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Effect of the Nature of the Polymer Matrix on the Luminescence of Tb(III) Complexes with β-Diketone Copolymers

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Abstract—The formation conditions and luminescence of Tb(III) complexes with synthesized copolymers of unsaturated acetylacetone derivatives with styrene and methyl methacrylate were studied. The luminescence intensity of these Tb(III) complexes was found to depend on the β-diketone substituent nature (CH_3, CF_3, C_6H_5) and structure (linear, branched) and the β-diketone to monomer ratio in the polymerizing mixture.

Keywords: β-diketone/styrene (methyl methacrylate) copolymers, terbium complexes with copolymers, luminescence

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INTRODUCTION

A promising class of new materials is represented by coordination compounds of lanthanides (Ln) with β-diketones (βd). They possess a narrow-band luminescence (~10 nm), which provides the color purity of the emission, with the color being determined by the central ion: red in the case of Eu(III) complexes, green for Tb(III) complexes, blue for Tm(III) complexes and so on. The Ln3+ ions chelated by β-diketones exhibit luminescence in both visible (Pr, Sm, Eu, Tb, Dy, Tm) and near-IR spectral region (Nd, Sm, Yb). This accounts for the wide use of Ln(III) coordination compounds as shift reagents in NMR spectroscopy, solar energy converters, laser and other materials, in fluorescence immunoassay, and for highly sensitive determination of micro and ultramicro quantities of Ln(III) in diverse objects [1–6]. β-Diketones are among the most well-known classes of complexing agents, but copolymers (CPs), obtained by unsaturated βd, have been described only in few publications [7–12].

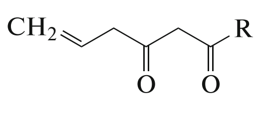
The inclusion of Ln(III) complexes into a polymer matrix substantially increases the luminescence intensity, most of all, as this suppresses diffusion of molecules of the complex in solutions, which leads to nonradiative transfer of the excitation energy [2, 13]. As shown for Tb(III) complexes with pyrazolecarboxylic acids [14], elimination of the intramolecular energy loss by displacement of H_2O from the inner coordination sphere of the complex increases the luminescence intensity (I_{lum}) threefold, while elimination of the diffusion upon sorption of the complexes increases the intensity 50-fold.

This study addresses the dependence of luminescence of Tb(III) complexes with βd copolymers on the nature of the polymer matrix, structure of unsaturated βd, and the βd to vinyl monomer (styrene, methyl methacrylate) ratio.

EXPERIMENTAL

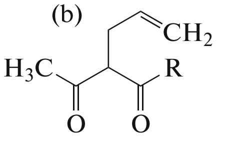
The copolymers were synthesized using (a) linear and (b) branched vinyl-βd and (c) 5-methyl-5-hexene-2,4-dione (MHD).

(a)



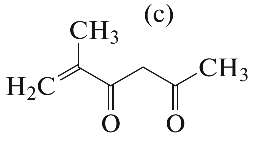
R: $-CF_3$ [1,1,1-trifluoro-7-octene-2,4-dione (TOD)], $-C_6H_5$ [1-phenyl-6-heptene-1,3-dione (PHD)]

(b)



R: $-CF_3$ [3-allyl-1,1,1-trifluoropentane-2,4-dione (ATPD)], $-C_6H_5$ [2-allyl-1-phenylbutane-1,3-dione (APBD)]

(c)



5-Methyl-5-hexene-2,4-dione (MHD)

The copolymers of unsaturated β-diketones with styrene (St) and methyl methacrylate (MMA) were synthesized as described in [15]. The vinyl-βd to vinyl monomer (St, MMA) volume ratios were 1 : 1, 1 : 2, 1 : 5, and 1 : 10. For evaluating the effect of the polymer matrix, the homopolymers of methyl methacrylate (polymethyl methacrylate, PMMA) and styrene (polystyrene, PSt) devoid of β-diketone groups were prepared under analogous conditions; for evaluation of the steric effect, 5-methyl-5-hexene-2,4-dione homopolymer (PMHD) with a β-diketone group in each macrochain unit was synthesized. The other βd do not form homopolymers [15].

