Effect of ultrasonic irradiation on luminescence properties of lanthanide–polyelectrolyte complexes

J. Kido* and Y. Okamoto†
Department of Chemistry, Polytechnic University, 333 Jay Street, Brooklyn, NY 11201, USA

and N. Yoshioka, H. Nishide and E. Tsuchida
Department of Polymer Chemistry, Waseda University, Shinjuku, Tokyo 169, Japan

(*Received 13 June 1991; revised 12 August 1991; accepted 29 August 1991*)

Luminescence properties of Tb^{3+}– or Eu^{3+}–polycarboxylate complexes in aqueous solution were investigated. The excitation bands near 300 nm for terbium– or europium–polyacrylate solutions were drastically enhanced by the addition of hydroxyl-radical generating reagents as well as ultrasonic irradiation. These spectral changes were attributed to the energy transfer from chromophore molecules formed by the hydroxyl radicals generated in both systems.

(**Keywords: luminescence; terbium; europium; polymer complex; hydroxyl radical; ultrasonic irradiation; aqueous solution**)

INTRODUCTION

The luminescence properties of lanthanide ions are extremely sensitive, termed hypersensitive, to their coordinative environment[1]. These metal ions, particularly Eu^{3+} and Tb^{3+}, have been used as luminescent probes to study ionomer structures[2–4] and ion binding properties of synthetic polyelectrolytes[5–10] as well as biopolymers[11–15]. Although the luminescence intensity of the ions is quite weak in aqueous solutions due to efficient luminescence quenching by hydrated water molecules, the intensity is enhanced upon binding to either polycarboxylate or polysaccharides.

Previously Yoshino *et al.* have reported the effect of ultrasonic irradiation on solutions of Tb^{3+} ion complexes with polycarboxylates[6]. They found that the luminescence properties of aqueous solutions of Tb^{3+} complexes of polycarboxylates such as polyacrylate (PAA) and maleic acid copolymers were drastically changed by ultrasonic irradiation. The excitation band of the Tb^{3+} ion at 310 nm (emission at 545 nm) was greatly enhanced upon ultrasonic irradiation. The results were interpreted in terms of changes in the binding mode of polycarboxylates by ultrasonic irradiation.

We have found that the addition of radical-forming reagents to solutions of Tb–PAA have also led to such enhancement of the Tb^{3+} excitation band. The luminescence spectral profile was identical to that observed for the sonicated Tb–PAA solution. However, the luminescent species exhibiting that particular excitation band at 310 nm in both systems have not been identified and the origin of the band still remains uncertain. We have attempted to clarify this ambiguity and the results are reported in this paper.

EXPERIMENTAL

Materials. PAA ($M_w = 2.5 \times 10^5$) and poly(methacrylic acid) (PMA) ($M_w = 3.0 \times 10^5$) were prepared by radical polymerization. The copolymer of maleic acid and ethylene (MAE) ($M_w = 2.5 \times 10^5$) was obtained from hydrolysis of the corresponding maleic anhydride copolymer purchased from Monsanto. Poly(vinyl alcohol) (PVA) ($M_w = 1.4 \times 10^4$), poly(ethylene glycol) (PEG) ($M_w = 1.0 \times 10^4$) and poly(sodium 4-styrenesulphonate) ($PStSO_3Na$) were obtained from Aldrich. Terbium chloride ($TbCl_3 \cdot 6H_2O$) and europium chloride ($EuCl_3 \cdot 6H_2O$) were purchased from Research Chemicals and used without further purification.

The pH values of the polymeric or monomeric acid solutions containing terbium chloride were adjusted to between 7 and 9.5 by the addition of NaOH.

Ultrasonic irradiation was carried out with a Bransonic 220 ultrasonicator (55 kHz). A polymer solution (10 ml) in a 20 ml vial with a stopper was placed in the centre of the sonicator bath with water at the sample solution level. The sample was then irradiated with ultrasound for a known period. The water temperature was kept at ~ 10°C by circulating cold water through a copper tube in the sonicator bath.

