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FLUORESCENCE PROPERTIES OF EUROPIUM AND TERBIUM TRIUNDECYLENATE-CONTAINING POLYMERS AND SOLUTIONS

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ABSTRACT

Europium triundecylenate, $\text{Eu}(\text{UA})_3$, and terbium triundecylenate, $\text{Tb}(\text{UA})_3$, were prepared by the method described in our previous paper. Either $\text{Eu}(\text{UA})_3$ or $\text{Tb}(\text{UA})_3$ was dissolved in methacrylic acid (< 20%) and copolymerized as a crosslinker with methyl methacrylate (> 80) by bulk polymerization in molds made of two glass plates. The fluorescence spectroscopy of these Eu- or Tb-containing polymers under ultraviolet/visible excitation light was investigated. The fluorescence spectroscopy of solutions of $\text{Eu}(\text{UA})_3$ or $\text{Tb}(\text{UA})_3$ in methacrylic acid was measured and compared with that of the solid-state Eu- or Tb-containing polymers. The fluorescence excitation and emission spectra of the solutions and polymers showed the characteristic features of free Eu^{3+} or Tb^{3+} . The lifetime fluorescence of the solutions and polymers with Eu^{3+} are also included.

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INTRODUCTION

Polymers containing rare earth metals have been studied by some researchers [1-4]. We have reported methyl methacrylate-methacrylic acid copolymers using either europium, terbium trimethacrylate as crosslinkers or europium, terbium trioctanonate as additives [5]. This paper is concerned with methyl methacrylate-methacrylic acid copolymers crosslinked by europium or terbium triundecylenate ($\text{Eu}(\text{UA})_3$, $\text{Tb}(\text{UA})_3$). The fluorescence properties of Eu- or Tb-containing solutions and solid-state polymers are discussed.

EXPERIMENTAL

Materials

Europia (Eu_2O_3) and terbia (Tb_4O_7) (>99.9%) were purchased from Shanghai and used without further purification. Methyl methacrylate (MMA), methacrylic acid (MA), and 2,2-azoisobutyronitrile (AIBN) were purified prior to use. Europium and terbium triundecylenate, $\text{Eu}(\text{OOC}(\text{CH}_2)_8\text{CH}=\text{CH}_2)_3$ and $\text{Tb}(\text{OOC}(\text{CH}_2)_8\text{CH}=\text{CH}_2)_3$, were prepared in our laboratory by using the method described in the literature [5]. Yield: ~75%. IR (KBr Wafer): $\nu(\text{C}=\text{O})$ 1702 cm^{-1} (disappears); $\nu_{\text{as}}(\text{OCO})$ 1540 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1430 cm^{-1} (appears).

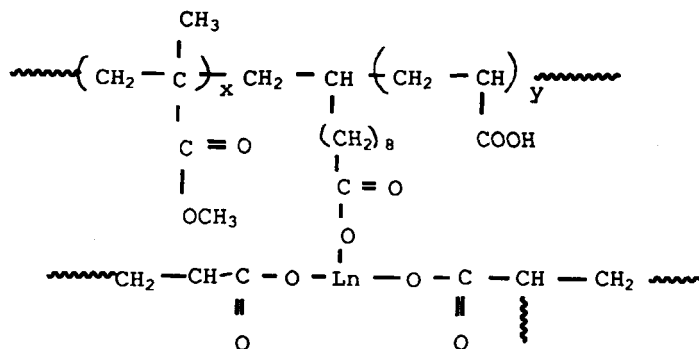
The data for the elementary analysis of the salts are listed in Table 1. The Ln wt% (Ln = Eu, Tb) was determined by ashing:

Eu- or Tb-containing polymers were prepared by a method similar to that reported in our previous paper [5]. Different amounts of $\text{Eu}(\text{UA})_3$ or $\text{Tb}(\text{UA})_3$ were dissolved in MA, then mixed with MMA. The mixture was copolymerized by radical bulk copolymerization in glass molds. The copolymers obtained were transparent plates. The Eu or Tb content in the

TABLE 1. Elementary Analysis

	Eu(UA) ₃			Tb(UA) ₃		
	C (%)	H (%)	Eu (%)	C (%)	H (%)	Tb (%)
Found	56.36	7.98	21.26	55.45	8.40	22.03
Calculated	56.48	8.19	21.65	55.92	8.11	22.40

copolymer is in the 0–5.5% range. The structure of the copolymer can be written as



Fluorescence Measurements

A Model RF-850 Hitachi fluorescence spectrometer was used to measure the spectra of the Eu- or Tb-containing polymers and solutions. The measurements were carried out under UV/Vis light at room temperature. The second harmonic (530 nm) of a pulsed YAG:Nd laser was used as the excitation source for the lifetime measurements.