Solutions of PMHD, PMMA, and PSt homopolymers with a concentration of 1 mg/mL were prepared by dissolving 50 mg of a polymer in 50 mL of dioxane purified according to [16].

A solution of $TbCl_3$ with a 1×10^{-3} mol/L concentration was prepared by dissolving an accurate weighed portion of high-purity Tb oxide (99.99%) in reagent grade HCl with subsequent removal of its excess and dissolution of the residue in distilled water.

All working solutions were prepared by diluting the stock solution in the appropriate solvent. Ammonium acetate buffer solutions were prepared according to [17] from 1×10^{-1} M solutions of acetic acid and ammonia. The pH of the solutions were checked using a pH-150MA pH-meter millivoltmeter.

The luminescence excitation spectra and the luminescence spectra of the reagents and Tb(III) complexes with them were measured on a Fluorolog FL3-22 Horiba Jobin Yvon (France) spectrofluorimeter with a 450 W xenon lamp and on an SDL-1 spectrometer (LOMO, Russia) with a DRSh-250 quartz mercury lamp. All measurements were carried out at room temperature (21–23°C). The Tb(III) luminescence spectra were recorded in the 470–640 nm range with $\lambda_{max} = 547$ nm ($^5D_4 \rightarrow {}^7F_5$ transition) [2].

The triplet energies of the organic reagents (E_{T1}) were calculated from the phosphorescence spectra of their Gd(III) complexes at 77 K [18].

RESULTS AND DISCUSSION

Since the luminescence of the Ln^{3+} ion in the complex is caused by the energy transfer from the excited ligand to the ion, it is important that the triplet energy E_{T1} be higher than the energy of the Tb(III) emission level ($E(^5D_4) = 20500$ cm^{-1}). The E_{T1} values found for the synthesized compounds are summarized in Tables 1 and 2.

A comparison of the E_{T1} values of PSt- and PMMA-based copolymers shows that they are close in magnitude and much higher than the energy of the Tb(III) emission level; thus, the excitation energy transfer from CPs to Tb(III) is possible. The high value E_{T1}(PMMA) = 25650 cm^{-1} indicates that this polymer matrix with carbonyl oxygen atoms, which are coordinated to Ln(III) ions [11], cannot accept the excitation energy, thus decreasing the luminescence.

As can be seen from Fig. 1, irrespective of the structure of βd (linear, branched) and for the same β-diketone to monomer ratio (1 : 5), the luminescence intensity of Tb(III) complexes with CPs is much higher for PMMA-based CPs than for PSt-based CPs. The maximum luminescence is attained when the CP concentration in the solution is 0.4 mg/mL. The optimal pH of the medium for Tb(III) complexes with any CP is 8.5. Table 3 presents the I_{lum} values of Tb(III) complexes with CPs composed of St and vinyl-β-diketones of various structures (linear and branched). A comparison of the I_{lum} values of Tb(III) complexes with various CPs, but with the same βd : St ratio demonstrates the advantage of branched βd, which probably gives rise to less pronounced steric hindrance to Ln^{3+} coordination to CP than linear diketones. The same is observed in the case of CPs based on PMMA (Table 4), for which I_{lum} of the Tb^{3+} ion is much higher than for the corresponding PSt-based CPs. This is attributable to an additional coordination, apart from the β-diketone coordination, of the MMA carbonyl oxygen atoms to the central ion [19].

Figure 2 shows the luminescence excitation and luminescence spectra of Tb(III) complexes with copolymers at different βd : St component ratios. Luminescence is found to be enhanced with decreasing β-diketone proportion from 1 : 1 to 1 : 10, i.e., on going to more sparse arrangement of βd in the CP chain, which promotes coordination of the Ln^{3+} ion to two or three ligand molecules [20]. The presence of the cyclic C_6H_5 substituent in βd (photoantenna) leads to more intense luminescence of Tb(III) complexes compared with that for the fluorinated CF_3 substituent. The luminescence of the Tb^{3+} ion is 3–4 times higher for PMMA-based copolymers than for analogous copolymers based on polystyrene (Tables 3 and 4).

