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Luminescence of Cerium(III) Polymer Complexes

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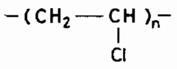
Abstract

New fluorescence films of complexes of Ce(III) with polyvinyl chloride (PVC) were prepared. The fluorescence properties of the PVC–Ce(III) films were compared with those of Ce(III) complexes with polymethylmethacrylate (PMMA) and with polystyrene (PS). The difference in the fluorescent properties between these three films was explained by assuming that the functional group coordinates with a Ce(III) ion in the polymers. The fluorescence films dispersed a crown ether (18•C•6); PVC–Ce(III)–18•C•6, PMMA–Ce(III)–18•C•6 and PS–Ce(III)–18•C•6 were also prepared. In the films containing both Ce(III) and the crown ether, competition between the crown ether and the coordination group in the polymer for the complexation with the Ce(III) ion was discussed. Another new complex of Ce(III) with poly(2-methacryloyloxymethyl-1,4,7,10,13,16-hexaoxacyclododecane) (PMA18•C•6) in which the crown ether moiety is attached directly to the methacryloyloxymethyl group was synthesized, and the fluorescence of the complex powder, PMA18•C•6–Ce(III) was also discussed.

Introduction

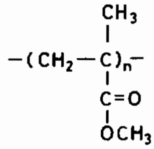
The fluorescent properties and the energy transfer in trivalent rare earth [RE(III)]–organic ligand complexes have been studied [1–5]. Fluorescence of divalent rare earth–crown ether ligand complexes has been well reported [6–12]. Okamoto *et al.* [13–16] and Nishide *et al.* [17] have reported the complexation of RE(III), such as Eu(III) and Tb(III), with polymers and the fluorescence properties of the polymer–RE complexes.

Recently, we have investigated the effect of the ligand substituent on RE(III) luminescence in the polymer films [18]. The transparent films fluoresce as red and green lights as the complexes of Eu(III)– and Tb(III)–β-diketone are uniformly dispersed into the PMMA matrix and irradiated by UV light. We also synthesized another Ce(III)–polymer complex which is a homogeneous film of polymethylmethacrylate containing Ce(III) or PMMA–Ce(III), which emits a strong UV fluorescence (380–390 nm) [19]. The luminescence of the complexes between Ce(III) and crown ethers has not yet been reported, although the complex has been prepared and the structure analysed in detail [20–23]. Other new fluorescent films were synthesized and the relationship was discussed between their fluorescence properties and the functional groups coordinating with Ce(III) in PVC (**1**), PMMA (**2**) and PS polymers (**3**). We have synthesized a new fluorescent material, PMA18•C•6–Ce(III), which is a complex of Ce(III) with PMA18•C•6 (**4**), and the fluorescence properties have been presented. It is noteworthy that there is a difference in the fluorescence properties for PMMA–Ce(III)–18•C•6 and PMA18•C•6–Ce(III), although both PMMA and PMA18•C•6 have almost the same polymer structure, except that the hydrogen of the methyl group attached to oxygen has been substituted by a crown ether (18•C•6).



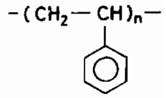
$-(CH_2-\underset{Cl}{CH})_n-$

PVC (**1**)

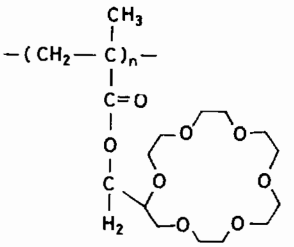


$-(CH_2-\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}})_n-$

PMMA (**2**)



PS (**3**)



PMA18•C•6 (**4**)

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Experimental

Materials

Methanol, ethanol, acetone, tetrahydrofuran (THF), PVC, PMMA, PS and 18·C·6 were obtained from Wako Pure Chemicals Ltd., Osaka, Japan. Anhydrous $CeCl_3$ and films of PVC–Ce(III), PMMA–Ce(III) and PS–Ce(III) were prepared by the method reported in ref. 19, except that the solvent for PVC was THF instead of acetone. The films containing both Ce(III) and the crown ether, namely PVC–Ce(III)–18·C·6, PMMA–Ce(III)–18·C·6 and PS–Ce(III)–18·C·6, were prepared in a similar manner, also described in ref. 19. The cerium metal content in all films was up to 0.1 wt.% at a transparency larger than 90%, and the molar ratio of the crown ether to the Ce(III) ion in the films containing both Ce(III) and 18·C·6 was up to 2.0.

