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The Fluorescence of Transparent Polymer Films of Rare Earth Complexes

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Abstract

Fluorescence films of rare earth (Eu^{3+} or Tb^{3+}) β-diketone chelates dispersed in a PMMA polymer matrix were prepared and their fluorescence properties were investigated. Dependence of rare earth contents on emission properties and transparencies of the films are also given. Influence of the substituents of the ligand on spectroscopic properties and fluorescence intensities were discussed. The strongest red and green fluorescence was obtained when DBM (dibenzoylmethane) was used as a ligand for the Eu-film and AcA (acetylacetone) for the Tb-film. The relation between the nature of ligands and efficiencies of energy transfer in the film systems was also studied.

Introduction

The fluorescence properties of rare earth complexes are of considerable interest in connection with energy transfer from an organic ligand to a rare earth ion [1–3]. These properties have also attracted many researchers from the viewpoint that rare earth chelate systems are important as laser materials. However, studies of fluorescence properties have mainly taken place in systems in solutions or crystallines of rare earth β-diketone chelates. Recently, Okamoto *et al.* [7–9] and Nishide *et al.* [10] have investigated the fluorescence properties of the rare earth polymer, but energy transfer from ligand to rare earth has not been considered in detail. In this paper, we report on fluorescence characteristics and the effects of the ligands listed below on the fluorescence intensities, and the energy transfer for rare earth ion containing polymethylmethacrylate (PMMA) films, dibenzoylmethane (DBM), benzoylacetone (BA), and acetylacetone (AcA). The films will be useful for agriculture because of their particular UV absorption and visible emitting properties.

Experimental

Materials

Three β-diketones (DBM, BA and AcA) were chosen as ligands for the PMMA polymer system. The ligands (special grade), acetone and PMMA were purchased from WAKO Pure Chemical Industries Ltd.

Anhydrous rare earth bromides were prepared by reaction of rare earth oxides (99.99%) with ammonium bromide, a mixture of which was fired in vacuum at 300–400 °C for 1 h.

Rare earth bromide and β-diketone (DBM, BA, or AcA) were dissolved into 10 ml of acetone (solution 1). 0.2 g of PMMA was also dissolved into 10 ml acetone (solution 2). A mixture of solution 1 and 2 was stirred and poured into a glass dish.

The transparent films were obtained while solvent acetone was slowly evaporated from the above solution and further dried under vacuum at room temperature for 10 h. The thickness of all of the films was approximately 0.05 mm.

Measurement Technique

Absorption spectra and transparencies of the films were observed by the use of a Shimadzu double beam spectrophotometer, model UV-180. Emission and excitation spectra were determined on a Shimadzu absolute spectrofluorophotometer, model RF-502, equipped with an automatic compensation and procalibration system.

Results and Discussion

Fluorescence of the Rare Earth Films

Figure 1 shows a fluorescence spectrum of transparent films containing Eu^{3+} ions. The spectrum is composed of 611 nm (the maximum emission peak, $^5D_0$–$^7F_2$), 545 nm ($^5D_1$–$^7F_0$), 580 nm ($^5D_0$–$^7F_0$) 595 nm ($^5D_0$–$^7F_1$), and 650 nm ($^5D_0$–$^7F_3$). The spectrum is not dependent on the type of β-diketone, and is roughly consistent with that of inorganic Y_2O_3:Eu, which was widely used as a red component of color TV. Normalized plots of the 611 nm emitting intensity against the Eu^{3+} ion content in the films

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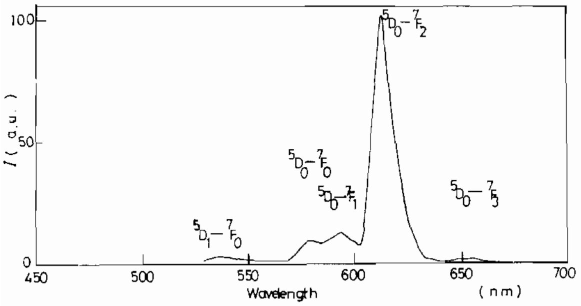


Fig. 1. Emission spectra of EuDBM–PMMA film. (λ_{ex} = 395 nm).

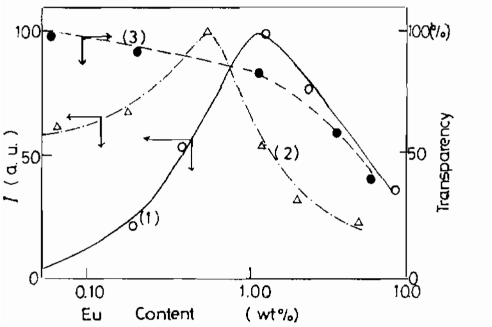


Fig. 2. The dependence of Eu content on fluorescence intensity and transparency in EuDBM–PMMA and EuBA–PMMA film systems. (1) Intensity *vs.* Eu content in EuDBM–PMMAA; (2) intensity *vs.* Eu content in EuBA–PMMA; (3) intensity *vs.* Eu content in EuAcA–PMMA. Transparency of PMMA film: 100%.

