professor Dr. Georg Manecke on his 70th birthday

SUMMARY

The complexation of europium ion(Eu^{3+}) with poly(methacrylic acid) and its copolymers was studied. Poly(methacrylic acid-co-acrylamide) formed the tris(carboxylate)-coordinate Eu complex with extra large overall complexation constant while poly(methacrylic acid)s did the bis-coordinate ones. Transparent and flexible film containing much Eu ion was prepared by casting the complex solution of poly(methacrylic acid-co-methylacrylate). On exposure to ultraviolet light (393 nm), the film relatively strongly fluorescenced a red color based on the tris-coordinate and uniformly dispersed Eu complex.

INTRODUCTION

Characteristic physicochemical properties of lanthanides are based on their inner 4f electrons, and composites of lanthanides and polymers have been often utilized as fluorescent, laser materials and plastic magnets. But they are what lanthanide metals or oxides were dispersed in the polymer matrixes and the polymer complexes with lanthanide ions where the ions coordinately bound to polymers have not been studied except a few reports by Okamoto et al. (1-3). There is much interest in the preparation of a polymer-lanthanide complex which is attempt to give an organic polymer with lanthanide functions.

In this paper, poly(methacrylic acid)(PMA) and its copolymers and europium ion(Eu^{3+}) were used as polymer ligands and a lanthanide ion, and effect of the polymer ligand on the Eu complexation was studied in aqueous solution. The complexation and fluorescent property of Eu ion in the poly(methacrylic acid-co-methylacrylate) film were also studied.

EXPERIMENTAL

Materials

Poly(methacrylic acid)(PMA), oligo(methacrylic acid)(OMA), poly(methacrylic aicd-co-methylacrylate)(MMA), poly(methacrylic acid-co-butylacrylate) (BMA) and poly(methacrylic acid-co-acrylamide)(MAA) were prepared by radical polymerization. Composition and molecular weight of the polymers were determined by elemental analysis and gel permeation chromatography respectively. Suffix indicated mole fraction of the methacrylic acid residue in the copolymer. Mol. wt. of PMA = 5.1×10^5, OMA = 6.4×10^3, $MMA_{0.35}$ = 1.6×10^5, $BMA_{0.44}$ = 6.0×10^4, $MAA_{0.35}$ = 3.5×10^5, $MAA_{0.28}$ = 3.5×10^5. Methacrylic acid(MA) was used after distillation. Analytical grade reagent of europium nitrate was used.

Polymer Complex Films

Methanol solutions of the copolymer and the europium salt were mixed and stirred for several hours. The complex solution was casted on teflon

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plate and dried under saturated methanol vapor for 2 days, under air atmosphere for a day, and in vacuo at 50°C for 2 days.

Potentiometric Titration

All titrations were carried out under nitrogen atmosphere using carbon dioxide-free waters. Hydrogen ion activities were determined with a glass electrode and TOA HM-15A type pH meter. Sodium nitrate was added as supporting electrolyte (0.1 M).

Spectral Measurements

IR spectrum of the films was measured with JASCO IRA-1. X-Ray diffractmetry and X-ray microanalysis were carried out with Rigaku Denki model 2026 and JEOL JXA-733 respectively. Fluorescence spectrum was measured with Hitachi model MPF-4 fluorescence spectrophotometer.

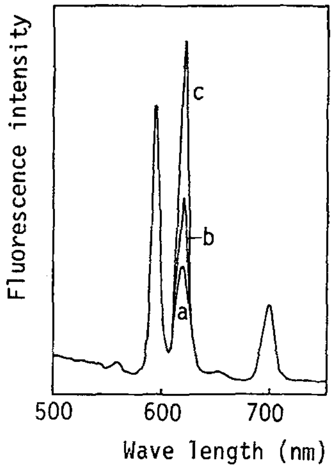

Figure 1. Fluorescence spectrum of the PMA-Eu complex solution (excitation: 393 nm)
pH=3.6, [Eu]=1 mM, [RCOOH of PMA] =0 (a), 2 (b), 10 (c) mM

RESULTS AND DISCUSSION

The fluorescence spectrum of the PMA-Eu complex solution was shown in Figure 1. While the wave lengths of peaks were not affected by the added PMA amount, only the fluorescence intensity at 617 nm (E_{617}) increased. The ratio of E_{617} to the fluorescence intensity at 591 nm (E_{591}), E_{617} / E_{591}, was plotted in Figure 2 with the molar ratio of the methacrylic acid residue in PMA to Eu ion ([RCOOH] / [Eu]) and with pH of the aqueous solution. E_{617} / E_{591} increased both with [RCOOH] / [Eu] and pH, which suggests E_{617} / E_{591} is corresponding to the complexation of PMA with Eu ion.

Potentiometric titration was carried out for the aqueous solution of Eu ion with PMA, OMA and MAA to get more detailed information of the complexation. PMA, OMA and MAA themselves and their Eu complexes behave as polyelectrolytes in aqueous solution, so that the modified Bjerrum method reported by Gregor (4) was used for calculation of following complexation constants.

