Fluorescent and photochemical properties of Tb^{III} complexes with acrylic acid-based macromolecular ligands

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The fluorescent and photochemical properties of Tb^{III} complexes with macromolecular ligands based on acrylic acid were studied. The photochemical behavior of the macromolecular Tb^{III} complexes with acrylic acid—alkyl methacrylate copolymers differs considerably from those of Tb^{III} complexes with polyacrylic acid and of low-molecular-weight analogs; in the former case, the intensity of Tb^{3+} photoluminescence noticeably increases during photolysis rather than decreases. It was found that the increase in the length of the alkyl group in the alkyl methacrylate favors the enhancement of the luminescence during the photolysis. The higher efficiency of the enhancement of the Eu^{3+} fluorescence during the photolysis of similar complexes of Eu^{3+} compared to the complexers of Tb^{3+} is due to the nature of the electrodipole "hypersensitive" $^5D_0$—$^7F_2$ transition in Eu^{3+}.

Key words: terbium, copolymers of acrylic acid and alkyl methacrylates, macromolecular complexes, luminescence spectra, photolysis.

In recent years, problems of the chemistry of macromolecular metal-containing complexes (MMC) have been attracting the steady attention of researchers.[1,2] The presence of steric hindrance can hamper the formation of coordination bonds between a metal and the 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 physicochemical properties of MMC. It has been found that the presence of coordinatively unsaturated structures in Eu^{III} complexes with copolymers of acrylic acid with alkyl methacrylates can have a substantial effect on the photochemical and luminescence properties of the polymeric complexes.[3,4]

In this paper, we report on the results of a study of the effect of the composition and structure of MML on luminescence and photochemical properties of Tb^{III} complexes with acrylic acid-based polymers.

Experimental

Polyacrylic acid (PAA) and copolymers of acrylic acid (AA) with ethyl and butyl methacrylates (EMA and BMA), were obtained by radical polymerization according to a previously described procedure.[5] 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.[6] The molecular weight of EMA was $1.7 \cdot 10^4$, that of BMA was $1.5 \cdot 10^4$, and that of PAA was $6.5 \cdot 10^4$. Below we present the content of AA in the copolymers (mol. %) and the content of Tb^{3+} in MMC (%), respectively: Tb-EMA (19.7; 12.6) (**1**); Tb-BMA (10.8; 5.6) (**2**); Tb-PAA (100; 5.5) (**3**); Eu-BMA (16.8; 5.3) (**4**).

Polymeric complexes with Tb^{III} were prepared by stirring for 1 h a dioxane solution of one of the above copolymers with an ethanolic solution of $TbCl_3 \cdot 6H_2O$, 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 °C *in vacuo*. The Tb content in the complexes was determined by the gravimetric method.

Fluorescence and fluorescence excitation spectra were recorded on a Hitachi-850 spectrophotometer; absorption spectra were obtained on a Specord M-40 spectrohotometer for films on quartz supports. IR spectra were recorded for samples as thin films between KBr glasses on a Specord 75-IR spectrophotometer. The lifetime τ of the Tb^{III} excited state was determined based on the analysis of the curves of the decay of the luminescence intensity induced by irradiation of a sample with a pulse of an LGI-21 nitrogen laser (t = 20 ns, λ = 337 nm). The signal obtained from a FEU-79 photomultiplier was recorded on the display of an S8-12 oscillograph. 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

Complexes of Tb^{III} with copolymers of AA with alkyl methacrylates are white powders, soluble in cyclohexanone and butanone and partially soluble in dioxane.

The IR spectra of the samples obtained serve as experimental evidence for the fact that Tb^{3+} ions are chemically bound to the functional groups of MML. The spectra of the copolymers and PAA exhibit an absorption band in the 1700 cm^{-1} region, which corresponds to stretching vibrations of nonionized and

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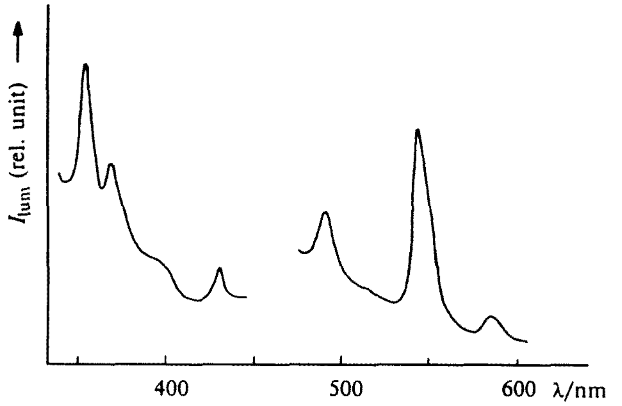

Fig. 1. Luminescence excitation and luminescence spectra of complex **1**.