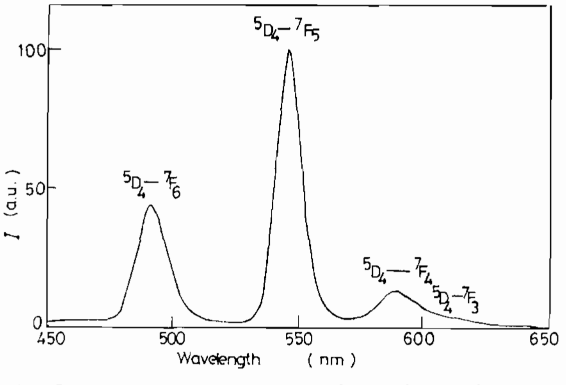


Fig. 3. Fluorescence spectrum of the films of TbAcA–PMMA system (λ_{ex} = 390 nm).

containing Eu–DBM and Eu–BA are shown in Figs. 1 and 2. That of the Eu–AcA film was not given because its intensity was too weak to observe. It is seen from Fig. 2(1) and (2) that the optimum region of the Eu contents for EuDBM- and EuBA-films are found to be about 1.2–1.5 and 0.5–0.6 wt.%, respectively. The dependence of Eu content on the emission intensity in the film system is also similar to that of inorganic oxide phosphors. The intensity gradually increases through a maximum and then decreases with increasing Eu content. This phenomenon is due to the concentration quenching mechanism corresponding to an electrostatic multipolar interaction [7].

Figure 2(3) shows the relation between the transparency and the Eu content for EuDBM-films. It can be noted that the transparency in the visible region lowers with increasing Eu content. Therefore, the fact that the emission intensity decreases with increasing Eu content is partly due to the decrease of the transparency, in addition to the concentration quenching mechanism.

Emission spectra of the film systems for TbDBM–, TbBA– and TbAcA–PMMA are shown in Fig. 3. The spectra consist of a very strong peak at 545 nm ($^5D_4-^7F_5$), weak peaks at 490 nm ($^5D_4-^7F_6$) 580 nm ($^5D_4-^7F_4$) and 620 nm ($^5D_4-^7F_3$) and are also similar to that of Tb^{3+}-actived inorganic oxide phosphors.

A Tb content dependence on the fluorescence intensity for the Tb-film containing ligands DBM, BA, and AcA is shown in Fig. 4(1), (2) and (3), respectively. From Fig. 4, the optimum Tb content was about 0.9, 1.8 and 0.4 wt.% for TbDBM- TBBA- and TBAcA-film, respectively. As discussed above for the Eu-film systems, there would be a similar concentration quenching mechanism for the Tb-films.

It is well known that rare earth ions are incorporated in β-diketone chelates by coordination through oxygen atoms acting as donors. Thus, the nearest neighbors of the rare earth ion would be oxygen atoms. In the Eu-films or the Tb-films, Eu or Tb ions are oxygen nearest neighbors. Therefore, the Eu- and Tb-films display fluorescence properties which resemble that of the inorganic oxide system.

The Tb content dependence of the transparency of the TbAcA-PMMA film is shown in Fig. 4(4). The situation of Tb-films is very similar to that of Eu-films.

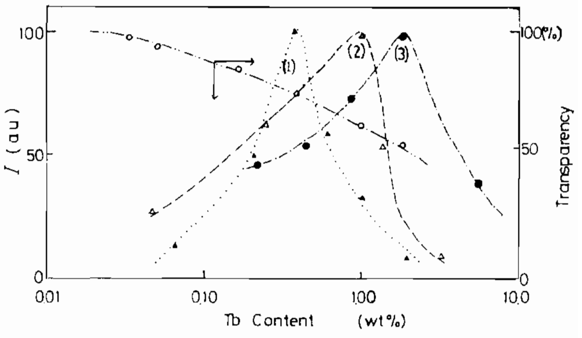


Fig. 4. The dependence of content on fluorescence intensity and transparency in Tb-film systems. (1) Intensity *vs.* Tb content in TbAcA–PMMA film; (2) intensity *vs.* Tb content in TbBA–PMMA film; (3) intensity *vs.* Tb content in TbDBM–PMMA film; (4) transparency *vs.* Tb content in TbAcA–PMMA film systems. Transparency of PMMA film: 100%.