RESULTS AND DISCUSSIONS

The Eu and Tb salts prepared were determined to be of the form $\text{Eu}(\text{OOC}(\text{CH}_2)_8\text{CH}=\text{CH}_2)_3$ and $\text{Tb}(\text{OOC}(\text{CH}_2)_8\text{CH}=\text{CH}_2)_3$ by elemental analysis, IR, and ashing. There are three double bonds per molecule of $\text{Eu}(\text{UA})_3$ and $\text{Tb}(\text{UA})_3$, which can be used as a crosslinking agent in free radical polymerization.

Because the molecule of $\text{Ln}(\text{UA})_3$ has a long hydrophobic chain, the solubility of $\text{Ln}(\text{UA})_3$ in methyl methacrylate–methacrylic acid (MMA-MA) mixture was much better than that of $\text{Ln}(\text{MA})_3$ and $\text{Ln}(\text{OCA})_3$, e.g., $[\text{Ln}(\text{OOC}(\text{CH}_2)_6\text{CH}_3)_3]$, in the same medium. Therefore, we were able to prepare copolymers with high concentrations of $\text{Eu}(\text{UA})_3$ and $\text{Tb}(\text{UA})_3$ in order to observe their fluorescence properties.

Figure 1 shows the fluorescence spectra of solutions of $\text{Eu}(\text{UA})_3$ in methacrylic acid. Besides the maximum excitation peak at 320 nm, the

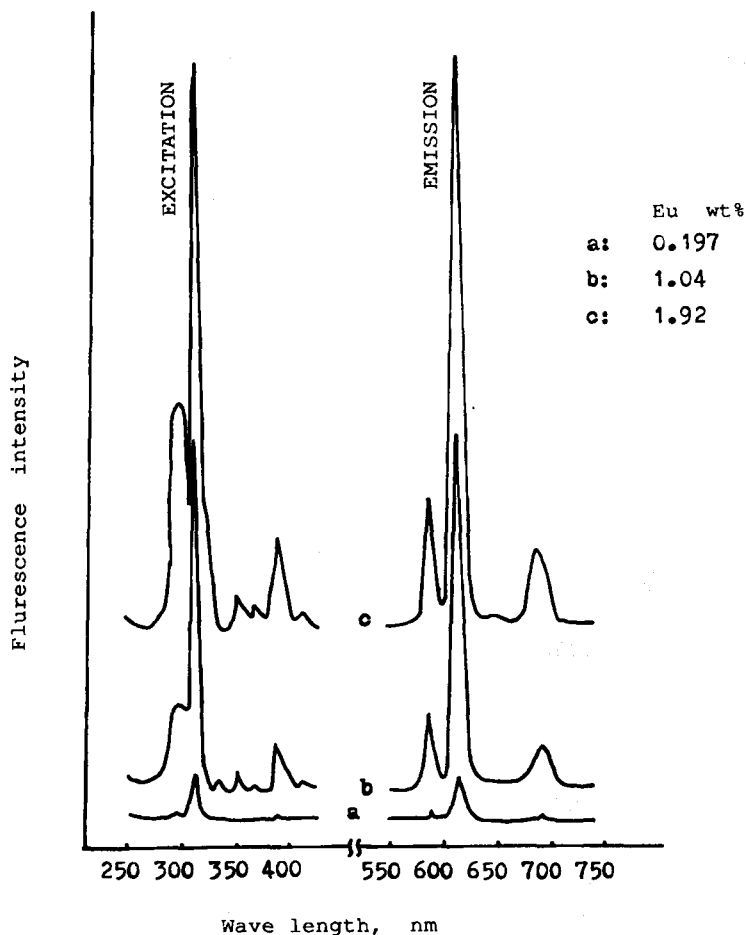


FIG. 1. Excitation and emission spectra of solutions of $\text{Eu}(\text{UA})_3$ in MA. $\lambda_{\text{EM}} = 616 \text{ nm}$, $\lambda_{\text{EX}} = 320 \text{ nm}$.

second largest peak at 290 nm can be clearly seen, but the polymers had only one broad peak at 290–340 nm (see Fig. 2). Figure 3 shows the relationship between fluorescence intensity and the europium content. The fluorescence intensity and the europium content have an approximately linear relationship within the concentration reached in our experi-

