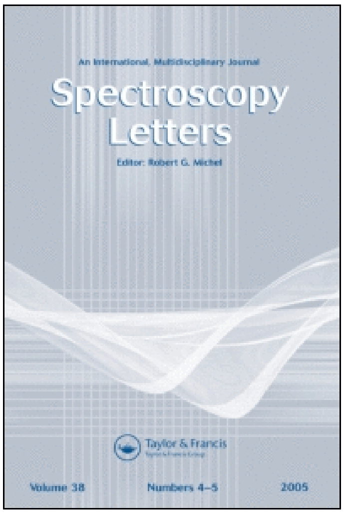

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FLUORESCENCE AND PHOTOCHEMICAL PROPERTIES OF Eu(III) POLY(ACRYLIC ACID-co-ETHYL METHACRYLATE) COMPLEXES

Key Words : Europium(III),Macromolecular complexes,
Copolymers of Acrylic Acid,Photolysis,
Luminescence Spectra

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ABSTRACT

The fluorescent and photochemical properties of Eu(III) with copolymers of acrylic acid and ethyl methacrylate were investigated. It was found that photochemical behavior of Eu^{3+} complexes with copolymers is essentially different from that Eu^{3+}complexes with polyacrylic acid-in the former Eu^{3+}luminescence intensity during photolysis noticeably enhances rather than reduces.

Two factors were supposed to cause the enhancement of Eu(III) luminescence efficiency during photolysis: one is responsible for decrease in the efficiency of the energy transfer from Eu^{3+} to -OH vibrational manifold and the other causes an increase in asymmetric binding site for Eu^{3+} ions.

INTRODUCTION

Synthesis and fluorescent properties of macromolecular complexes in which rare earth ions are directly bonded to polymeric chain have been extensively studied, since these complexes can be used as luminescent and laser materials of good quality [1-5]. However, photochemical behavior of such lanthanide polymer complexes has not been so far investigated in detail.

It has been recently observed that the luminescence intensity of Eu(III) complexes with copolymers of acrylic acid and alkyl methacrylates is noticeably enhanced upon UV-irradiation[6,7].

In the present work we have prepared Eu(III) polymer complexes which contain copolymer ethyl methacrylate-acrylic acid as coordinating ligand and discussed their luminescence and photochemical properties by comparing them with those of the corresponding complex of Eu(III) with polyacrylic acid (PAA).

EXPERIMENTAL

Synthesis of copolymers ethyl methacrylate-acrylic acid (EMAA) and their macromolecular complexes with Eu was described previously⁶⁾. Composition of the above copolymers was determined from the carboxyl groups content. Molecular mass of the polymers was calculated by Staudinger method, the average molecular mass being equal to $2{,}0 \times 10^4$. Transparent films of Eu(III) complexes were obtained by pouring the cyclohexanon solutions of the compounds studied onto glass or KBr plates. The polymer complexes were dried in vacuum at 50°C. IR spectra of complexes prior to and after UV-irradiation at room temperature in the form of films on KBr plates were measured by using Specord 75 IR (Karl Zeiss) spectrophotometer. Emission spectra were determined on the SDL-1(LOMO) spectrometer, with a DRSh-250 mercury lamp used as an excitation source.

Fluorescence lifetimes were obtained by using the pulsed output (337 nm) of a nitrogen laser (LGI-21) and capturing the emission-decay curves with SF-12 oscillograph. The lifetimes for luminescence decay obtained in this fashion were reproducible to within 10-15% .

Photolysis was carried out by irradiating the transparent films of the polymer complexes with nonfiltered light of the DRT-250 mercury lamp.

RESULTS AND DISCUSSION

The Table given below shows the composition of the copolymer-Eu^{3+} complexes obtained.

The binding of Eu(III) by carboxylate groups induces significant changes in IR spectrum of EMAA. The intensity of the band at 1700 cm^{-1} assigned to the stretching vibrations of non-coordinated carboxylate-groups is decreasing and an absorption band at 1540-1560 cm^{-1} appears which corresponds to the asymmetrical $\nu_{as}(COO^{-})$ stretching vibrations of ionized carboxylate groups.