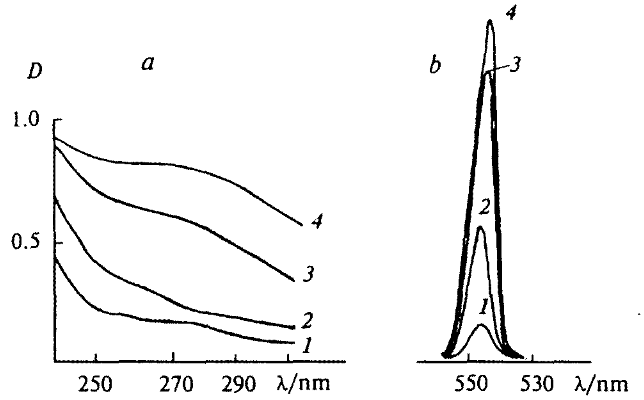

Fig. 2. Effect of UV irradiation on the absorption spectrum (*a*) and fluorescence intensity (*b*) of complex **2**. Duration of the irradiation at 300 K, h: 0 (the initial complex, *1*); 1 (*2*); 6 (*3*); 12 (*4*); λ_{lum} = 545 nm (the $^5D_4$—$^7F_5$ transition).

noncoordinated COOH groups. Following the interaction of Tb^{3+} with MML, the intensity of this band decreases, while a band in the 1550—1570 cm^{-1} region corresponding to asymmetrical ($\nu_{as}COO^-$) stretching vibrations of ionized carboxyl groups[5] appears instead.

When exposed to UV radiation, all the MMC of Tb^{3+} and films obtained from them luminesce with green light. Luminescence spectral patterns of the complexes are sets of discrete lines corresponding to Stark $^5D_4$—^7F_j transitions of Tb^{3+} (Fig. 1). The most intense line corresponds to the $^5D_4$—$^7F_5$ transition (λ_{lum} = 545 nm). Analysis of the excitation spectra indicates that there is no intramolecular energy transfer from the levels of MML to the resonance levels of Tb^{3+}.

UV irradiation of the polymeric films of the Tb^{3+} complexes with homo- and copolymers results in a decrease in the intensities of the main absorption band in the IR spectra; simultaneously, the integral intensity of the $\nu_{as}COO^-$ bands at 1520—1530 cm^{-1} for the MMC with PAA and at 1550—1570 cm^{-1} for MMC with the copolymers increase. A band in the 270—280 nm region due to carbonyl chromophores[7] arises in the electronic absorption spectra, which points to photodestruction of the MML (Fig. 2, *a*).

Photoirradiation exerts an effect on fluorescence characteristics, which can be judged from the changes in the intensity of the Stark $^5D_4$—$^7F_5$ transition (λ_{lum} = 545 nm) and in $\tau(Tb^{III})$ in the excited state. Irradiation of the Tb MMC with copolymers with unfiltered UV light leads to enhancement of fluorescence in the Tb^{III} band with λ = 545 nm (Fig. 2, *b* and Fig. 3). Thus, photochemical behavior of the Tb^{3+} MMC under consideration, like that of the previously studied complexes of Eu^{3+} with acrylic acid copolymers,[3] differs substantially from the behavior of the low-molecular-weight analogs and of Tb^{3+} and Eu^{3+} complexes with PAA, namely, during the photodestruction of the metal-containing polymer, the intensity of the fluorescence of the ion does not decrease but, conversely, 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 Tb^{3+} observed during the photolysis cannot