The results demonstrated that PMMA-based copolymers should be preferred over PSt-based copolymers for observation of intense luminescence of Ln^{3+} ions. The PMHD and PMMA homopolymers are less efficient, as the complexing group is present in every polymer unit, which sterically hampers the formation of polymer complexes. The Tb^{3+} ion, being coordinated to the >C=O groups of PMMA, provides additional stabilization of the polymer complexes, which is absent for the PSt matrix. It is noteworthy that the luminescence of the Tb^{3+} ion sorbed by PMMA is 5–8 times lower than that for complexes with PMMA-based copolymers.

The copolymers form strong chelates, whereas PMMA forms donor-acceptor complexes, which are less strong than the chelates. The possibility of additional excitation energy transfer from PMMA (E_{T1} = 25650 cm^{-1}) to Ln^{3+} ions with lower energies of the emission levels should also be borne in mind.

Table 1. Characteristics of copolymers of β-diketones with styrene*

βd (R)	βd : St ratio	λ_{exc}, nm	λ_{phos}, nm	E_{T1}, cm^{-1}
MHD (R = CH_3)	PMHD	372	438	26520
	1 : 5	315	431	23200
	1 : 10	315	432	23150
OD (R = CH_3)	1 : 5	291	400	25000
	1 : 10	294	407	24691
TOD (R = CF_3)	1 : 1	294	404	24390
	1 : 5	290	411	23866
PHD (R = C_6H_5)	1 : 5	284	405	21505
	1 : 10	292	407	24509
APD (R = CH_3)	1 : 5	294	404	24390
	1 : 10	297	407	24154
ATPD (R = CF_3)	1 : 1	294	405	23809
	1 : 5	294	411	23923
APBD (R = C_6H_5)	1 : 5	287	405	21551
	1 : 10	292	407	25000

* $c_{Gd} = 1 \times 10^{-4}$ mol/L; $c_{\beta d} = 0.3$ mg/mL; pH 8.5; $T = 77$ K.

Table 2. Characteristics of copolymers of β-diketones with methyl methacrylate*

βd (R)	βd : MMA ratio	λ_{exc}, nm	λ_{phos}, nm	E_{T1}, cm^{-1}**
MHD (R = CH_3)	PMHD	377	438	26520
	1 : 5	317	404	23810
	1 : 10	313	407	23760
TOD (R = CF_3)	1 : 2	287	416	24038
	1 : 5	296	420	23809
PHD (R = $-C_6H_5$)	1 : 5	294	412	24272
ATPD (R = CF_3)	1 : 2	297	417	23981
	1 : 5	301	418	23923
APBD (R = C_6H_5)	1 : 1	288	421	23753
	1 : 2	292	419	23866
	1 : 5	294	416	24038

* $c_{Gd} = 1 \times 10^{-4}$ M; $c_{\beta d} = 0.3$ mg/mL; pH 8.5; $T = 77$ K.
** E_{T1}(PMMA) = 25650 cm^{-1}.