Measurements. Luminiescence spectra were taken with a Perkin–Elmer MPF-44B or a Jasco FP-770 spectrofluorometer. U.v. absorption spectra were taken with a Cary 2300 or a Shimadzu UV-240 spectrophotometer.

RESULTS AND DISCUSSION

Addition of sodium polyacrylate to an aqueous solution of $TbCl_3$ led to the enhancement of the luminescence

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* Present address: Department of Materials Science and Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan
† To whom correspondence should be addressed

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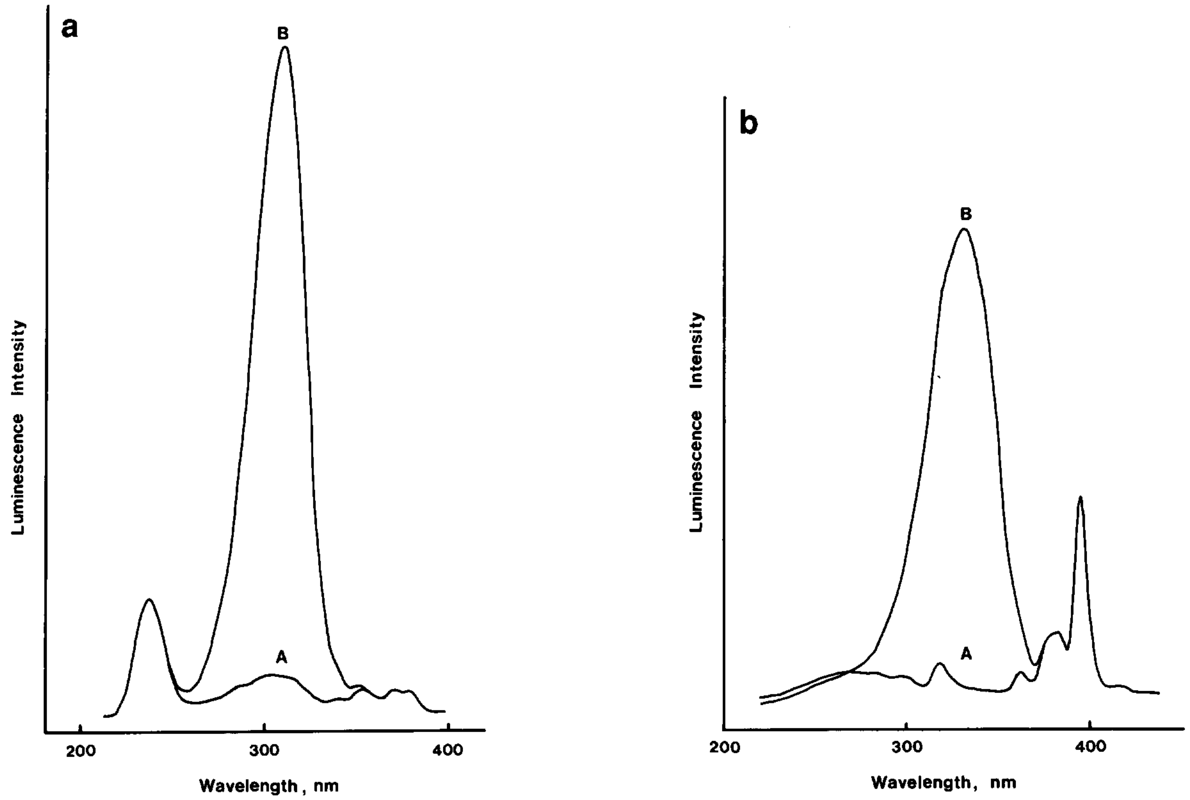

