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SYNTHESIS AND CHARACTERIZATION OF POLYMERS CONTAINING RARE EARTH METALS

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ABSTRACT

Europium and terbium salts of methacrylic acid (MA) and octanoic acid (OCA) were prepared by a method similar to that described in the literature. Either $Eu(MA)_3$ or $Tb(MA)_3$ with three double bonds (C=C) was used as a crosslinker containing rare earth metal ions, but the octanoic acid salts were used as additives. The salts were dissolved in methacrylic acid (<20%) and then copolymerized with methyl methacrylate (>80%) using AIBN (0.2 wt%) as initiator. The two types of polymers, one containing $Eu(MA)_3$ or $Tb(MA)_3$ and the other with $Eu(OCA)_3$ or $Tb(OCA)_3$, were synthesized by bulk copolymerization in molds made of two glass plates and characterized. The fluorescence spectroscopy of these polymers under ultraviolet/visible excitation light was investigated. The fluorescence excitation and emission spectra of the polymers showed the characteristic spectra of the free Eu^{3+} or Tb^{3+}. The fluorescence intensity of the rare earth metal ions increased with increasing rare earth metal content. Fluorescence measurements for $Eu(MA)_3$, $Tb(MA)_3$, and $Eu(OCA)_3$ polymers do not display fluorescence quenching behavior within the range of the rare earth metal content used in our experiments. But for $Tb(OCA)_3$ polymers, this phenomenon was observed, illustrating that ionic aggregates exist in $Tb(OCA)_3$ polymeric systems.

INTRODUCTION

Low molecular weight organic complexes of rare earth metals have been extensively studied for their fluorescence and laser properties. Polymer complexes with rare earth metals were investigated by Wolff and Pressley [1] and Nellay [2]. Polymers or copolymers in which rare earth metals are directly bonded to the polymeric chain have been studied by Okamoto, Ueba, and Banks [3-6]. Work related to the above has been done by Shen, Bao, Jian et al. [7-9].

This paper is concerned with the synthesis and characterization of crosslinked poly(methyl methacrylate-*co*-methacrylic acid) with europium methacrylate or terbium methacrylate as the crosslinker, and with europium octanoate or terbium octanoate as the additive.

Our main purposes are 1) to prepare Eu or Tb-containing poly(methyl methacrylate-*co*-methacrylic acid) materials with fluorescence properties under UV/vis light excitation; 2) to compare the fluorescence properties of two types of polymers, one containing $Eu(MA)_3$ or $Tb(MA)_3$ as the crosslinker, and the other containing $Eu(OCA)_3$ or $Tb(OCA)_3$ as the additive.

EXPERIMENTAL

Materials

Europia (Eu_2O_3) and terbia (Tb_4O_7) (>99.9%) were purchased from Shanghai and used without further purification. Europium and terbium methacrylate, $Eu[OOC-C(CH_3)=CH_2]_3$ and $Tb[OOC-C(CH_3)=CH_2]_3$ [$Eu(MA)_3$ and $Tb(MA)_3$] were prepared in our laboratory by the method described in the literature [10, 11]. Yield: about 80%. $Ln(MA)_3$ (Ln = Eu, Tb). IR(KBr): $\nu_{(C=O)}$, 1702 cm^{-1} (disappeared); $\nu_{(C=C)}$, 1623 cm^{-1} shifted to 1644 cm^{-1}; δ(OCO), 660 cm^{-1}; $\nu_{(OCO)}$, 1540 cm^{-1} (newly produced).

Europium and terbium octanoate, $Eu[OOC(CH_2)_6CH_3]_3$ and $Tb[OOC(CH_2)_6CH_3]_3$ [$Eu(OCA)_3$ and $Tb(OCA)_3$] were synthesized following routes similar to the above. Yield: about 80%. $Ln(OCA)_3$ (Ln = Eu, Tb). IR(KBr): $\nu_{(C=O)}$, 1702 cm^{-1} disappeared); δ(OCO), 684-712 cm^{-1}; $\nu_{(OCO)}$, 1540 cm^{-1} (newly produced).

The data for elementary analysis of these salts are listed in Table 1.