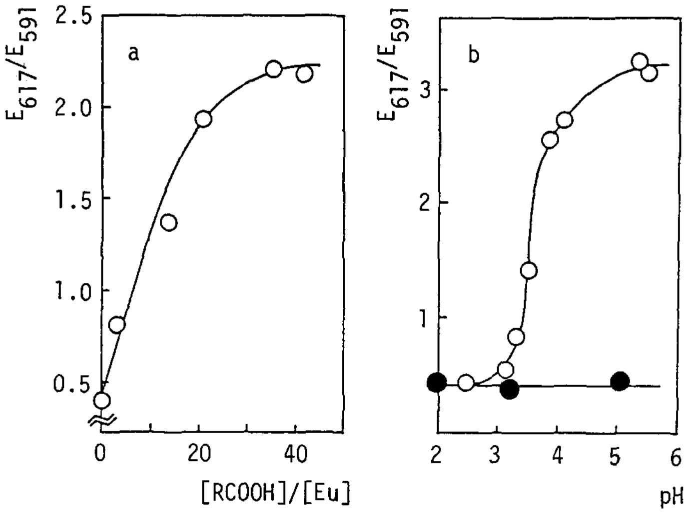

Figure 2. Effect of the added PMA amount (a) and pH (b) on the fluorescence intensity (exitation: 393 nm)
(a) pH 3.6, [Eu]=1 mM
(b) [Eu]=1 mM, [RCOOH of PMA]=20 mM

$$\mathrm{RCOOH} + \mathrm{Eu}^{3+} \xrightleftharpoons{k_1} \mathrm{RCOOEu}^{2+} + \mathrm{H}^+ \tag{1}$$

$$\mathrm{RCOOH} + \mathrm{RCOOEu}^{2+} \xrightleftharpoons{k_2} (\mathrm{RCOO})_2\mathrm{Eu}^+ + \mathrm{H}^+ \tag{2}$$

$$\mathrm{RCOOH} + \mathrm{RCOOEu}^{+} \xrightleftharpoons{k_3} (\mathrm{RCOOH})_3\mathrm{Eu} + \mathrm{H}^+ \tag{3}$$

Successive formation constants k_i and overall formation constant

$$\beta_n = \prod_{i=1}^{n} k_i \tag{4}$$

for the complexation of Eu ion with the corboxylic acids are summarized in Table 1. k_1 and k_2 for the Eu complex with PMA was ca. 10 times larger than those with the low molecular MA. But the third step of the carboxylate-complexation was not observed and β_n was limitted to ca. 10^9. It is assumed that the PMA chain can not easily form the tris-coordinate complex with its three carboxylate groups due to the steric hindrance of the polymer chain and the "large" Eu ion. The k_n and β_n values for the OMA-Eu complex were approximately equal to those of PMA, and moleculr weight, at least in this mol. wt. region, of the polymer ligand did not influenced the complexation constants. On the other hand, the Eu ion complexation proceeded to the third step for MAA; β_n was ca. 10^3 times larger than those of PMA and MA, and the MAA formed very stable tris-coordinate complex with Eu ion. It is considered that the comonomer residue in MAA decreases steric hindrance for the complexation.

Table 1

Complexation Constants of Poly(methacrylic acid)s with Eu ion

Ligand	pK_a	$\log k_1$	$\log k_2$	$\log k_3$	$\log \beta_n$
PMA	6.1	4.6	4.3	-	8.9
OMA	6.2	4.7	4.4	-	9.1
$MAA_{0.35}$	5.7	4.2	3.8	3.4	11.4
MA	4.5	3.2	2.6	2.4	8.2

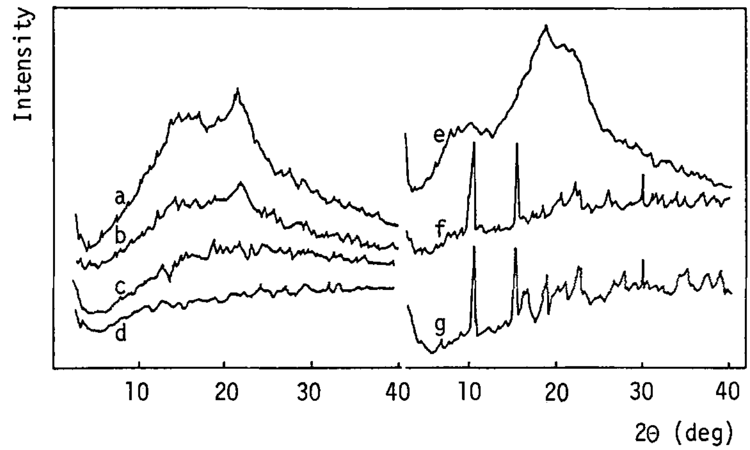

Figure 3. X-Ray diffract patterns of the $MMA_{0.35}$ and $BMA_{0.44}$-Eu complex films $MMA_{0.35}$ (a), the $MMA_{0.35}$-Eu complex: [RCOOH]/[Eu] =50 (b), 20 (c), 3 (d), $BMA_{0.44}$ (e), the $BMA_{0.44}$-Eu complex: [RCOOH]/[Eu]=3 (f), europium nitrate (g)

Polymer-Eu complex films were prepared by casting the methanol complex solutions containing various amount of Eu ion. Only $MMA_{0.35}$ gave flexible and transparent complex films independent of the Eu ion content.