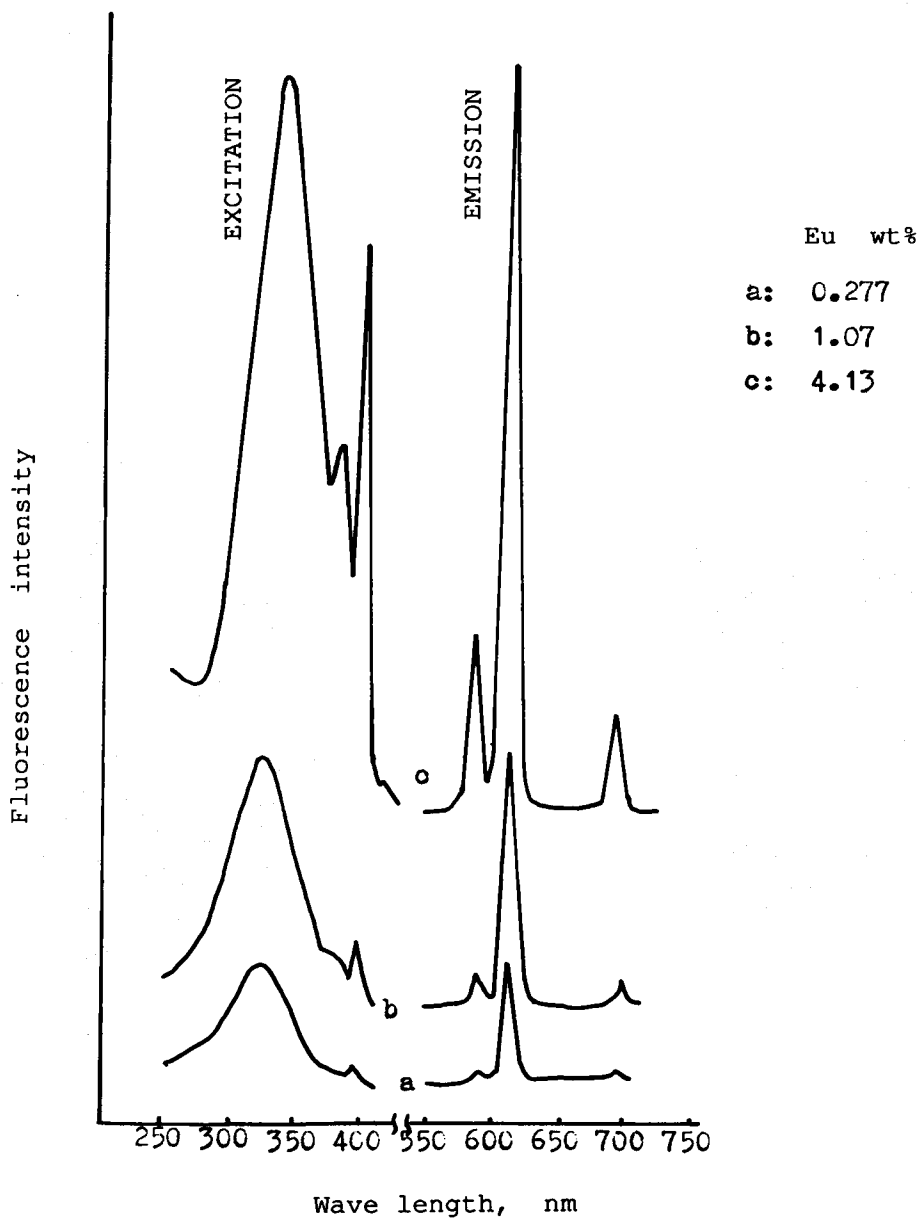


FIG. 2. Excitation and emission spectra of $\text{Eu}(\text{UA})_3$ polymers. $\lambda_{\text{EM}} = 616$ nm, $\lambda_{\text{EX}} = 327$ nm.