Eu^{3+} or Tb^{3+}-containing polymers: Different amounts of $Eu(MA)_3$ or $Tb(MA)_3$ were dissolved in 1.0 mL methacrylic acid. 5.0 mL methyl methacrylate was prepolymerized at 70°C with AIBN as initiator (0.2 wt%) for 30 min to increase the viscosity. The salt solutions were added to the prepolymer-

TABLE 1. Elementary Analysis (in %)

	$Eu(MA)_3$		$Tb(MA)_3$		$Eu(OCA)_3$		$Tb(OCA)_3$	
	C	H	C	H	C	H	C	H
Calculated	35.40	3.71	34.80	3.65	48.08	7.90	47.53	7.81
Found	36.00	3.86	35.88	3.61	47.51	8.44	47.09	8.04

ized solutions, then the mixtures were vigorously stirred and poured into glass molds which were made from two glass plates 3 mm apart. The edges of the molds were sealed with Teflon tape. The polymerization was carried out at 45°C for 24 h, successively at 60, 80, and 105°C for 2 h to complete the polymerization. The polymers obtained were all hard and transparent plates.

$Eu(OCA)_3$-polymer and $Tb(OCA)_3$-polymer blends. Poly(methyl methacrylate-*co*-methacrylic acid) (PMMA/MA)-$Eu(OCA)_3$ and PMMA/MA-$Tb(OCA)_3$ were prepared by our laboratory. $Eu(OCA)_3$ or $Tb(OCA)_3$ ($\leqslant$3 wt%) was dissolved in methacrylic acid (<20%) and added to the prepolymerized methyl methacrylate solution, then polymerized under the same conditions as the above.

Fluorescence Measurements

A Model RF-850 Hitachi fluorescence spectrometer was used to measure the spectra of the Eu or Tb-containing polymers. The plate samples were placed in the solid holder attached to the instrument. The measurements were carried out at room temperature under UV/vis excitation light. The sample thickness was 3 mm and there was no moisture absorbed in the samples.

RESULTS AND DISCUSSION

The composition and structure of $Eu(MA)_3$ and $Tb(MA)_3$ were determined by elemental analysis, IR, and ashing. There are three double bonds per $Eu(MA)_3$ or $Tb(MA)_3$ molecule, which thus can be employed as cross-linking agents in free-radical polymerization.

From IR results, the spectra of methacrylic acid and octanoic acid have an absorption peak at 1702 cm^{-1} caused by the $\nu_{(C=O)}$. Upon formation of the salts, the peak at 1702 cm^{-1} disappeared and a new peak appeared at 1540 cm^{-1}, corresponding to the $\nu_{s(OCO)}$.

TG and DTA curves of $Eu(MA)_3$ and $Tb(MA)_3$ are similar and show that their heat resistance is good; there was no weight loss up to 200°C.

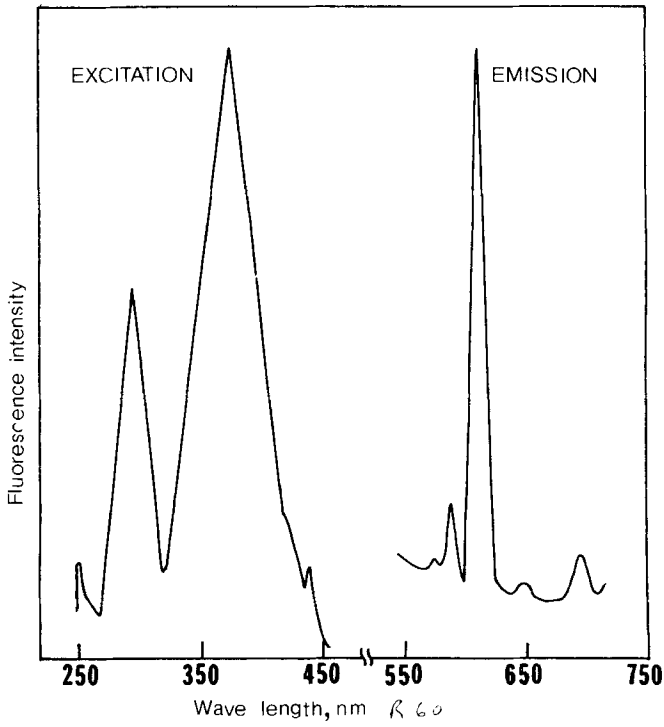

FIG. 1. Excitation and emission spectra of $Eu(MA)_3$ polymers. λ_{EM} = 616 nm, λ_{EX} = 375 nm.

