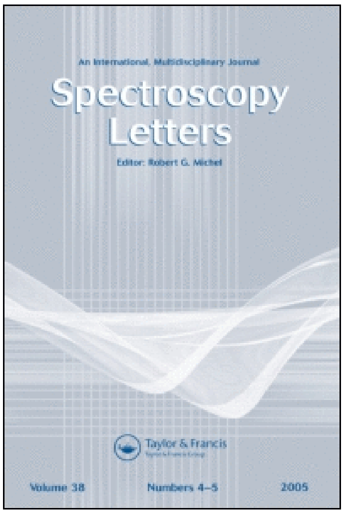

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Enhancement of Luminescence in the Photolysis Of Eu(III) Poly(Acrylic Acid-co-Butyl Methacrylate) Complexes

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ENHANCEMENT OF LUMINESCENCE IN THE PHOTOLYSIS OF Eu(III) POLY(ACRYLIC ACID-co-BUTYL METHACRYLATE) COMPLEXES

Key words: europium, copolymers of acrylic acid and butyl methacrylates, macromolecular complexes, luminescence spectra, IR-spectra, photolysis

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ABSTRACT

The fluorescent and photochemical properties of Eu(III) with copolymers of acrylic acid and butyl methacrylate were investigated. It was found that photochemical behavior of Eu^{3+} complexes with copolymers is essentially different from those of Eu^{3+}

with polyacrylic acid - in the former Eu^3 luminescence intensity during photolysis noticeably enhances rather than reduces. It has been found that the presence of steric hindrances and coordinatively unsaturated structures in the initial complexes with copolymer and peculiarities of the photodecomposition of macromolecular ligand favors the enhancement of the luminescence during the photolysis

INTRODUCTION

In the recent years, problems of the chemistry of macromolecular metal-containing complexes (MMC) have been attracting a steady attention of researchers[1,2]. The presence of steric hindrance can hamper the formation of coordination bonds between metal and chelating fragment of a macromolecular ligand (MML), thus leading to a change in the local concentration of functional groups of the MML, and affect the physico-chemical properties of MMC[3] . It has been found that the presence of coordinatively unsaturated structures in Eu^{3+} MMC can have a substantial effect on the photochemical and luminescence properties of MMC.[4]

To continue our investigation of Ln^{3+} MMC with acrylic acid copolymers[5,6] , we report on the results of study of the effect of the composition and structure of

MML on luminescence and photochemical properties of Eu(III) complexes with acrylic acid-based polymers.

EXPERIMENTAL

Polyacrylic acid(PAA) and copolymers of acrylic acid (AA) with butyl methacrylate (BMAA) were obtained by the radical polymerization according to a previously described procedure[6]. The composition of the copolymers was calculated based on the percentage of carboxyl groups; the molecular weights of polymers were determined by the Staudinger method. The molecular weight of BMAA was $1.5 \cdot 10^4$ while the molecular weight of PAA was $6.5 \cdot 10^4$. The content of acrylic acid in the copolymer was 16.8 mol%.

Polymeric complexes with Eu^{3+} were prepared by 1h stirring of a dioxane solution of one of the above polymers with an ethanolic solution of $EuCl_3 \cdot 6H_2O$, to which an ethanolic solution of ammonia was preliminarily added to pH 7. After stirring, the mixture was poured into a large amount of distilled water, the product was washed with water and ethanol and dried for 48 h at 60 ^{0}C *in vacuo*. The Eu content in the complexes was determined by the gravimetric method.

Emission spectra were determined on the SDL-1 (LOMO) spectrometer, with a DRSh-250 mercury lamp used as an excitation source. IR spectra of MMC prior to and after UV-irradiation at room temperature in the form of films on KBr were measured by using Perkin-Elmer (Model 577)r. Absorption spectra were obtained on a Specord M-40 (Karl Zeiss) spectrophotometer for films on quartz supports. Photolysis was carried out by irradiating the samples with the unfiltered light of a DRT-250 mercury lamp. The distance from the lamp to the sample was 20 cm.