Figure 1 Excitation spectra of (a) Tb^{3+}-PAA and (b) Eu^{3+}-PAA, in aqueous solutions (A) before and (B) after ultrasonic irradiation for 1 h. [PAA] = 50 mN, [Ln^{3+}] = 1 mM, pH ~9.5, λ_{em} = 545 nm for Tb^{3+} and λ_{em} = 615 nm for Eu^{3+}. The intensity scale is arbitrary

intensity of the Tb^{3+} ion. This enhancement is caused primarily by the replacement of hydrated water molecules to the Tb^{3+} ion with carboxylate ligands. Water molecules act as efficient luminescence quenchers, hence displacement of such molecules from the first coordination sphere of the Tb^{3+} ion results in increasing luminescence intensity as well as luminescence lifetime[16,17]. It was reported[6] that the luminescence properties of Tb-polycarboxylate solutions were further changed by irradiation of the solutions with ultrasonic waves. In the cases of PAA and MAE, the broad excitation bands peaking at 310 nm for Tb^{3+} and 330 nm for Eu^{3+} were greatly enhanced as shown in *Figure 1*. The intensity increased with irradiation time and gradually decreased upon standing at room temperature or heating at 60°C for 30 min.

We found that the addition of a radical-generating reagent, $K_2S_2O_8$, to a Tb–PAA solution followed by incubation at 60°C greatly enhanced the excitation bands at 310 nm which also decreased upon ageing (*Figure 2*)*. The spectral profile is identical to that for the sonicated Tb–PAA solutions. The luminescence intensity at 310 nm increased with incubation time and was proportional to the concentration of $K_2S_2O_8$ added.

Other radical-generating reagents were also examined in the Tb–PAA system and the results are summarized in *Table 1*. Among these reagents, the luminescence intensity at 310 nm was enhanced only by the addition of $K_2S_2O_8$, $(NH_4)_2S_2O_8$ or H_2O_2. These reagents are known to generate hydroxyl radicals in aqueous solution after decomposition by heating. On the other hand, systems which do not involve hydroxyl radical formation such as aqueous azobis(2-amidinopropane) dihydrochloride (AAPD), and methanolic azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) solutions did not cause any spectral changes. These results suggest that hydroxyl radical formation is essential for causing such enhancement in the luminescence of Tb^{3+}-polymer complexes. The concentration of hydroxyl radical generated by the addition of $K_2S_2O_8$ was determined by the spectroscopic method of Gutteridge and Wilkins[18], and

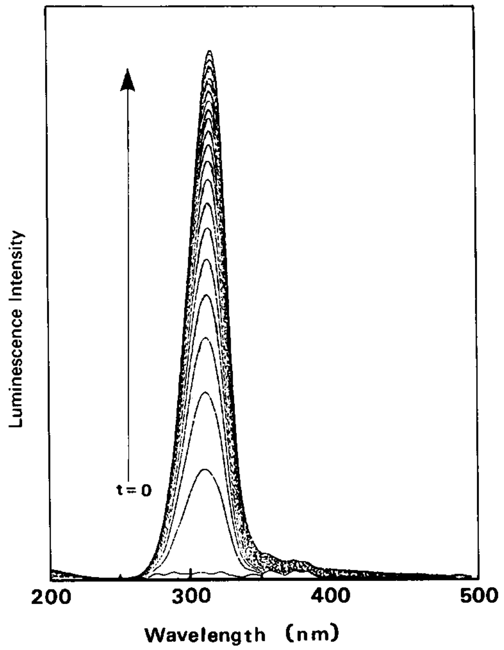

Figure 2 Time course in the excitation spectra of Tb^{3+}-PAA in the presence of $K_2S_2O_8$ at 60°C. [PAA] = 30 mN, [Tb^{3+}] = 1 mM, [$K_2S_2O_8$] = 1 mM, pH ~8.0. The time interval between each scan is 10 min, and the intensity scale is arbitrary

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* Incubated below 40°C no spectral changes were observed, indicating that no reaction took place between the complex and $K_2S_2O_8$