X-Ray diffraction patterns of the MMA film, the BMA film and their Eu complex films were shown in Figure 3. In the case of $MMA_{0.35}$, hollow peak due to stereoregularity of the polymer disappeares as the Eu content increases (Figure 3: b,c,d). The sharp peakes of europium nitrate (g) is not also obserbed. But for the $BMA_{0.44}$-Eu film with higher Eu content (f), the peaks of europium nitrate was remained. This suggests that Eu ion is uniformly dispersed in the $MMA_{0.35}$ film in the wide range of the Eu ion content.

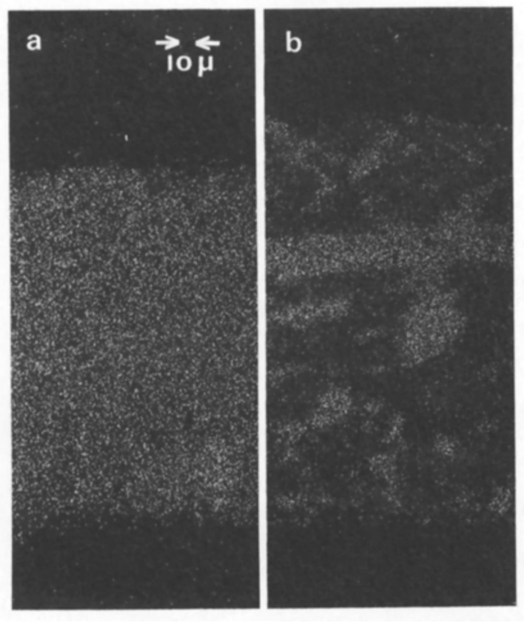

Figure 4. Distribution of Eu ion in the $MMA_{0.35}$ (a) and $BMA_{0.44}$ (b) film (photographs by X-ray micro analysis)

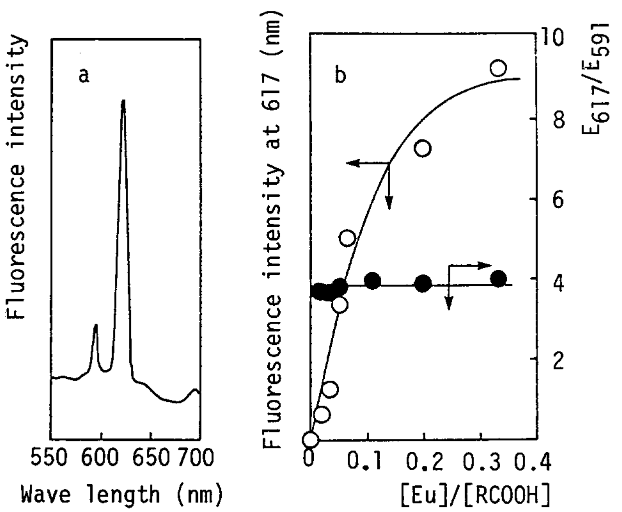

Figure 5. Fluorescence spectrum of the $MMA_{0.35}$ film (a) and effect of the Eu content in the film on the fluorescence intensity (b) (exitation: 393 nm)

The distribution of Eu ion in the films was measured with X-ray microanalysis (Figure 4). The photographs also support that Eu ion is uniformly dispersed in the $MAA_{0.35}$-Eu film and is partially isolated as its salt form in the $BMA_{0.44}$-Eu film.

The complexation of Eu ion in the $MAA_{0.35}$ film was also confirmed by its IR spectrum. $\nu_{C=O}$(-COOH) appeared at 1700 cm^{-1} for the $MMA_{0.35}$ film and $\nu_{C=O}$($-COO^-$) did at 1630 cm^{-1} for the $MMA_{0.35}$-Na salt film. On the other hand $\nu_{C=O}$($-COO^-$) of the $MMA_{0.35}$-Eu complex film shifted to lower wave number (1620 cm^{-1}), which suggested the complexation between carboxylate and Eu ion in the film.

The $MMA_{0.35}$-Eu film strongly fluorescenced a red color on exposure to ultraviolet light of wave length 393 nm and showed the sharp spectrum as shown in Figure 5 (a). Effect of the Eu ion content in the film on the fluorescence intensity was given Figure 5 (b). While E_{617} increased with the Eu ion content, the fluorescence intensity ratio (E_{617} / E_{591}) was relatively large and constant. This result means that Eu ion formed the tris-coordinate Eu complex in a wide Eu ion containing range in the MMA film.

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