

STUDY ON FLUORESCENCE BEHAVIOUR OF Eu^{3+} CONTAINING POLY(METHYL METHACRYLATE)*

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ABSTRACT

Fluorimetry has been used to characterize ionomers synthesized by copolymerization of methyl methacrylate, methacrylic acid and europium methacrylate (EMA). Under excitation of UV light at 375 nm no self-quenching was found in fluorescence of EMA containing ionomers at 615 nm within the concentration range of 1.6×10^{-2} to 11.49×10^{-2} mol%. This means that the distance between two Eu^{3+} ions is larger than 5 nm. In the same concentration range self-quenching took place in europium octanoate (EOA) containing poly(methyl methacrylate) in which EOA was doped as an additive.

INTRODUCTION

Fluorimetry has long been used in the studies of biological macromolecules^[1,2]. For instance, since the extent of nonradiative energy transfer is a sensitive function of the distance separating the donor and acceptor chromophores, the phenomenon can be used to measure their separation. This principle was used to determine the distance between Tb^{3+} and Co^{2+} ions bound to specific sites in the enzyme thermolysin and the result obtained was found to be in good agreement with its known molecular structure^[3]. In recent decades, this powerful research tool has also been applied in the study of the structure of synthetic polymers^[4]. When two polymers are labelled with donor and acceptor chromophores, respectively, and a film is cast from a solution containing a mixture of the two, nonradiative energy transfer from the donor to the acceptor should be small if the two polymers are segregated into two phases, but will be extensive if they form a single phase^[5]. Generally speaking, energy absorbed by a chromophore may be transferred to a second chromophore up to 5 nanometers away if the emission spectrum of the donor overlaps the absorption spectrum of the acceptor^[6].

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Rare earth ions possess many energy levels and have been used as fluorescence source for various materials doped with them. In most situations the levels of one kind of rare earths are all the same^[7]. One of the rare earth ions absorbs the incident energy and then fluorescence emission can be transferred to another through nonradiative energy transfer so long as the distance between the two ions is within the critical distance for quenching^[8]. This kind of quenching is usually called self-quenching or concentration quenching. A study of the energy transfer between Eu^{3+} ions in a lattice has shown that energy transfer occurs over more than 0.7 nm from Eu^{3+} (S_6) ions to Eu^{3+} (C_2) ions and as far as about 0.6 nm at 300 K from Eu^{3+} (C_2)- Eu^{3+} (C_2) interactions^[9]. These distances are both very short as compared with the distance between Eu^{3+} ions in homogeneously doped inorganic glasses with Eu^{3+} , for which no concentration quenching was found up to 7.7 mol% of Eu^{3+} content^[10]. On the other hand, the phenomenon of energy transfer between rare earths may be useful in understanding the structure of ionomers although some research works have been done concerning self-quenching of rare earths in organic glasses^[11]. In this work, a new type of amorphous ionomer based on poly(methyl methacrylate) containing Eu^{3+} was synthesized. Discussion on the relationship between the Eu^{3+} content and the properties of the ionomer are based on the measurements of fluorescence of the ionomers.

EXPERIMENTAL

Preparation of ionomers

Ionomers were prepared by random copolymerization of the component monomers: methyl methacrylate (MMA) and europium methacrylate (EMA). EMA was synthesized by the method reported elsewhere^[12]. The process of copolymerization is described below:

Different amounts of EMA were dissolved in methacrylic acid (MA) and solutions with different Eu^{3+} contents were obtained. MMA was prepolymerized in bulk with AIBN as initiator (0.2 wt%) for 30 min and then mixed with the salt solution (50/5, v/v, about 11 mol% of MA) under vigorous stirring. The copolymerization was carried out in specified molds, designed for the preparation of samples for different measurements, at 45°C for 24 h and consecutively at 60, 80 and 100°C for 2 h to complete the reaction.