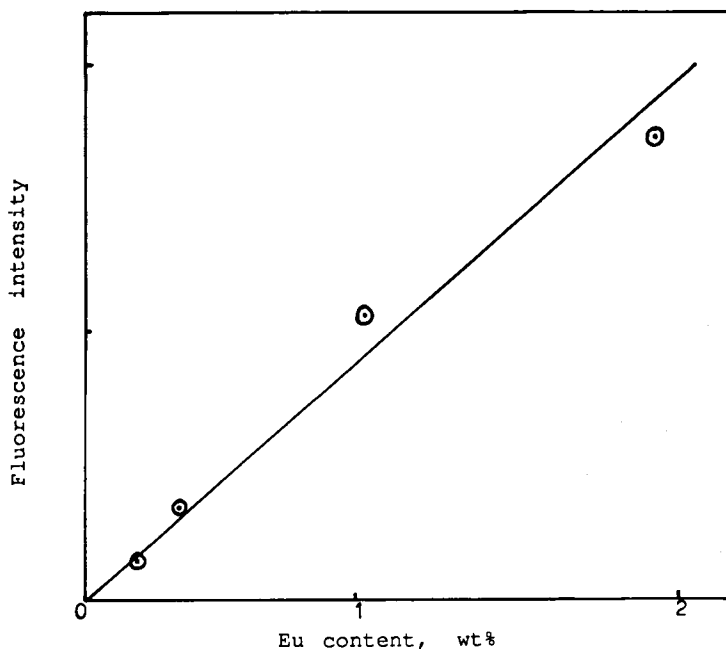


FIG. 3. Relationship between fluorescence intensity and Eu content in solution of $\text{Eu}(\text{UA})_3$ in MA.

ment. The fluorescence intensity of the solution of $\text{Tb}(\text{UA})_3$ in MA was too low to be detected.

Fluorescence spectra of $\text{Eu}(\text{UA})_3$ -containing polymers are shown in Fig. 2. The polymers reached their maximum excitation at 325 nm, and the characteristic line of their emission appeared at 616 nm (corresponding to a ${}^3\text{D}_0 \rightarrow {}^7\text{F}_2$ transition). There was a second large excitation peak at 390 nm, which cannot be seen for $\text{Eu}(\text{MMA})_3$ or $\text{Eu}(\text{OCA})_3$ polymers.

The fluorescence spectra of $\text{Tb}(\text{UA})_3$ -containing polymers indicated that the maximum excitation wavelength changed from 295 nm at a low content of $\text{Tb}(\text{UA})_3$ to 247 nm at a high content of $\text{Tb}(\text{UA})_3$ (Fig. 4). This could be explained as the following: The polymer matrix becomes more rigid with increasing $\text{Tb}(\text{UA})_3$ content, and the movement of Tb thus becomes more restricted and a higher energy is needed to excite the f-electrons. The maximum emission was at 547 nm for all $\text{Tb}(\text{UA})_3$ -containing polymers.