RESULTS AND DISCUSSION

The IR spectra of the samples obtained serve as an experimental evidence for the fact that Eu^{3+} ions are chemically bound to the functional groups of MML. The spectra of BMAA and PAA exhibit an absorption band in the 1700 cm^{-1} region, which corresponds to stretching vibrations of nonionized and noncoordinated COOH groups. Following the interaction of Eu^{3+} with MML, the intensity of this band decreases, while a band in the 1520-1560 cm^{-1} region corresponding to asymmetrical stretching vibrations of ionized carboxyl groups ($\nu_{as}COO^-$) appears instead. The ($\nu_{as}COO^-$) band exhibited several inflections with maximum near 1525, 1560 cm^{-1} which may indicate the nonequivalent coordinated carboxyl groups.

When exposed to UV radiation, all the MMC of Eu^{3+} and films obtained from them luminesce with red light. The most intense line corresponds to the $^5D_0$ - $^7F_2$ transition (λ_{lum} = 612 nm). Analysis of the excitation spectra indicates that there is no intramolecular energy transfer from the levels of MML to the resonance levels of Eu^{3+}.

Irradiation of the Eu^{3+} MMC with BMAA with unfiltered UV light leads to enhancement of luminescence in the Eu^{3+} band with λ =612 nm (Fig.1). Thus, photochemical behavior of Eu^{3+} MMC with BMAA under consideration differs substantially from the behavior of the low-molecular-weight analogs and Eu complexes with PAA, namely, during the photodestruction of the metal-containing polymer, the intensity of the fluorescence of the ion does not decrease but, controversially, substantially increases.

No variations in the structure of the luminescence excitation spectra were found during UV irradiation of the samples; therefore, the increase in the luminescence intensity of Eu^{3+} observed during the photolysis cannot be explained by intensification of the transfer of the electronic excitation energy from the levels of MML and photodestruction products to the levels of Eu^{3+}.

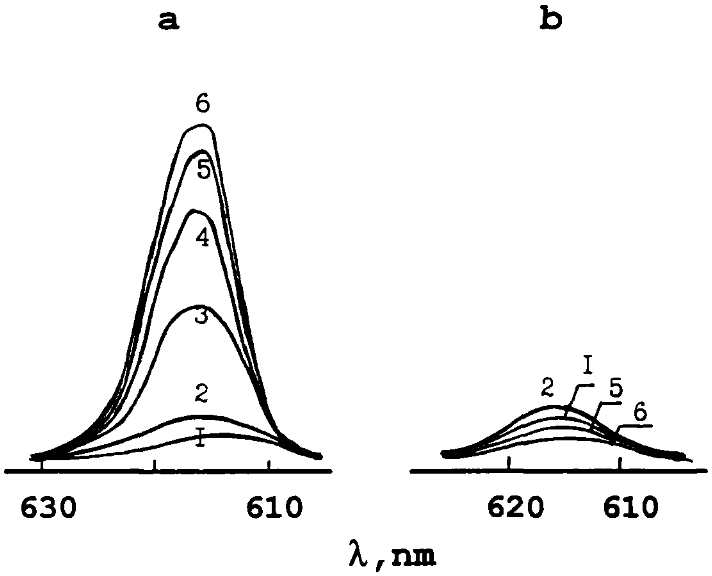

FIG.1. Effect of UV irradiation on the fluorescence intensity of (a) Eu-BMAA ($[Eu^{3+}]$ = 2.0 wt.%); (b) Eu-PAA ($[Eu^{3+}]$ = 5.4 wt.%). Duration of irradiation at 300K, h: 0 (initial complex,1); 1(2);4(3); 7(4); 10(5); 13(6); λ_{lum} = 615 nm ($^5D_0$ -$^7F_2$ transition)

UV irradiation of the polymeric films of the Eu^{3+} complexes with BMAA results in a decrease in the intensities of the main absorption band in the IR spectra and the similar process is much more effective in the case of Eu^{3+} with PAA; simultaneously, the intensities of the ν(OH) bands of the acid at 2500-2700 cm^{-1} and 3100-3300 cm^{-1} almost disappear and $\nu_{as}COO^-$ bands at 1520-1540 cm^{-1} for the MMC with PAA and at