Table 1 Intensity of the excitation band at 310 nm[a] for the Tb–PAA system in the presence of various radical generators

Reagent[b]	Solvent	Relative intensity[c]
$K_2S_2O_8$	Water	100
$(NH_4)_2S_2O_8$	Water	66
H_2O_2	Water	23
AAPD	Water	0.33
AIBN	Methanol	0
BPO	Methanol	0

[a] $\lambda_{em} = 545$ nm
[b] [Reagent] = 1 mM
[c] [PAA] = 30 mN, $[Tb^{3+}] = 1$ mM, pH = 8. Luminescence spectra were taken after incubation at 60°C for 30 min

Table 2 Intensity of the excitation band at 310 nm[a] for Tb^{3+} complexes of various ligands in the presence of $K_2S_2O_8$

Ligand[b]	Relative intensity[c]
PAA	100
PMA	1.4
PVA	0.72
$PStSO_3Na$	0.71
PEG	0
Acrylic acid	0
Propionic acid	0
Maleic acid	0
1,3,5-Pentanetricarboxylic acid	1.1

[a] $\lambda_{em} = 545$ nm
[b] [Ligand] = 30 mN
[c] $[K_2S_2O_8] = 1$ mM, $[Tb^{3+}] = 1$ mM, pH = 8. Luminescence spectra were taken after incubation at 60°C for 30 min

was found to be proportional to the enhancement of luminescence intensity in the Tb–PAA system. It is, therefore, possible to determine the hydroxyl radical concentration in aqueous solution by using the Tb–PAA complex.

The effect of ligand structure on the enhancement of luminescence intensity by radical generators were investigated with various polymeric and monomeric ligands. $K_2S_2O_8$ was added as a hydroxyl radical generator for the Tb^{3+} complexes, and the results are summarized in *Table 2*. In the cases of PMA, PVA, $PStSO_3Na$, PEG and pentanetricarboxylic acid, the effect of $K_2S_2O_8$ was negligible compared with PAA. This is reasonable since the Tb^{3+} ion does not form complexes with PVA and PEG, and only weakly forms a complex with $PStSO_3Na$ in aqueous solutions. Consequently, any structural changes in these polymers do not have any influence on the luminescence properties of the Tb^{3+} ion. In the case of PMA, the effect of adding the radical generator was found to be negligible. It should be noted that ultrasonication also had no effect on the luminescence of the Tb–PMA system. The binding properties of both PAA and PMA are quite similar: the Tb^{3+} ion is condensed onto the polymer by site binding with three to four hydrated water molecules[7]. Therefore, any differences seen with hydroxyl radicals are not due to polymer configuration or complex structure. A structural difference between these polymers is the presence of the methyl group for PMA and the presence of the α-hydrogen for PAA. The effect of such differences will be discussed later in this paper.

The excitation peak at 310 nm in Tb^{3+} luminescence is referred to as a hypersensitive band. However, there are very few reports concerning this band[8,19] and detailed photophysical properties are still unknown. On the other hand, broad excitation bands often result from luminescence sensitization by a chromophore, that is, absorbed energy by the organic molecules is transferred to the metal ion in a non-radiative or radiative manner[20–22]. Such intra- or intermolecular energy transfer occurs to the metal ion emissive levels from a higher energy singlet or triplet state of the organic molecule. Since the broad excitation band such as seen for Eu^{3+}–PAA after sonication in *Figure 1* has not been reported as an intrinsic Eu^{3+} excitation band, the broad bands near 300 nm in Tb or Eu are likely to be the consequence of sensitization by chromophores. However, polymer molecules such as PAA and MAE do not possess any chromophores to transfer energy to the metal ion. Thus, if the excitation bands near 300 nm are due to sensitization, the sensitizing organic groups should be produced upon ultrasonic irradiation or by the addition of hydroxyl radical-forming reagents. It is known that ultrasonic irradiation of aqueous polymer solutions yields hydroxyl radicals[23] and it may follow that chromophore molecules will be produced by the chemical reactions of hydroxyl radicals.