PMA18·C·6 was obtained by radical polymerization of methacryloyloxymethyl–18·C·6 with the same method as described in ref. 24. The PMA18·C·6–Ce(III) complex was prepared by impregnating 0.1 g of the PMA18·C·6 in 0.1 M methanolic solution of $CeCl_3$ for 20 h. Finally, the PMA18·C·6–Ce(III) complex powder was obtained by filtering and drying the 'gel' under vacuum for several hours.

Measurement Techniques

Absorption spectra and transparencies of the films were observed by the use of a Shimadzu double-beam spectrophotometer, model UV-180. Emission and excitation spectra were determined on a Shimadzu absolute spectrofluorophotometer, model RF-502, equipped with an automatic compensation and procalibration system.

The fluorescence lifetimes for both films and powder were measured using a Horiba time-resolved spectrofluorometer NAES-1100 equipped with a high pressure hydrogen lamp (pressure 1 MPa, half-width of the pulse <2 ns). IR spectrum analysis was carried out for nujol mulls of KBr pellets with an FTIR-3 spectrometer. The Ce(III) content in the PMA18·C·6–Ce(III) powder was determined by the usual EDTA titration method.

Results and Discussion

Characterization of Polymers Obtained

The transparent films of the complexes were synthesized by casting from acetone solutions for PMMA and PS or from the THF solution for PVC containing Ce(III) ions and 18·C·6. All polymers which dispersed the Ce(III) ions and 18·C·6 were the films having a 0.03 mm thickness, and the Ce(III) ions and 18·C·6 which have a homogeneous distribution. The Ce(III) average content was 0.68 wt.% for all the films (about 0.60, 0.65 and 0.75 wt.% for the PS, PMMA and PVC film systems, respectively), and the optimum molar ratio of Ce(III) to 18·C·6 was about 1:1. The films had a transparency of >90% in the visible region. IR spectra were also observed, but because the solubility of the Ce(III) ion and the 18·C·6 is low the variation of the spectra is too small to be measured for films having a higher transparency. Our original purpose was to prepare a film of PMA18·C·6–Ce(III), however, a powder of the complex was obtained. When PMA18·C·6 was impregnated into a methanol solution of $CeCl_3$ for several hours, the rubber-like product was gradually transformed to a 'gel' state. Elasticity of the complex and its capability of forming a film were considerably reduced because of the complexation. The Ce(III) content in the PMA18·C·6–Ce(III) complex was about 18.6 wt.%.

Luminescence of the Films

It seems to be necessary to know the luminescence mode of all the polymers used as ligands for a Ce(III) ion before considering the fluorescent properties of the complexes of Ce(III) with the polymers. The luminescence and excitation spectra of these polymers are shown as individual em_0 and ex_0 in Figs. 1, 2 and 3. The luminescence intensity is stronger for PS than for PVC and PMMA, because the former occurs from the π^*–π transition of a phenyl moiety, and the latter from the π^*–n transition. When Ce(III) ions were introduced into PVC, a strong emission band was observed. This band differs from that of uncomplexed PVC, as indicated in Fig. 1, and is presumably due to an overlap of two symmetrical bands with a peak separation of about 1600 cm^{-1}, which are assigned to a transition from 5d to 4f with a doublet ($^2F_{5/2}$ and $^2F_{7/2}$) [25]. As described in ref. 19, because the fluorescence originates from the Ce(III) ion complexed with a carbonyl group in PMMA, the PVC–Ce(III) fluorescence is also expected to be generated by complexation of the Ce(III) with a chloride ion in the PVC–Ce(III) films,