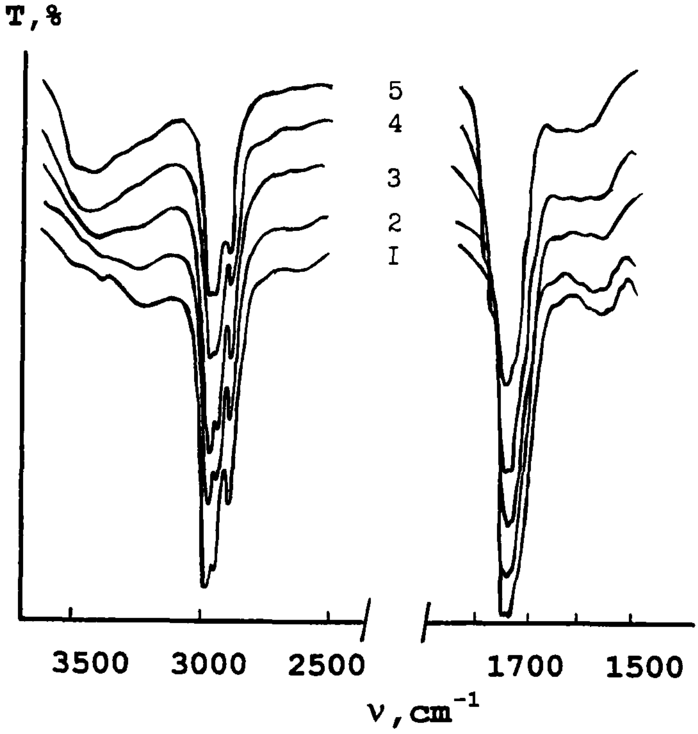

FIG.2. Effect of UV irradiation on infrared spectra of Eu-BMAA complex ([Eu^{3+}] = 2.0 wt.%). Duration of irradiation at 300 K, h: 0 (initial complex,1); 1(2); 4(3); 7(4); 10(5); 13(6)

1520-1560 cm^{-1} for MMC with the BMAA increase that shows the increase of carboxylate ions asymmetrically connected with Eu^{3+} (Fig.2). A band in the 270-280 nm region due to carbonyl chromophores appears in the electronic absorption spectra, which indicates to the photodestruction of the MML.

The main products of copolymer (BMAA) photolysis were shown to be monomers: butyl methacrylate and AA.[8] The appearance of IR absorption band at the range 1615-1625 cm^{-1} proves the olefins presence in photoproducts. The appearance of free AA able to form additional coordination bonds weakens the effect of polymeric chain and reduces the part of coordinatively-unsaturated structures. The appearance of the additional maximum in the IR spectrum at 1580 cm^{-1} ($\nu_{as}COO^-$) (Fig.2) with its increasing intensity in the photolysis indicates the change of coordination of carboxylate groups in this process. Unlike the BMAA the PAA photolysis is characterized by the formation of peroxo-radicals and hydroperoxo groups which are difficult to form luminescent complexes with Eu^{3+}. Moreover, the relatively low BMAA photodecomposition rate in comparison with the PAA can be accounted for photochemical stabilization mechanism of formation of poly(n-butyl methacrylate) consisting in cyclic anhydride group formation which causes the photoreaction break. That is confirmed by the emerging of absorption band ν (C=O) at 1750 cm^{-1} at prolonged irradiation.

Investigation of the luminescent properties of MMC of lanthanide's with homo- and copolymers of AA indicates that MMC with copolymers contain higher local concentrations of functional groups and metal ions (ion aggregates) than complexes with PAA. Thus, the lanthanide MMC with AA-based copolymers are characterized by larger numbers of coordinatively unsaturated structures than MMC with PAA, that results in their different photochemical properties. In fact, the luminescence intensity of Eu^{3+} polyacrylate remained virtually unchanged during UV irradiation, and it decreased upon prolonged irradiation(see Fig 1). Apparently, when the initial complexes are formed, more bulky substituents cause greater steric hindrance and, hence, a larger number of coordinatively unsaturated structures appear. MML are destroyed during the photolysis of MMC, and this decreases steric hindrance and increases the number of carboxylate ions asymmetrically bound to Eu^{3+}. Consequently, the processes occurring in the polymer during its photolysis should be more intense in complexes containing larger numbers of coordinatively unsaturated structures.

Recently, we have reported the results of EXAFS investigations of Eu-BMA complexes[7]. The first coordination sphere of Eu contains from six to eight O atoms located at an average distance of 2.47 Å. Then the polymeric complexes are photolyzed, the Eu-O interatomic distance increase by 0.15 Å. The increase in the Eu-O average distance observed in the photolysis probably favors a decrease of the efficiency of the process of nonradiative dissipation of $Eu^{3+}$of electronic excitation of on high-frequency vibrations of MML and ,therefore, an increase of the intensity of the ion photoluminescence.

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