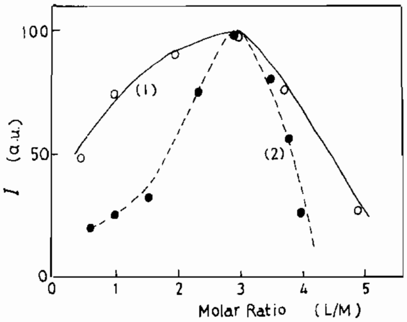


Fig. 5. The dependence of molar ratio [DBM/Eu] (1) and [AcA/Tb] (2) on fluorescence intensities in the Eu-films and the Tb-films.

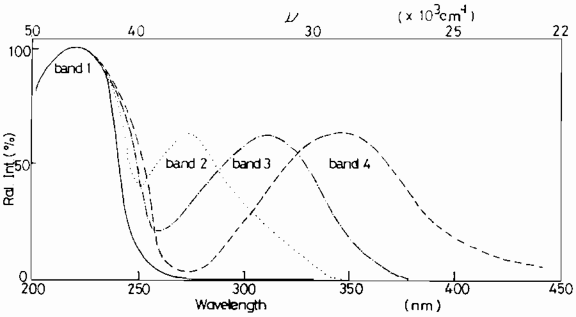
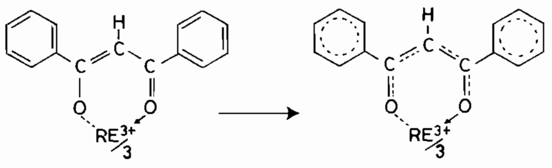


Fig. 6. Relative absorption spectra of the PMMAA and the RE-chelate–PMMA films. RE = Eu or Tb; the film thickness: 0.03 nm.

It is observed that the optimum mole ratio of ligand to rare earth at the maximum fluorescence intensity is found at about 3, as shown in Fig. 5(1) and (2) for EuDBM- and TbAcA–PMMA films. This fact suggests that in the film system the number of atoms on 8 coordination to Eu^{3+} or Tb^{3+} ion is 6, although there are publicated numbers for precipitating chelates of the EuDBM system [4].

Absorption and Excitation of Film Systems

The absorption spectra of rare earth film systems are shown in Fig. 6. Spectra of rare earth diketone PMMA film are composed of two bands, one of which corresponds to π^*–n absorption of the PMMA matrix (band 1). But band 2, band 3, and band 4 in Fig. 6 are due to the same kind of electronic transition, probably a π^*–π, associated with a conjugated system. All the double bonds in the complex are placed alternately and form a large π electron conjugate system [4]:



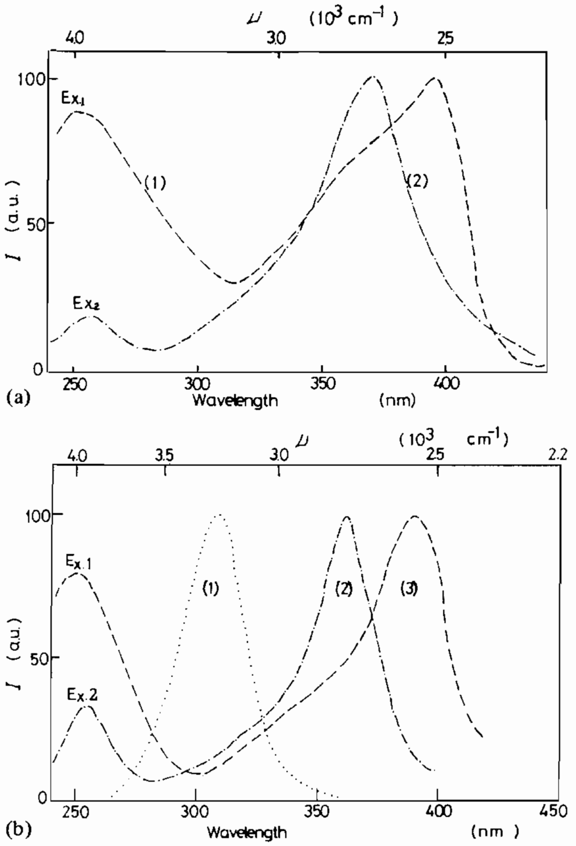
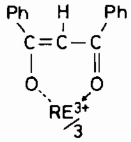
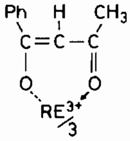
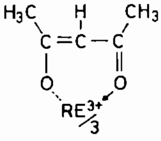


Fig. 7. (a) The excitation spectra of Eu^{3+} having different ligands in PMMA systems (λ_{em} = 611 nm). (1) EuDBM; (2) EuBA. (b) The excitation spectra of Tb^{3+} having different ligands in PMMA systems (λ_{em} = 545 nm).