Europium and terbium octanoate dissolve well in methacrylic acid compared to $Eu(MA)_3$ and $Tb(MA)_3$. It is important that the mutual solubility of these salts and the other monomers involved in copolymerization be considered. The latter salts will separate out and are not well-distributed in polymeric systems such as terbium octanoate.

DSC results of those polymers showed that the heat stability of Eu-containing polymers is improved compared to pure polymers. T_g was raised about 50°C by addition of 3 wt% to PMMA (T_g = 105°C) $Eu(OCA)_3$ blends; 70°C for 0.4 wt%/$Eu(MA)_3$, but for Tb-containing polymers, $Tb(MA)_3$ polymers, and $Tb(OCA)_3$-polymer blends, we did not find T_g to be changed noticeably.

The excitation and emission spectra of $Eu(MA)_3$ and $Tb(MA)_3$ polymers and of $Eu(OCA)_3$ and $Tb(OCA)_3$ polymer blends were found to be identical

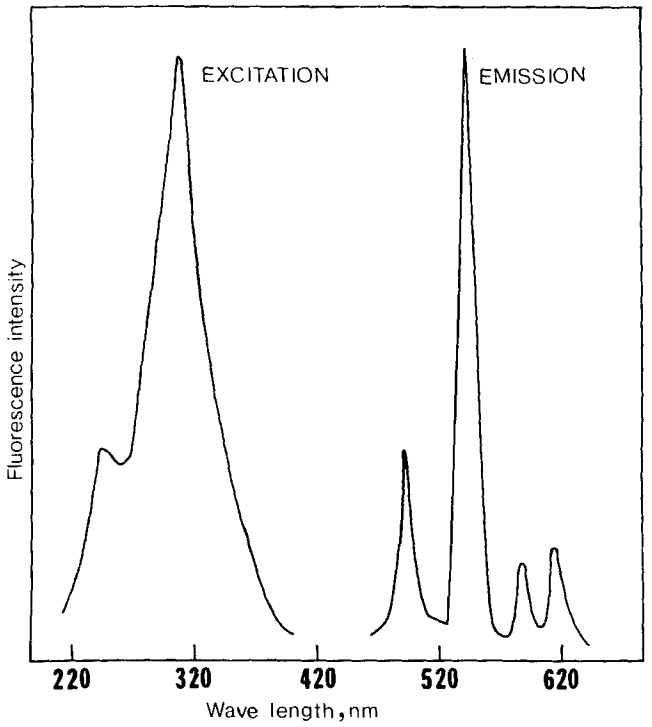

FIG. 2. Excitation and emission spectra of $Tb(MA)_3$ polymers. λ_{EM} = 546 nm, λ_{EX} = 301.7 nm.

(Figs. 1-4). The excitation spectra for $Tb(OCA)_3$ polymer blends were broad compared to those of $Eu(OCA)_3$ polymer blends, in agreement with published results [4].

All the fluorescence emission spectra show the characteristic spectra of the Eu^{3+} or Tb^{3+}. Eu-containing polymers reach their maximum excitation at 375 nm, and the characteristic line of its emission appears at 615 nm (corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition), even with a Eu content as low as 30 ppm in copolymers. Tb-containing polymers have their maximum excitation at 301.7 nm, maximum emission at 546 nm (corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition), even with a Tb content as low as 40 ppm

For Eu^{3+} and Tb^{3+} polymers, the fluorescence intensity increases with increasing Eu or Tb content in the low concentration range. The relationship