The u.v. absorption spectra of MAE solutions in the presence or absence of the Tb^{3+} ion, and before and after sonication, are shown in *Figure 3*. After sonication a broad band peaking at 280 nm appeared. In addition to the band at 280 nm, another broad band appeared at 310 nm in the presence of Tb^{3+} ion. This band at 310 nm was also seen as a shoulder in the Tb–PAA system although it is not as distinctive. The intensity of these absorption bands at 310 nm seems to be proportional to

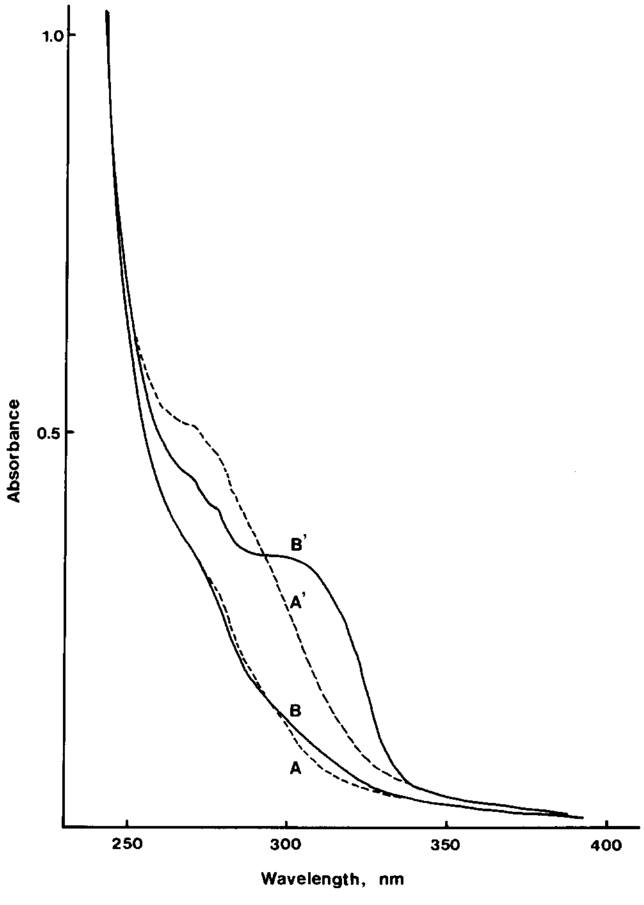

Figure 3 U.v. absorption spectra of Tb^{3+}–MAE in aqueous solutions. [MAE] = 50 mN, pH = ~9.5; (----), in the absence of Tb^{3+} (A) before and (A') after sonication; (——), in the presence of 2 mM Tb^{3+} (B) before and (B') after sonication