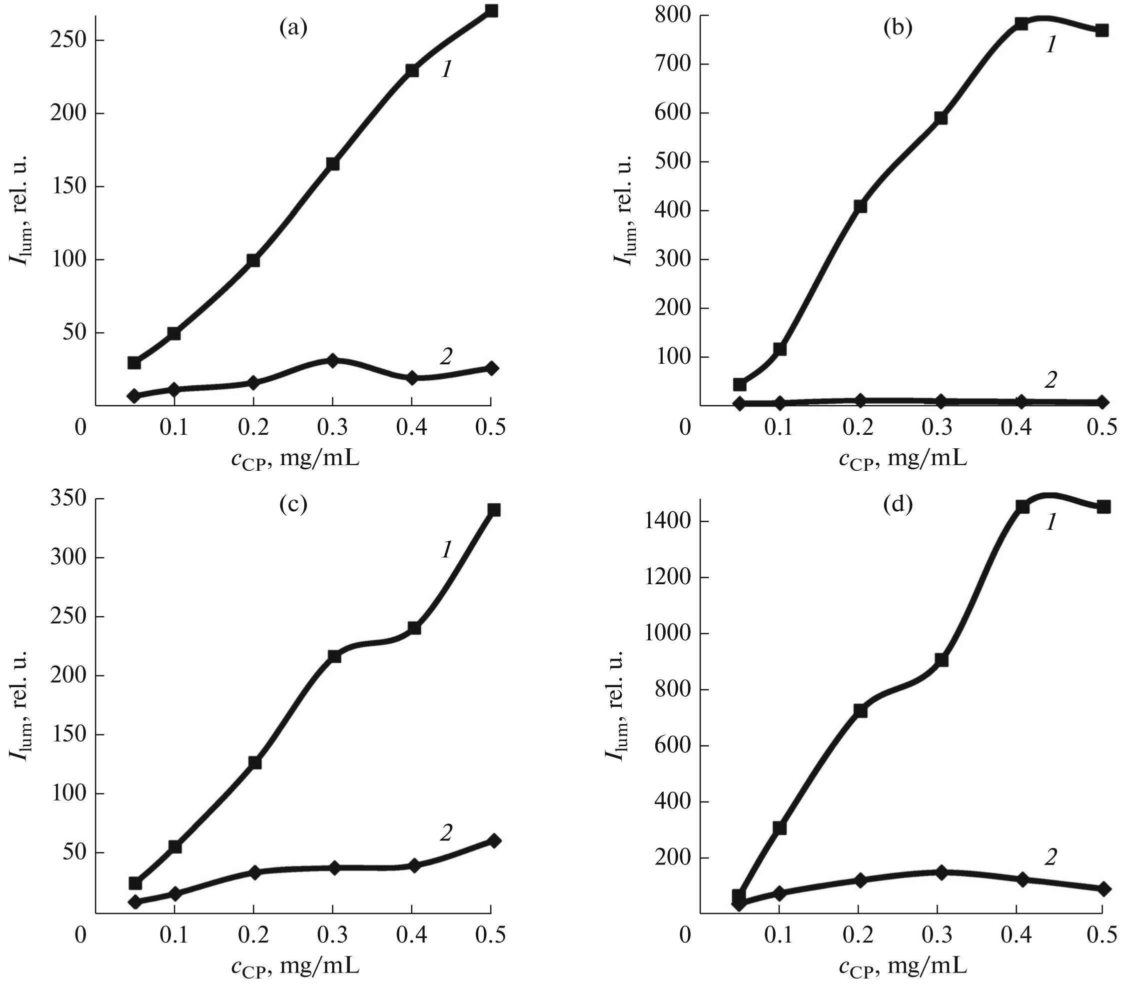


Fig. 1. Luminescence intensity of Tb(III) complexes with copolymers: (*1*) PMMA, (*2*) PSt incorporating (a, b) linear or (c, d) branched βd with the substituents: (a, c) CF_3 and (b, d) C_6H_5 for the βd : monomer ratio of 1 : 5 vs. amount of the copolymer in the solution ($c_{Tb} = 1 \times 10^{-4}$ mol/L; conditions of recording the luminescence are identical).

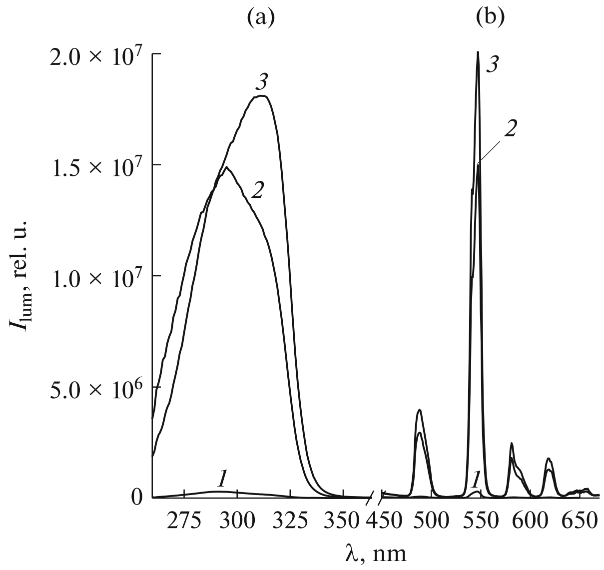


Fig. 2. (a) Luminescence excitation spectra, λ_{lum} = 547 nm and (b) luminescence spectra of the Tb(III) complexes with (*1*) PMMA, λ_{exc} = 290 nm and (*2*, *3*) copolymers: (*2*) MHD : MMA = 1 : 5, λ_{exc} = 295 nm and (*3*) MHD : MMA = 1 : 10, λ_{exc} = 313 nm. ($c_{Tb} = 1 \times 10^{-4}$ mol/L, c_{CP} = 0.1 mg/mL; conditions of recording the spectra are identical).