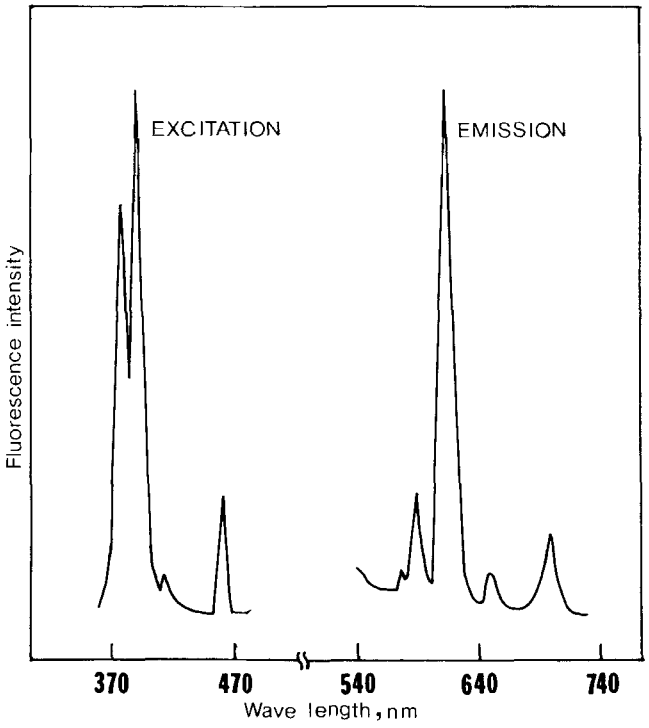

FIG. 3. Excitation and emission spectra of $Eu(OCA)_3$ polymers. λ_{EM} = 615 nm, λ_{EX} = 396 nm.

between fluorescence intensity and the rare earth content in the polymers is shown in Fig. 5. For the $Eu(OCA)_3$ polymer blends, it was observed that the fluorescence intensity increased linearly with increasing europium content in the polymers, but the relationship between the fluorescence intensity and Tb content in the polymer for $Tb(OCA)_3$ polymer blends were nonlinear, as shown in Fig. 6. The results indicate that ionic aggregate may exist in this system.

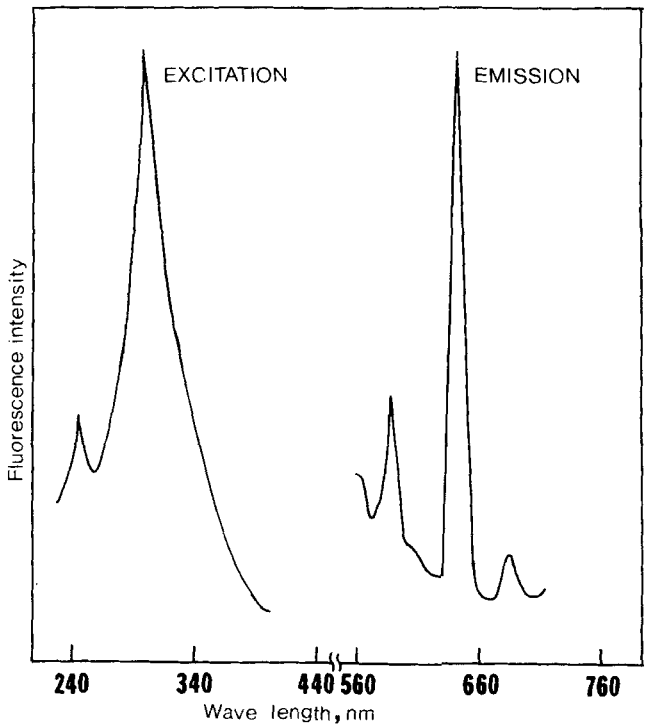

FIG. 4. Excitation and emission spectra of $Tb(OCA)_3$ polymers. λ_{EM} = 546 nm, λ_{EX} = 305 nm.

The characteristic fluorescence emission intensity for $Eu(MA)_3$-containing polymers was at least 10 times stronger than that of $Eu(OCA)_3$ polymer blends with the same Eu content (0.1 wt%). For $Tb(MA)_3$ polymeric systems the fluorescence emission intensity was about 3 times greater than that of $Tb(OCA)_3$ polymer blends at the maximum excitation with the same Tb content (0.1 wt%).