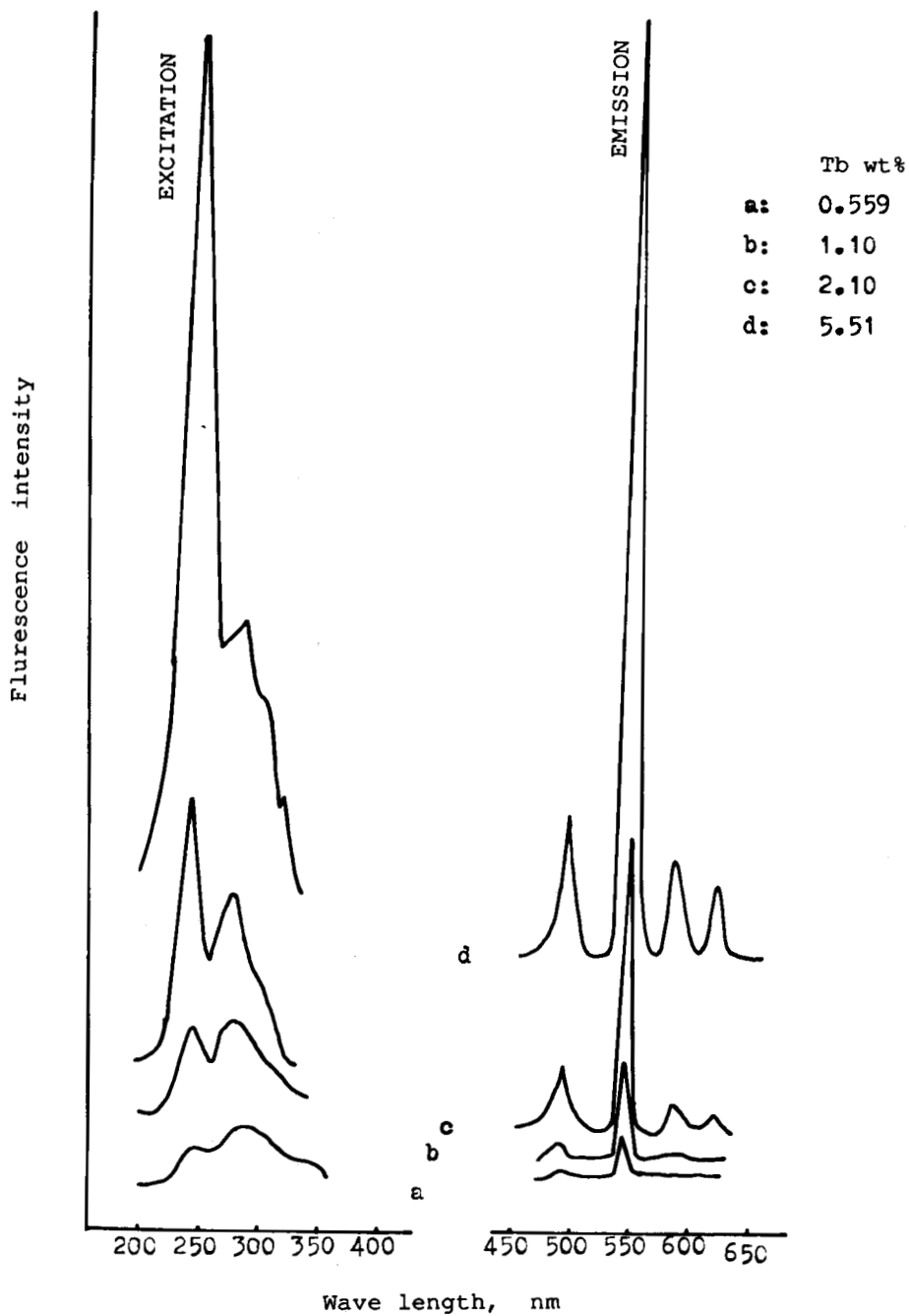


FIG. 4. Excitation and emission spectra of Tb(UA)₃ polymers. $\lambda_{EM} = 547$ nm, $\lambda_{EX} = 247$ nm.

Figure 5 shows the relationship between the fluorescence intensity of Ln-containing polymers and the Ln content (Ln = Eu, Tb). Fluorescence intensity increased linearly with an increase in Ln content up to 5.51 wt%. This indicates that $\text{Ln}(\text{UA})_3$ is distributed uniformly in the system and that ionic aggregation did not exist.

The measured decay curves for the fluorescence were approximately exponential. The lifetime obtained from the fluorescence curve was 0.5 ms for solid salts $[\text{Ln}(\text{UA})_3]$, solutions, and polymers.

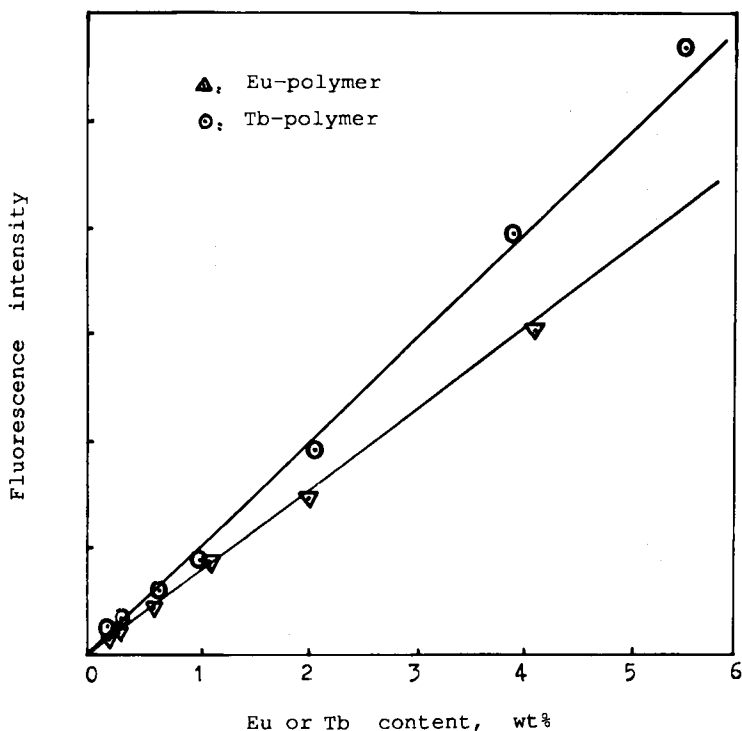


FIG. 5. Relationship between fluorescence intensity and Ln content in polymers.

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