For comparison, europium octanoate (EOA) and the EOA containing poly(methyl methacrylate) (PMMA), in which EOA as an additive, were also synthesized by the procedure mentioned above. The polymers obtained were all hard and transparent and the Eu^{3+} contents for them are listed in Table 1.

Measurements

A model RF-850 Hitachi fluorescence spectrometer was used to measure the visible emission of Eu^{3+} -containing samples. The plate samples with a thickness of 3 mm were placed in the solid holder attached to the instrument. The measurements were carried out at room temperature under excitation of UV light at 375 nm. The visible fluorescence at 615 nm was observed and the change of the relative fluorescence intensity with Eu^{3+} concentration was recorded.

Table 1 Eu^{3+} content in ionomers based on poly (methyl methacrylate)*

EMA-containing	Ionomer mol% $\times 10^{-2**}$	EOA-containing	PMMA mol% $\times 10^{-2**}$
EMA1	1.60	EOA1	1.65
EMA2	3.20	EOA2	3.28
EMA3	6.48	EOA3	6.57
EMA4	9.84	EOA4	9.78
EMA5	11.49	EOA5	11.53

* MA content in ionomers is about 11 mol%

** Calculated in terms of the mole number of Eu^{3+} in each sample

RESULTS AND DISCUSSION

According to the procedure described in the experiment section, copolymerization was performed by mixing three monomers i.e. methyl methacrylate (MMA), methacrylic acid (MA) and europium methacrylate (EMA), and the copolymer containing EMA was obtained. In terms of the model reported before^[13,14], the random copolymer structure with a longer chain of MMA and separated EMA would be formed as EMA is a monomer with a bulk substituent and would have higher steric hindrance for another EMA to attack. On the other hand, for europium octanoate (EOA) containing system, an aggregate would be formed because EOA is inert to polymerization reactions and can move close as an additive during the polymerization process. At the same time, as Eu^{3+} is one of the larger rare earth cations, it could have multiple 7—9 coordinated types of sites and lower site regularities^[7]. When it is introduced into copolymers, the flexible polymer chains would gathered round Eu^{3+} and the free carbonyl or ester groups would able to take part in coordination^[15]. All these expectations seem to be in according with the following experimental findings.

Eu^{3+} containing ionomers exhibit their maximum excitation at 375 nm and the characteristic line of emission appears at 615 nm, corresponding to the $5\text{D}_0 \rightarrow 7\text{F}_2$

transition, as shown in Fig. 1. The intensity of the emission is increased with increase of Eu^{3+} concentration as shown in Fig. 2. More interesting is that the linear relationship has a slope of 0.90 calculated by least square method for the EMA containing ionomer, as can be seen in Fig. 2-a. Hence, when the number of Eu^{3+} ions is doubled the intensity of the fluorescence of Eu^{3+} is also doubled, and no self-quenching takes place. According to the analysis on nonradiative energy transfer between chromophores^[6], surrounded Eu^{3+} ion no other Eu^{3+} ions exist within 5 nm. In the model of ionomers proposed by Eisenberg^[16], one multiplet is considered as an aggregate consisting of several ion pairs and containing only ionic materials. As Eu^{3+} is a trivalent ion one Eu^{3+} would be surrounded by three anions within the diameter of the multiplet (ca. 0.6 nm) and a single cation ion multiplet could be formed according to the result above. Around this multiple PMMA chains are distributed homogeneously. From this structure it could be expected that this single cation ion multiplet may have the same "anchor" function as that of the ion pair multiplet in ionomers and may be even stronger as all elastic forces of polymer chains have been concentrated on one ion.