The effect of Eu^{3+} concentration on the magnitudes of luminescence intensity and lifetime in Eu-EMAA complexes are illustrated in Fig.1. The Eu^{3+} concentration ranged from 2 to 20 wt.% and the data were acquired by using excitation wavelength of 365 nm and emission wavelength of 615 nm. It was found that,although the luminescence intensity increased with increasing Eu^{3+} content,reached a maximum at 12-15 wt % of ions ,and then decreased with a further increase of ion content, the luminescence lifetime remained constant at 220µs over the entire range.The insensitivity of the emission lifetime to the total Eu^{3+}concentration is a strong evidence of the existence of a well defined metal-ion binding site which nature is independent on the Eu^{3+} amount.

TABLE

Composition of Eu(III) Poly(acrylic acid-co-ethyl methacrylate) Complexes

Compound	Composition of the copolymer (AA mol.%)	$[Eu^{3+}]$ in complex (wt.%)
I	23,0	4,6
II	23,0	13,5
III	23,0	19,7
IV	40,1	3,9
V	40,1	11,2
VI	40,1	18,8
VII	60,9	4,3
VIII	60,9	9,3
IX	60,9	16,2
X	100,0	12,3

Recently, we have reported the results of EXAFS investigations of Eu-EMAA complexes with acrylic acid (AA) content from 20 up to 60 mol. % 8).The carboxylate groups of AA predominantly form monodentate bonds with average Eu-O distances of 2,46Å and Eu-Eu distances of 4,23Å.

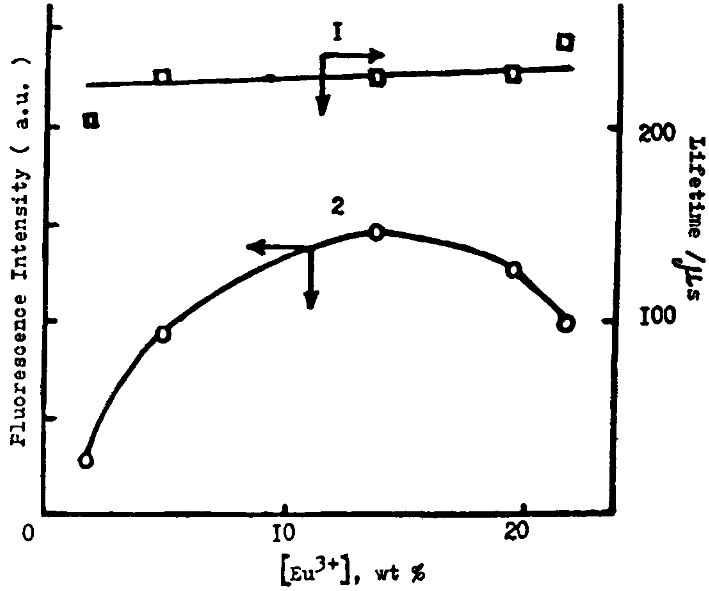

FIG.1. Eu^{3+} luminescence intensity (excitation wavelength 365 nm and emission wavelength 615 nm) and luminescence lifetime as a function of Eu(III)concentration for the Eu-EMAA complexes; (AA content 23,0 mol %)

We believe it is interesting to analyse the kinetics of photodecomposition of the macromolecular complexes studied,based on the records of changes in Eu^{3+} luminescence intensity ($^5D_0$ - $^7F_2$ transition, λ = 615nm). Study of Fig.2(a,b,c,d) shows that a photochemical behavior of the Eu-EMAA complexes studied is essentially different from that of Eu-PAA complex: in the former Eu^{3+} luminescence intensity during the polymer photodestruction noticeably enhances rather than reduces. Upon UV-irradiation the Eu^{3+} luminescence in-