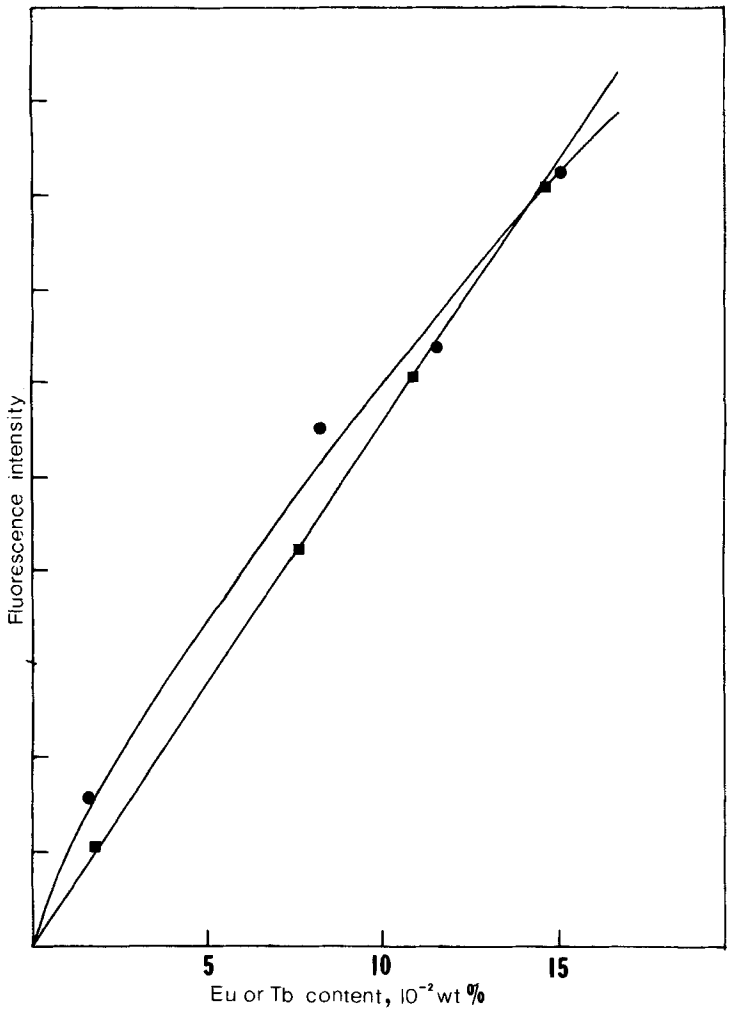

FIG. 5. Relationship between fluorescence intensity and content of Eu in $Eu(MA)_3$ polymers (■) and Tb in $Tb(MA)_3$ polymers (●).

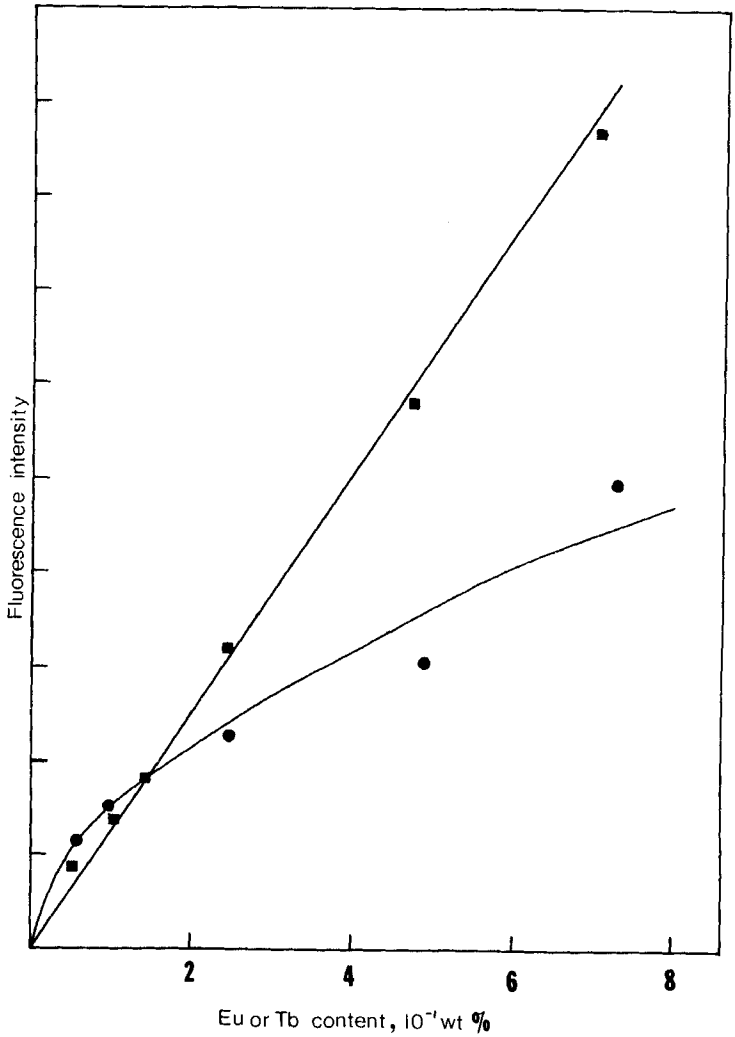

FIG. 6. Relationship between fluorescence intensity and content of Eu in $Eu(OCA)_3$ polymer blends (■) and Tb in $Tb(OCA)_3$ polymer blends (●).

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