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Ultraviolet Fluorescence of Polymer Films Containing Cerium Ions

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Abstract

Transparent films of Ce^{3+}–polymethylmethacrylate (PMMA) were prepared. The films exhibit an ultraviolet emission (380–390 nm) by a 255 nm excitation. The fluorescence in the Ce^{3+}-films originated from Ce^{3+} complexed with the PMMA polymer; an energy transfer from the PMMA matrix to Ce^{3+} ions in the Ce^{3+}-films seems to take place. Effects of Ce^{3+} contents on fluorescence properties of the Ce^{3+}-films are also discussed.

Introduction

The fluorescence and the energy transfer of complexes containing trivalent rare earths (RE^{3+}) have been investigated [1–3]. Recently Okamoto *et al.* [4–6] and Nishide *et al.* [7] have studied the fluorescence of the rare earth metal-containing polymers. However, no reports on the fluorescence of Ce^{3+} in an organic polymer system have yet been published, although Ce^{3+}-activated inorganic materials were previously reported.

In this paper, we report the results of our investigation of the absorption, excitation and emission properties of the Ce^{3+}-films. Transparent ultraviolet emitting films might be useful for some light traps in agriculture.

Experimental

Materials

Methanol, acetone and PMMA were obtained from WAKO Pure Chemical Ltd.

Anhydrous $CeCl_3$ was prepared from $CeCl_3 \cdot nH_2O$ (99.99%) which was mixed with an excess of NH_4Cl and fired at 500 °C for 1 h in a hydrogen atmosphere.

Anhydrous $CeCl_3$ powders were dissolved into 2 ml of methanol (solution 1) 0.2 g of PMMA were dissolved into 20 ml of acetone (solution 2). Both solutions were mixed and diluted again with acetone to 30 ml. The mixed solution was stirred and poured into a glass dish. Transparent films were obtained while acetone slowly evaporated. Finally, the transparent films were dried in vacuum for several hours at room temperature. The cerium metal content in the Ce^{3+} film system is up to 3 wt.% at the appropriate transparence.

Measurement Techniques

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

The fluorescence lifetimes of the Ce-films 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). X-ray microanalysis was carried out with a HITACHI X-650 EDX for confirmation of uniform distribution of Ce^{3+} ions.

Results and Discussion

Transparent soft UV-fluorescence films were prepared by casting from acetone solutions of PMMA containing Ce^{3+} ions. Anhydrous $CeCl_3$ compounds as a source of trivalent cerium ions may be replaced by anhydrous $CeBr_3$ for preparing the films. All the films have a 0.05 mm thickness and transparency of >90% in the visible region. The Ce^{3+} content was 0.1–3.0 wt.% in the Ce^{3+}-films. A photograph of EDX showed evidence of a uniform distribution of Ce^{3+} ions in the film.

The emission and excitation spectra of the Ce^{3+}-film and anhydrous $CeCl_3$ are shown in Fig. 1. It is obvious that the luminescence properties of the anhydrous $CeCl_3$ powder and the film containing Ce^{3+} differ considerably from each other. Two emission bands (350 and 385 nm) of the Ce^{3+}-film have longer wavelength than those (340 and 365 nm) of the anhydrous $CeCl_3$ powder. The separation between the two bands was larger for the Ce^{3+}-films than for the $CeCl_3$ powder, and the emission intensity at shorter wavelength for the Ce^{3+}-films

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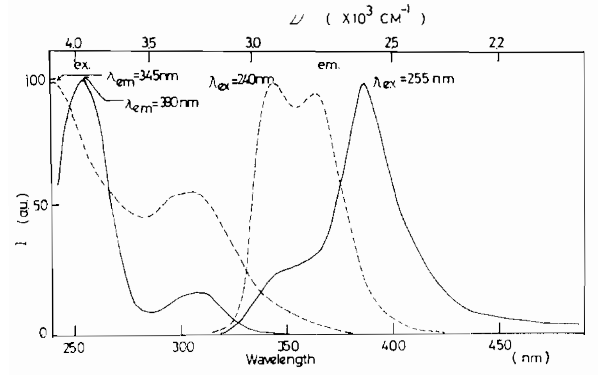

Fig. 1. Excitation and emission spectra of powder $CeCl_3$ (– – –) and Ce^{3+}-film (——).

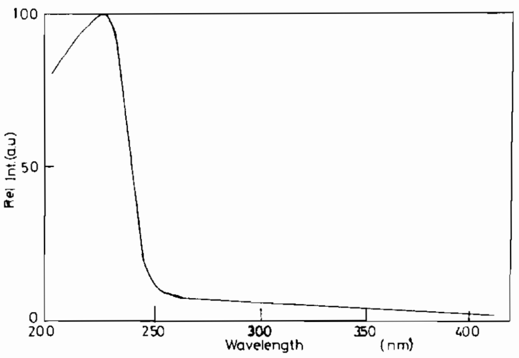

Fig. 2. Relative absorption spectra of Ce^{3+}-films in UV region.