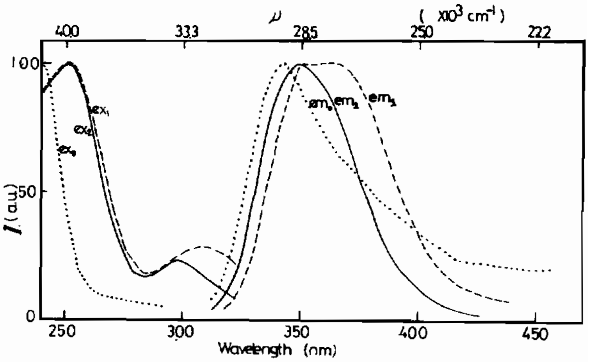

Fig. 1. Excitation and emission spectra of: PVC–Ce(III)–18·C·6 (——), PVC–Ce(III) (- - - -), excitation 255 nm; PVC, (·······), excitation 240 nm.

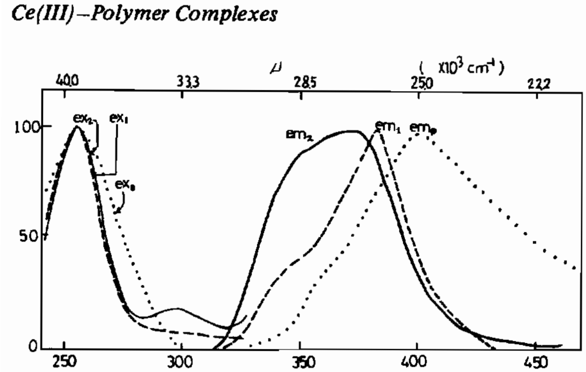

Fig. 2. Excitation and emission spectra of: PMMA–Ce(III)–18·C·6 (——), PMMA–Ce(III) (- - - -), excitation 255 nm; PMMA) (·······), excitation 255 nm.

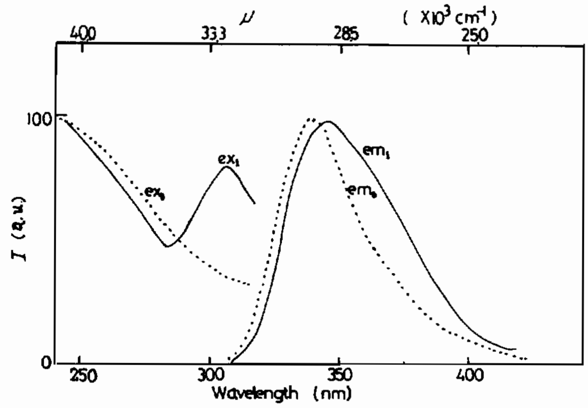

Fig. 3. Excitation and emission spectra of: PS–Ce(III)–18·C·6 (——), PS–Ce(III) and PS (,,,,,,,) excitation 240 nm.

although the coordinating capability of a chloride ion seems to be weak. The shape of the emission band does not vary with Ce(III) content, in contrast to the PMMA–Ce(III) film [19].

The position of the emission band of Ce(III) varies with the splitting of the 5d level. The stronger the ligand field, the larger is the splitting of the 5d level [25]. Because the strength of the ligand field for a C=O group is known to be greater than for Cl^- [26], the emission band is situated at a longer wavelength for PMMA–Ce(III) than that for PVC–Ce(III).

When the Ce(III) ion was introduced into the PS film under the same conditions, the emission spectrum and the intensity did not differ from PS itself. It seems likely that complexation between the Ce(III) ion and PS does not occur. The phenyl moiety cannot coordinate to the Ce(III) ion, since a phenyl ring does not have a lone pair of electrons. A strong fluorescence band was observed at 338 nm which originates from a phenyl group [27], although the Ce(III) ions were dispersed in the PS film.