The absorption band of films containing the metal complexes does not show any difference on changing the rare earth (Eu or Tb); the absorption band of the ligand parts in the films also shows no significant difference in comparison with corresponding free ligand molecules [4]. It is also seen from Fig. 6 that the absorption peak shifted gradually to a longer wavelength when the methyl group of β-diketone was gradually substituted for a phenyl group. The shift of the absorption peak is due to an increase in the length of the conjugated system as a whole. The excitation spectrum of the Eu-films and Tb-films at an optimum rare earth content are shown in Fig. 7. It is observed that the excitation spectra of rare earth films correspond to their absorption spectra. One of the two bands corresponds to absorption of PMMA itself and the other to that of the rare earth chelates in the films. No excitation band corresponding to absorption of PMMA for the TbAcA-film system was observed. From the above results, we see that the energy transfer to rare earth ions occurred not only from the β-diketone, but also from PMMA used as a matrix.

TABLE I. Dependence of the Fluorescence Intensity of the Rare Earth in the Film Systems on the Nature of the β-Diketone Used as Ligand

Film system:	REDBM–PMMA chelate	REBA–PMMA chelate	REAcA–PMMA chelate
			
Relative intensity:			
Eu-film	1.00	0.66	(0.01)
Tb-film	0.40	0.50	1.00

Energy Transfer

As mentioned above, the fluorescence of Eu^{3+} or Tb^{3+} is exhibited when they are excited with UV light absorbed by the ligand in the film system. The facts can be explained by a model of the intramolecular energy transfer from a ligand to a rare earth ion, as reported previously for solutions or crystallines of rare earth chelates [1–3, 12, 13]. However, the fluorescence intensity of the rare earth in our film systems varies considerably with the nature of the β-diketone used as a ligand. In other words, the substitution of a β-diketone in a film has drastically influenced the efficiency of the energy transfer. The intensities for the Eu-film and Tb-film system were found to vary as shown in Table 1. Crosby *et al.* have suggested that, for rare earth chelates, the triplet state of the complexes played an important role in the energy transfer from the ligand to rare earth ions [14]. Sato *et al.* have demonstrated that the fluorescence yield shows an optimum energy difference between the lowest triplet energy level of the complex and the resonance level of the rare earth ion [15]. From refs. 12 and 14, the energy level of the triplet state of the EuDBM– and Tb–PMMA systems seems to position at nearly 20 500 cm^{-1}. Similarly, those of the triplet state of REBA–PMMA and REAcA–PMMA system (RE = Eu or Tb) are roughly 21 500 and 25 000 cm^{-1}, respectively, as sketched in Fig. 8. The fact that the EuDBM–PMMA has an emission intensity that is stronger than that of EuBA– and EuAcA–PMMA in the Eu-film systems suggests that there might be an optimum energy difference between the triplet state energy and the resonance level of the Eu^{3+} ion.

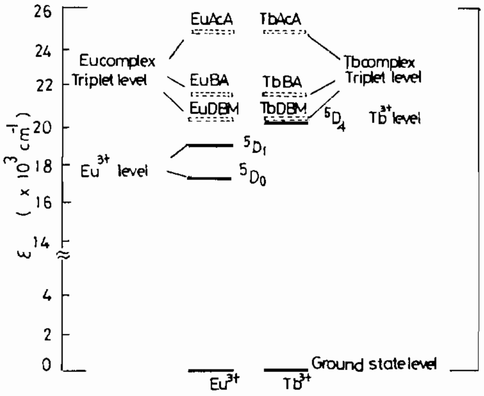


Fig. 8. The triplet state energy of the Eu-film and the Tb-film systems and resonance levels of corresponding RE ion (the solid lines indicate resonance levels and shadow lines connect the triplet levels of RE chelates in the film systems).

The triplet state energy of EuBA and EuAcA increases gradually to a higher position than that of EuDBM. Thus, under the resonance mechanism, the exchange interaction of the lowest excited state ($^5D_0$) level of the Eu^{3+} ions must be diminished gradually. Therefore, fluorescence intensities of the Eu-film system decreased in order of EuDBM–, EuBA–, and EuAcA–PMMA. The fluorescence intensities of the Tb-film systems gradually increase in order of TbDBM–, TbBA–, and TbAcA–PMMA. The lowest fluorescence intensity was observed for the TbDBM-PMMA film system. The situation of the Tb-film system was also explained by the conclusion given in ref. 15. The energy difference between the triplet state of TbDBM and the $^5D_4$ level of the Tb^{3+} ion is so small that it induces a thermal deactivation process [15]. The largest fluorescence intensity of Tb-film systems was observed for the TbAcA–PMMA system, because there might be an optimum energy difference between the triplet state of TbAcA and $^5D_4$ level of Tb^{3+} ion. In addition, the fluorescence intensity of TbDBM and TbBA–PMMA has showed 10 time and 30 time increase respectively, but that of TbAcA–PMMA film has given only a smaller increase when the temperature is lowered from room temperature to LN_2 temperature. This fact may also be explained by the above discussion.

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