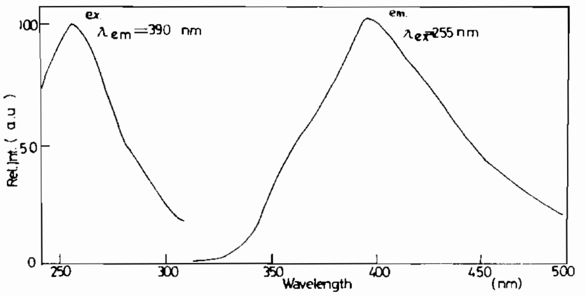

Fig. 3. The excitation and fluorescence spectra of PMMA film alone.

was smaller than for the anhydrous $CeCl_3$ powder. This fact indicates explicitly the difference in the condition of the Ce^{3+} ions when the anhydrous $CeCl_3$ powder was dispersed into the PMMA polymer. This is because the environment of Ce^{3+} ions was varied from an inorganic host to an organic polymer matrix. The maximum excitation band of the Ce^{3+} fluorescence in the Ce^{3+}-films corresponds with the absorption spectrum of the Ce^{3+}-films, as shown in Fig. 1 (solid line) and Fig. 2. Figure 3 shows excitation and emission spectra of PMMA alone; the shape of emission band differs from that of the Ce^{3+}-film, and the fluorescence intensity is approximately 1% as much as that of Ce^{3+}-fluorescence in the Ce^{3+}-film. The absorption band of the Ce^{3+}-films is in agreement with that of the PMMA polymer, having a peak at about <230 nm. But an f–d absorption in Ce^{3+} is too weak in comparison with the PMMA, so that nearly all the excitation energy in the UV region seems to be absorbed by the PMMA matrix in the Ce^{3+}-film system (see Fig. 2). Thus, there may be 'complexation' between the carbonyl groups of PMMA and the Ce^{3+} ions in the Ce^{3+}-film system, notwithstanding that a carbonyl group in PMMA is usually considered to be chemically inactive. Unfortunately, the solubility of Ce^{3+} ions in the transparent films is too small to measure the variation of IR spectra. Nevertheless, the complexation between the polymers containing a carbonyl group and Ce^{3+} in the Ce^{3+}-film was indirectly examined based on the fluorescence properties of the Ce^{3+}-film system. Because of the complexation, the efficient energy transfer from the organic polymer to Ce^{3+} ions was assumed to take place.

Intramolecular energy transfer from a ligand to the central metal ion in RE^{3+}–organic complexes has been widely studied [8]. The absorption of the PMMA originates from the transition of π^*–n of the carbonyl groups in the polymer. The absorbed energy is transferred to the central metal ion in the complex system via the lowest 'triplet' state of the ligand. Because the efficient energy transfer from the PMMA ligand to a 5d level of the Ce^{3+} ion takes place, an intense Ce^{3+}-fluorescence was observed for the Ce^{3+}-films.

The fluorescence emission of the Ce^{3+} ion originates from a transition of 4f–5d and the ground state of a Ce^{3+} ion is a doublet ($^2F_{5/2}$ and $^2F_{7/2}$) with a separation of about 2000 cm^{-1}. Thus, each emission band is expected to show two peaks with a separation about 1600–3300 cm^{-1}. The separation decreases with increasing Ce^{3+} content in the film (Fig. 4) because the doublet character of the emission band depends on the Ce^{3+} concentration [9].

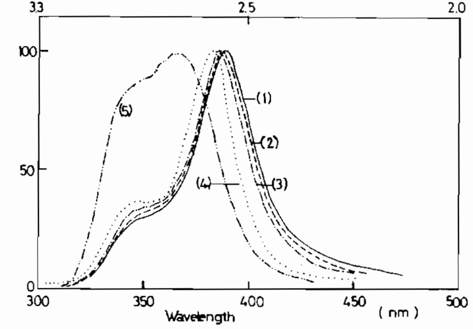

Fig. 4. The dependence of emission spectra on Ce^{3+} ion content in Ce^{3+}-film system. (1) 0.11%; (2) 0.22%; (3) 0.33%; (4) 1.10%; (5) 3.0%.

It is well known that in the case of an inorganic oxide lattice the emission of Ce^{3+} usually peaks in the near UV region [9]. Ce^{3+} ions are complexed with PMMA by coordination through a donor atom of oxygen when anhydrous CeCl$_3$ powder is introduced in the PMMA polymer. Neighbourhoods of Ce^{3+} ions in the Ce^{3+}-films would be similar to those in inorganic oxide hosts. Therefore, spectroscopic characteristics of the Ce^{3+} in the film systems also have close similarity to those inorganic oxide matrices. It is noteworthy that the emission spectra and intensities apparently depend on the Ce^{3+} ion content in the Ce^{3+}-films (Fig. 4). This is because the next neighbours of Ce^{3+} ions vary gradually with increasing Ce^{3+} content, so that the ligand field for Ce^{3+} ions in the films would change. Thus, the splitting of a 5d level of the Ce^{3+} ions has been affected.

The emission decay of Ce^{3+} in Ce^{3+}-films excited at 255 nm was fairly exponential in nature with a decay constant of 19 ns, but that of anhydrous CeCl$_3$ powder is much longer, *i.e.*, 30 ns. Fluorescence of PMMA alone is too weak for the emission decay to be observed with the same measurement method.

For comparison, with a trivalent rare earth ion having f–f transition, a β-diketone (for example, dibenzoylmethide (DBM)) was used as ligand for Ce^{3+} ions in the PMMA matrix. But no fluorescence was observed in the Ce–DBM-systems, although Eu^{3+}–, and Tb^{3+}–DBM-PMMA systems showed an intense fluorescence at an excitation by UV light [10]. The β-diketone complex characteristics of rare earth ions having an f–d transition seem to differ drastically from that of the complex with RE^{3+} having the f–f transition. As Eu^{2+} or Yb^{2+} complexed with DBM was introduced in the PMMA matrix, the Eu^{2+} or Yb^{2+} fluorescence was not observed either.

The Ce^{3+}-films would exhibit a strong response to radiation from a low pressure mercury vapour lamp because the excitation peak of Ce^{3+}-films is approximately equal to the lamp radiation.

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