It is well known that because the ionic diameter (2.4 Å) of the Ce(III) ion is comparable with the cavity size (2.6 Å) of an 18·C·6 ring, Ce(III)–18·C·6 complexes with a 1:1 molar ratio easily occur [20–23], and hence the addition of Ce(III) and 18·C·6 in the previously mentioned polymers is of interest. When the Ce(III) ion together with the 18·C·6 were dispersed in the films of PVC and PMMA, a variation in the fluorescent properties was indicated. For the former, PVC–Ce(III)–18·C·6, the emission band shifted to a shorter wavelength, its half-width became narrower, and the fluorescent intensity increased by about 4 times. For PMMA–Ce(III)–18·C·6, however, the emission spectrum was composed of a relatively broad band centered at about 370 nm and a shoulder at 350 nm. The fluorescence intensity was almost equal to that of PMMA. It can be seen from the results that the crown ether has a different influence on the fluorescent properties for the films of PVC–Ce(III)–18·C·6 and of PMMA–Ce(III)–18·C·6. Since PMMA has stronger and better coordination capabilities than PVC, the degree of influence of the crown ether on the fluorescence properties is smaller for PMMA than for PVC. The fluorescence of the Ce(III)–18·C·6 complex was mainly observed for the PVC–Ce(III)–18·C·6 film because the complexation of Ce(III) with a chloride ion is very weak, but for the PMMA–Ce(III)–18·C·6 film, the coordination of the Ce(III) ion with a carbonyl group and a crown ether ring presumably occurs to the same extent.

We have also observed the luminescence of Ce(III) in methanol and ethanol solutions. When $CeCl_3$ powder together with the crown ether was dissolved in these solutions, the fluorescences of the solutions displayed remarkably different characters. Figure 4 shows the excitation and emission spectra of the methanol solution containing 18·C·6 and Ce(III). The emission band em_1 is composed of an overlap of two bands, and the maximum is the same wavelength as em_0, which originates from the solvated Ce(III), but the band at 337 nm corresponds to that of the complex of the Ce(III) ion with the crown ether. The emission band in the ethanol solution was, however, only generated from the complex of the

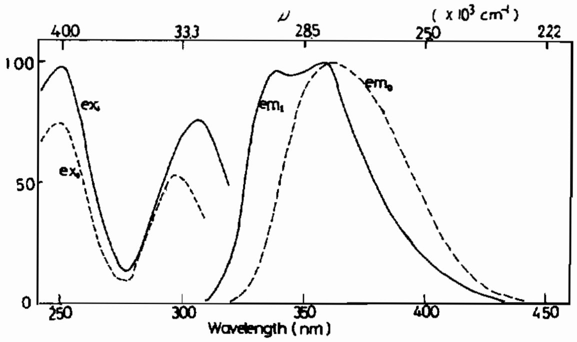

Fig. 4. Excitation and emission spectra of: Ce(III)–18·C·6 (——) and $CeCl_3$ (- - - -) in methanol, excitation 250 nm.

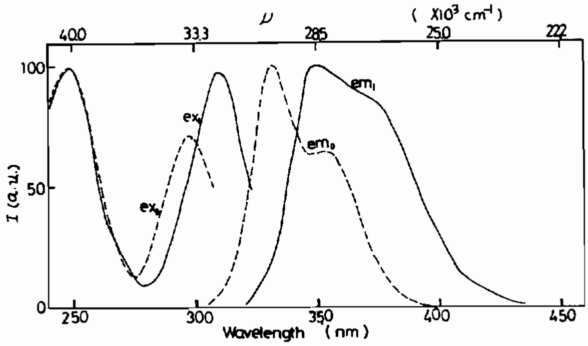

Fig. 5. Excitation and emission spectra of Ce(III)–18•C•6 (——) and $CeCl_3$ (- - - -) in ethanol, excitation 250 nm.