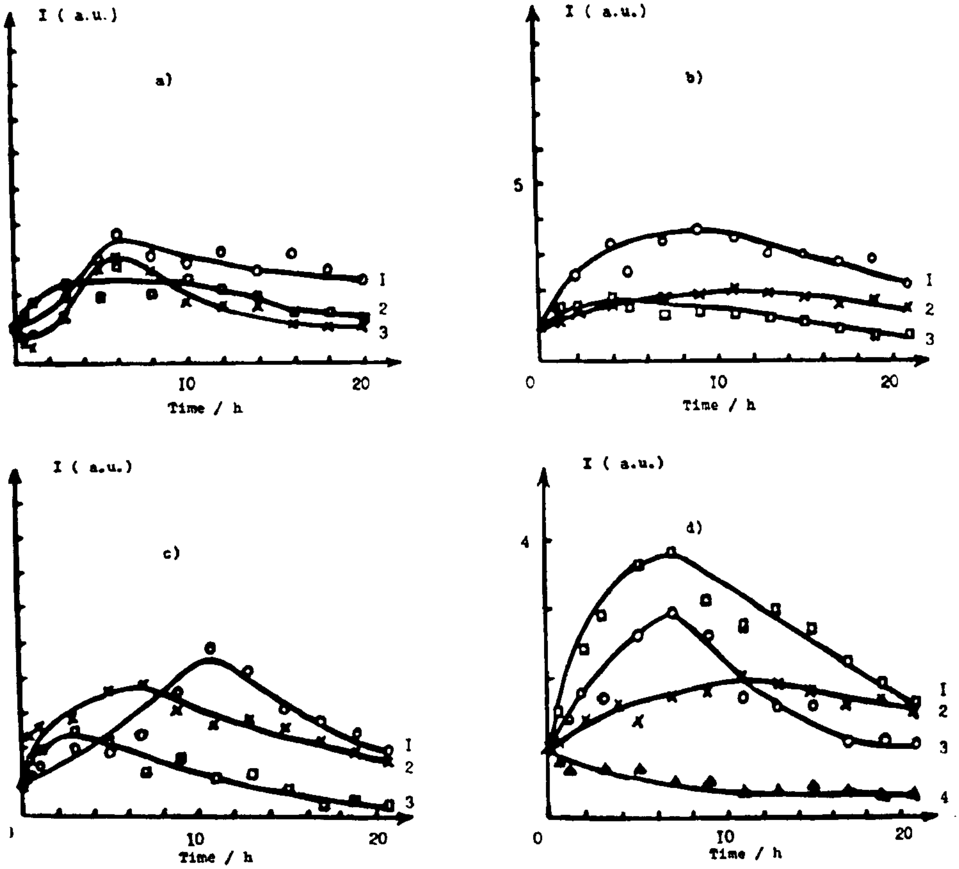

FIG.2. Dependence of emission intensity of Eu^{3+} on time of irradiation of Eu-EMAA complexes at 300K: a) 1 - VII; 2 - VIII; 3 - IX; b) 1 - IV; 2 - V; 3 - VI; c) 1 -I; 2 - II; 3- III; d) 1- II; 2- V;3- VIII;4 - X; (see Table).

tensity rises by 2-5 times depending on the composition of the macromolecular complex.Such differences in a photochemical behavior of Eu-EMAA and Eu-PAA complexes confirm that several effects take place in the process which can be summarized as follows:

(i) It is known that nonradiative quenching pathway through energy transfer to the -OH vibrational manifold of macromolecular ligand and coordinated water molecules represent the dominant mode of radiationless deactivation of the emissive $^5D_0$ state9) . Insertion of the comonomer into PAA polymer chain makes molecular vibration of the complexes decrease ($\nu(OH) = 3400cm^{-1}$; $\nu(COOCH_3) = 1700cm^{-1}$). Lifetime measurements indicate that Eu-PAA complex is more influenced by OH-groups than Eu-EMAA during photolysis (Fig.3).

(ii) Insertion of the comonomer into PAA chain results in a decrease of quenching by the energy transfer between Eu^{3+}ions. Since Eu^{3+} does not coordinate comonomer,it prevents Eu^{3+} ions from localizing.