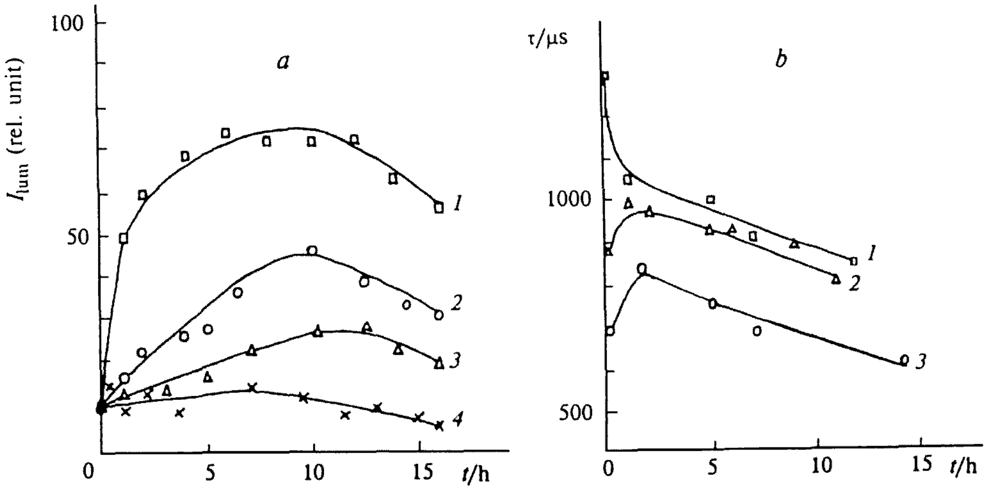

Fig. 3. Dependence of the luminescence intensity (*a*) of complexes **4** (*1*); **2** (*2*); **1** (*3*); and **3** (*4*) and dependence of the lifetime of the Tb^{3+} excited state (*b*) in complexes **3** (*1*); **1** (*2*); and **2** (*3*) on the duration of UV irradiation.

be explained by intensification of the transfer of the electronic excitation energy from the levels of MML and of photodestruction products to the levels of Tb^{3+}.

The efficiency of the enhancement of Tb^{3+} luminescence is affected by the size of the alkyl groups in the methacrylate molecules; with similar metal concentrations in the complexes under study, the maximum luminescence is observed during the photolysis of the complex with BMA (see Fig. 3, *a*). 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 Tb^{3+}. According to the Jadd—Offelt theory,[8] the increase in the asymmetry of the environment of Tb^{3+} enhances the Stark transitions in Tb^{3+}. Consequently, the processes occurring in the polymer during its photolysis should be more intense in complexes containing larger numbers of coordinatively unsaturated structures.

Investigation of the fluorescent properties of MMC of lanthanides 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 polyacrylates.[9] Thus, the lanthanide MMC with AA-based copolymers are characterized by larger numbers of coordinatively unsaturated structures than the MMC with homopolymers, which results in their photochemical properties being different. In fact, the luminescence intensity of Tb^{3+} polyacrylate remained virtually unchanged during UV irradiation, and upon prolonged irradiation, it decreased (see Fig. 3, *a*).

The data on the photochemical behavior of MMC obtained from the analysis of the variation of the fluorescence intensity I_{fl} generally correlate with those obtained from the measurements of $\tau(Tb^{III})$; however, the rates of the variation of τ and I_{fl} are substantially different: the I_{fl} value increases up to 10 h of UV irradiation, whereas τ starts to decrease even after 3 h of irradiation (see Fig. 3, *b*). Apparently, the variations of τ make it possible to follow the photochemical transformations mainly in the local environment of Tb^{3+}, *i.e.*, in the anionic sphere constituted by the carboxylate ions of PAA, whereas the fluorescence intensity reflects the overall photodestruction occurring in MMC (variation of the efficiency of the energy migration along the polymer, variation of the optical density of MMC during photodestruction, *etc.*).

In the study of Eu^{3+} MMC with AA-based copolymers, it was shown that the efficiency of the enhancement of Eu^{3+} fluorescence during UV irradiation is affected by two factors: the decrease in the efficiency of the degradation of the electronic excitation energy of Eu^{3+} at high-frequency vibrations of MML during the photolysis and the increase in the degree of asymmetry of the local environment of the ion.[3]

Comparison of the photochemical behaviors of Tb^{3+} and Eu^{3+} MMC having similar compositions shows that the Eu^{3+} complex is characterized by more efficient enhancement of photoluminescence during UV irradiation (see Fig. 3, *a*). Apparently, this is mainly caused by the fact that the induced electrodipole transitions in Eu^{3+} are forbidden, and, hence, the dependence of the intensity of some transitions (especially, $^5D_0$—$^7F_2$ in luminescence) on the odd crystal field parameters, eliminating the prohibition with respect to parity, is more pronounced than that for other lanthanides.[8] Therefore, the increase in the asymmetry of the local environment of the lanthanide ion occurring during the photodestruction of MML should have a greater effect on the "hypersensitive" electrodipole $^5D_0$—$^7F_2$ (Eu^{3+}) transition than on the $^5D_4$—$^7F_5$ (Tb^{3+}) transition, which is partially a magnetic-dipole transition.[8]

Thus, our study of the luminescence and photochemical properties of Tb^{3+} complexes with copolymers of acrylic acid with alkyl methacrylates confirmed the fact found previously[3,4] for similar complexes of Eu^{3+} that the photochemical behavior of these complexes differs substantially from that of low-molecular-weight analogs and of complexes with PAA, namely, that the intensity of luminescence of Tb^{3+} during the photodestruction of MMC markedly increases rather than decreases. The efficiency of the enhancement of Tb^{3+} photoluminescence depends on the composition and the structure of the initial MMC: an increase in the length of the alkyl radical in alkyl methacrylates favors an increase in the efficiency of the enhancement of luminescence.

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