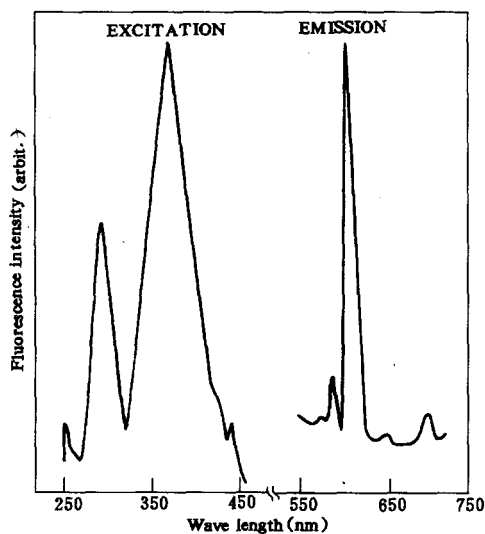


Fig. 1 Excitation and emission spectra of EMA containing ionomers

$$\lambda_{\text{EM}} = 615 \text{ nm}, \lambda_{\text{EX}} = 375 \text{ nm}$$

By comparison, EOA was prepared and blended into the ionomers through a procedure similar to that used in EMA preparation in the same Eu^{3+} concentration range. The fluorescence measurement of EOA containing PMMA was also performed and the result can be seen in Fig. 2-b. Within the same Eu^{3+} concentration range, the fluorescence intensity of EOA containing PMMA is lower than that of the EMA

containing ionomers; evidently, some fluorescence self-quenching by energy transfer between Eu^{3+} ions results from a closer distance between the ions. This structure difference can be traced back to the random copolymerizations in which EMA was incorporated into three polymer chains (for intra-macromolecular cross-linking, the structure is similar). The electrostatic interaction between EMA units is too weak to overcome the steric hinderance of crowded polymer chains around it, and the distance between two Eu^{3+} ions is larger than 5 nm. In EOA containing PMMA, Eu^{3+} ions could be held together by electrostatic interactions between them as EOA could move freely as an additive. When the distance between Eu^{3+} ions is within 5 nm self-quenching by nonradiative energy transfer can take place.

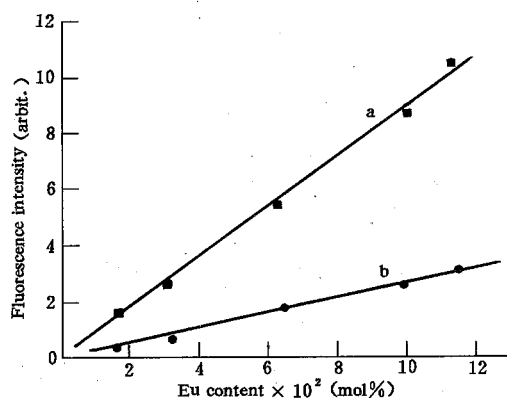


Fig. 2 Relationship between fluorescence intensity and Eu^{3+} content in (a) EMA containing ionomers and (b) EOA containing sample

CONCLUSIONS

Two kinds of Eu^{3+} containing polymers were synthesized, one containing EMA and the other containing EOA. From the chemical structures of EMA and EOA it could be deduced that EMA was incorporated into the macromolecular chains and Eu^{3+} containing ionomers formed. Six chains would be connected to one EMA unit either inter or intra-macromolecular cross-linking reaction takes place through the double bonds in EMA. This makes it possible that a crowded aggregate of polymer chains around each Eu^{3+} group can be formed. By contrast, for EOA containing PMMA, EOA is inert for free radical polymerization and could move freely as an additive between polymer chains. Fluorimetry results have been shown that for the EMA containing ionomers, no self-quenching was observed within $1.6 \times 10^{-2} \sim 10.0 \times 10^{-2}$ mol% of Eu^{3+} concentration range. In the plate sample with a thickness of 3 mm used in the fluorescence measurements, the distance apart from two Eu^{3+}

ions was longer than 5 nm. Self-quenching phenomenon was observed ion EOA containing PMMA, which resulted from the possibility that EOA could move as an additive and forms a cluster in PMMA.

Keywords:

Polymethyl methacrylate; Eu^{3+} containing; Fluorescence behaviour

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