Table 3. Dependence of I_{lum} of Tb(III) complexes with PSt-based copolymers and various vinyl-β-diketones on the amount of the copolymer*

Tb(III) complexes with CPs		I_{lum}, rel. u. for c_{CP}, mg/mL					
βd (R)	βd : St ratio	0.05	0.1	0.2	0.3	0.4	0.5
MHD (R = CH_3)	PMHD**	0.8	0.9	0.6	0.6	0.5	0.4
	1 : 5	2.8	4.1	3.1	3.0	2.8	2.6
	1 : 10	5.8	5.0	4.5	4.0	3.1	1.8
TOD (R = CF_3)	1 : 1	8.6	11.4	20	23.8	25.7	30.0
	1 : 2	8.6	10.5	13.3	14.8	16.2	17.1
	1 : 5	7.1	11.4	16.2	31.4	19.6	26.2
	1 : 10	4.4	5.2	5.6	10.9	11.6	13.8
PHD (R = C_6H_5)	1 : 2	5.0	7.3	7.6	10.2	8.5	6.5
	1 : 5	5.3	6.2	11.1	10.0	8.8	7.6
	1 : 10	6.4	5.7	8.4	10.2	8.8	5.1
ATPD (R = CF_3)	1 : 1	84.0	185.0	410.0	503.0	594.0	632.0
	1 : 2	15.0	36.0	89.0	128.0	172.0	94.0
	1 : 5	8.0	15.0	33.0	37.0	39.0	60.0
	1 : 10	61.0	84.0	172.0	100.0	61.0	116.0
APBD (R = C_6H_5)	1 : 2	5.1	5.7	7.1	7.3	8.4	6.4
	1 : 5	38.0	75.0	122.0	150.0	125.0	91.0
	1 : 10	7.1	7.7	7.7	9.5	11.1	8.2
	PSt**	0.5	0.6	0.8	1.2	1.1	1.0

* $c_{\text{Tb}} = 1 \times 10^{-4}$ mol/L, $\lambda_{\text{exc}} = 365$ nm, $\lambda_{\text{lum}} = 545$ nm.
** PMHD, PSt are the homopolymers of 5-methyl-5-hexene-2,4-dione and styrene, respectively.

Table 4. Dependence of I_{lum} of Tb(III) complexes with PMMA-based copolymers and various vinyl-β-diketones on the amount of the copolymer*

Tb(III) complexes with CPs		I_{lum}, rel. u. for c_{CP}, mg/mL					
βd (R)	βd : MMA ratio	0.05	0.1	0.2	0.3	0.4	0.5
MHD (R = $-CH_3$)	PMHD**	26	28	42	40	38	37
	1 : 5	136	155	141	134	139	127
	1 : 10	160	225	223	220	215	210
TOD (R = CF_3)	1 : 2	50	77	167	206	262	320
	1 : 5	30	50	100	166	230	271
PHD (R = C_6H_5)	1 : 5	44	117	409	590	783	770
ATPD (R = CF_3)	1 : 2	47	78	224	292	324	388
	1 : 5	24	55	126	216	240	340
APBD (R = C_6H_5)	1 : 2	26	51	172	568	968	981
	1 : 5	66	308	726	906	1452	1452
	PMMA**	25	30	40	55		135

* $c_{\text{Tb}} = 1 \times 10^{-4}$ mol/L, $\lambda_{\text{exc}} = 365$ nm, $\lambda_{\text{lum}} = 545$ nm.
**PMHD, PMMA are homopolymers of 5-methyl-5-hexene-2,4-dione and methyl methacrylate, respectively.

Thus, unlike the complex formation of Ln^{3+} with monomeric β-diketones in solutions, the formation of complexes with CPs is possible if the fixed complexing groups occupy appropriate geometric positions, thus governing both the positions of β-diketone groups and the proper CP matrix. Therefore, Ln^{3+} ions exhibit more intense luminescence in the complexes with CPs that are less crowded with β-diketones.

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