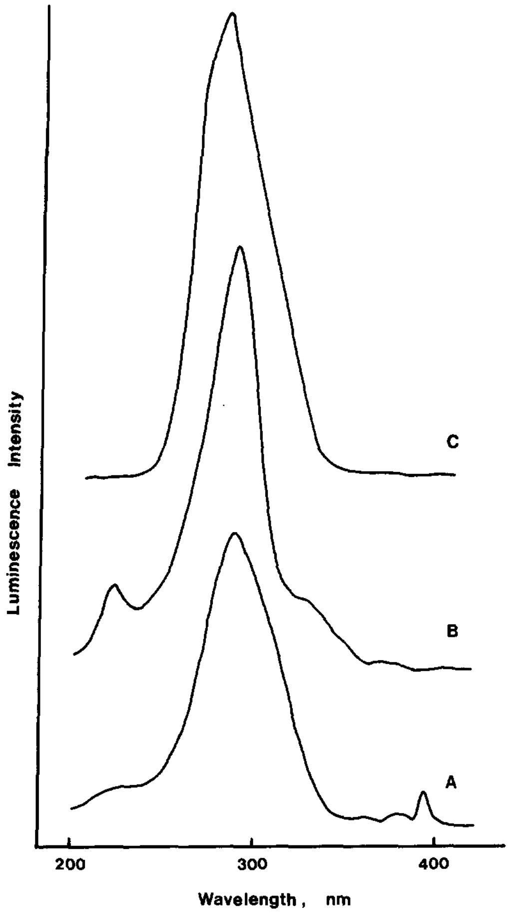

Figure 4 Excitation spectra of Tb^{3+} or Eu^{3+} complexes of carbonyl-containing ligands in aqueous solutions. (A) [1,3-Acetonedicarboxylic acid] = 0.1 N, [Eu^{3+}] = 2 mM, pH ~7, λ_{em} = 613 nm; (B) [1,3-Acetonedicarboxylic acid] = 0.1 N, [Tb^{3+}] = 2 mM, pH ~7, λ_{em} = 543 nm; (C) [Succinic semialdehyde] = 5 mN, [Tb^{3+}] = 2 mM, pH ~7, λ_{em} = 543 nm. The intensity scale is arbitrary

that of the excitation bands at 310 nm; the luminescence intensity of the 310 nm band for Tb–MAE was much greater than that for Tb–PAA. Because the absorption bands at 310 nm were only observed in the presence of Tb^{3+} ion, it is likely that the band at 310 nm is a charge transfer band of the Tb^{3+} complexes. The PMA system, which did not exhibit the 310 nm excitation band even after sonication, lacks the absorption band at 310 nm even in the presence of Tb^{3+} ion. The results suggest the existence of chromophore molecules in the cases of PAA and MAE.

As mentioned earlier, one of the differences between PMA and PAA is the existence of the α-hydrogen (to the carboxylic group) in the polymer main chain. Therefore, it is reasonable to assume that the formation of the chromophore involves the α-hydrogen in the polymer main chain. It is known that the α-hydrogen is easily abstracted by an external radical via a chain transfer mechanism resulting in the production of a free radical at that position. The formation of the chromophore is assumed to be due to such a reaction.

We tested some carbonyl-containing ligands as possible chromophore molecules. Carbonyl groups are common defects in the polymer backbone initiating polymer degradation, and sensitizing Ln^{3+} luminescence[24–26]. Thus, luminescence spectra of some Tb^{3+} complexes of monomeric carboxylic acids containing ketone or aldehyde groups were taken and are shown in *Figure 4*.

A broad band near 300 nm is observed for Tb– or Eu–acetonedicarboxylate and Tb–succinic semialdehyde. The band is broader and much more intense than the intrinsic 4f–4f Tb^{3+} absorption. Since these transitions are not intrinsic Tb^{3+} or Eu^{3+} transitions, luminescence sensitization by the ketone or aldehyde moiety of the ligands takes place. Although the locations of the peaks are not exactly the same as found in the irradiated Tb^{3+}–polymer complexes, these results support the possibility of energy transfer from carbonyl groups in the polymeric systems.

The results show that the effect of ultrasonic irradiation observed in Tb–PAA is well reproduced by the addition of hydroxyl radicals. It is concluded that the luminescence excitation bands around 300 nm in Tb^{3+} as well as in the Eu^{3+}–polymer complex solutions after ultrasonic irradiation do not originate from intrinsic Tb^{3+} or Eu^{3+} 4f–4f transitions but are energy transfer bands of the complexes. The chromophore molecules are formed by ultrasonic irradiation, and are slowly decomposed by reduction or oxidation in aqueous solution. Consequently the excitation band enhanced by ultrasonic irradiation decreases upon standing at room temperature or heating. The complex species, however, could not be identified due to the low concentrations of the particular complex molecules.

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