(iii) If the enhancement of Eu^{3+} emission intensity during photolysis depended solely on the change of the energy transfer to -OH vibrational manifold of macromolecular ligand,the enhancement of emission in Eu-EMAA complexes of equal AA-content would decrease with a decrease in Eu^{3+} concentration (because complexes of low Eu^{3+} concentrations contain a greater

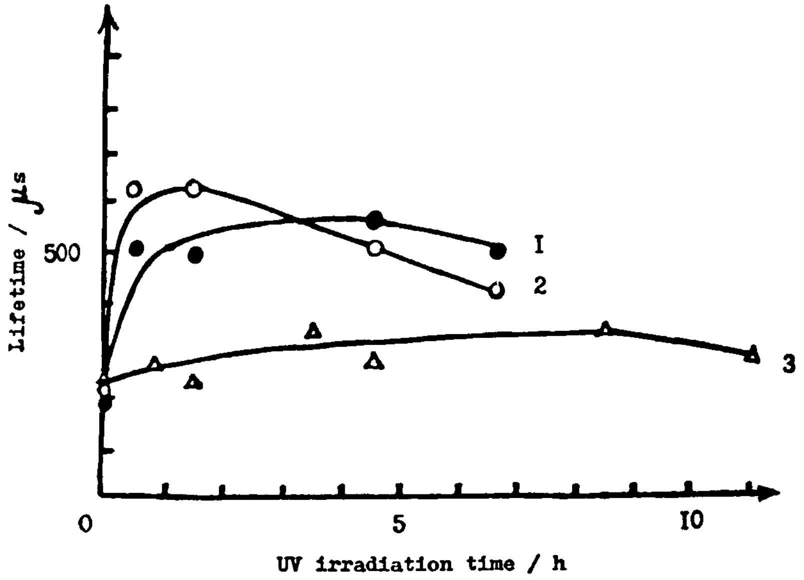

Fig.3. Dependence of luminescence lifetime on time of irradiation of Eu(III) polymer complexes at 300K: 1 - II; 2 - I; 3 - X (see Table)

number of OH- quenchers per each europium atom). On the contrary, Fig.2(a-c) shows that the enhancement of Eu^{3+} emission during photolysis increases with a decrease in Eu^{3+} concentration. These facts suggest two factors for the emission enhancement: one is responsible for energy transfer to -OH vibrational manifold while the other is due to the change of the Eu^{3+} local site. Due to steric hindrances,in synthesizing polymer complexes structures of unsaturated coordination are formed. Photolysis of macromolecular complexes causing destruction of the macromolecular ligand ,promotes decrease of a number of steric hindrances and increases the number of carboxylate ions asymmetrically bound to Eu^{3+}.Since Eu^{3+} does not coordinate comonomer,insertion of bulky comonomer into PAA chain makes it easier to form coordinatively unsaturated structures.As a result,the above processes of increase in the asymmetry of the Eu^{3+} environment during photolysis must be more noticeable in complexes of low AA-content.

Since initial macromolecular complexes of low Eu^{3+} concentration contain a greater number of the carboxylate groups per Eu^{3+} ion, a greater probability for formation of asymmetric binding site for Eu^{3+} ion must exist during photodecomposition of such complexes.

Such conclusion is confirmed by analyzing the experimental dependences of Eu^{3+} emission intensities on UV-irradiation for polymer complexes of different metal and acrylic acid content (Fig.2,). Fig.2(a,b,c) show that in Eu-EMAA complexes of equal AA-content, the emission enhancement increases with the decrease in metal concentration. Upon photolysis of Eu-EMAA comlexes (Fig.2d,compounds II,V,VIII,X) of similar Eu^{3+} concentrations,the enhancement of luminescence intensity is less noticeable with a increase in AA-content.For example,in complex I (Fig.2,d) having a minimum AA-content (23,0 mol.%) emission becomes 4 times more intense after UV-irradiation,while in complex V (40,1 mol.% AA) the emission intensity increases only by ? times.Finally, in complex X (100 mol % AA),there is no enhancement of Eu^{3+} luminescence intensity at all (moreover,emission intensity decreased during photolysis)

The results obtained in this work demonstrated that efficiency of enhancement of Eu^{3+} luminescence intensity in Eu-EMAA complexes during UV-irradiation depends on composition and structure of the complexes. Low metal and AA-content cause a decrease in the efficiency of the energy transfer from Eu^{3+} to -OH vibrational manifold and increase asymmetric binding site for Eu(III) ion during photolysis. This results in increased Eu^{3+} luminescence efficiency.

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