Ce(III) ion with the crown ether, as indicated in em_1 of Fig. 5. The reason for this is that methanol has such a strong solvation capability that the complexation of Ce(III) with the crown ether is partly reduced, but the solvation of ethanol is weaker than methanol. The fluorescent properties in ethanol solution were related only to the complex of Ce(III) with the crown ether. It can, therefore, be concluded that the above-stated solid film 'solvent' seems to be like a methanol or ethanol solvent for the complexation. The crown ether competes with the coordination group of the solid film 'solvent' in the polymer system.

As shown in em_1 of Fig. 3, a weaker band at 345 nm is observed for the PS–Ce(III)–18•C•6 film. The intensity of the band is considerably weaker than that of PVC–Ce(III)–18•C•6, because the excitation energy may be mainly absorbed by the aromatic groups of PS and may not transfer to Ce(III).

The fluorescence lifetime was increased by adding 18•C•6 to the PVC–Ce(III) and PMMA–Ce(III) films. This is taken to show that a proportion of a radiation-less transition was reduced [17].

Luminescence of Powder Sample

ex_1 and em_1 in Fig. 6 indicate the excitation and emission spectra of the PMA18•C•6–Ce(III) powder, which differ from those of PMA18•C•6 (see ex_0 and em_0 in Fig. 6); the fluorescence intensity is drastically stronger for the complex than for the ligand. The position of the maximum emission band for the complex is the same as the 350 nm shoulder of the emission band for PMMA–Ce(III)–18•C•6, which originates from the Ce(III)–18•C•6 complex (see Fig. 2). From the fluorescent properties of PMA18•C•6–Ce(III), it is presumed that the Ce(III) ions are complexed with the crown ether group. It is noteworthy that the 385–390 nm emission band generated from the complexes of Ce(III) with the carbonyl group is almost no longer observed, although there are two possibilities for the Ce(III) to complex with the carbonyl or the 18•C•6 groups in the PMA18•C•6 ligand. The emission spectrum is composed of a sharp band centered at 350 nm, which indicates the complexation of Ce(III) with a 18•C•6 group in PMA18•C•6. The complexation between Ce(III) and the crown ether group is also supported by the IR spectrum of PMA18•C•6–Ce(III), in which the ν_{as}(CCO) vibration shifts about -15 to -20 cm^{-1} toward lower wavenumbers upon complexation between Ce(III) and PMA18•C•6. This gives evidence for a moderate interaction between the polyether and the metal ion [20, 28].

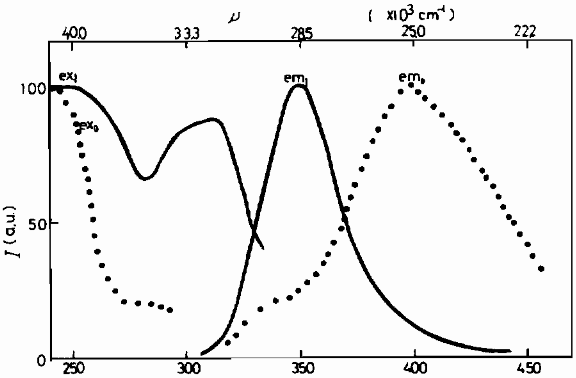

Fig. 6. Excitation and emission spectra of PMA18•C•6–Ce(III) (——), excitation 250 nm; and PMA18•C•6 (·······), excitation 240 nm.

This phenomenon may be accounted for by the obviously different existence state of the polyether in the two polymers, as described in ref. 19. For the PMMA–Ce(III) film, the luminescence of Ce(III) generates from the UV absorption of the PMMA matrix, and the energy transfers from the polymer to the Ce(III). As shown in Fig. 6, the excitation spectrum of the PMA18•C•6–Ce(III) powder is composed of two bands, one of which, the 310 nm band, is due to a direct excitation of the Ce(III) ion; another of which, the 250 nm band, only partly overlaps that of the PMA18•C•6 ligand. It seems, therefore, that the fluorescence of the Ce(III) ions complexed with the 18•C•6 group is mainly generated from a direct excitation of Ce(III).

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