

Unique luminescence properties of Eu^{3+} -doped polyimide

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Abstract

Luminescence properties of Eu^{3+} -doped 6FDA-6F polyamic acid (PAA) and polyimide (PI) films were investigated. Eu^{3+} -doped PAA films showed a luminescence assigned to Eu^{3+} just after preparation. However, the luminescence intensity decreased with increases in UV-irradiation treatment time. On the other hand, Eu^{3+} -doped PI films showed unique luminescence properties. The films showed no luminescence just after preparation. However, the luminescence intensity ascribed to Eu^{3+} increased with increases in the UV-irradiation treatment time. In contrast, the luminescence intensity decreased with elevation of the heat-treatment temperature and disappeared at 220 °C. After the luminescence vanished, the luminescence intensity again increased with increases in the UV-irradiation treatment time. The luminescence of the matrix similarly changed upon UV-irradiation and thermal treatment. It is proposed that luminescence properties of Eu^{3+} -doped PI films is based on a reversible changes in the luminescence of the matrix caused by UV-irradiation and thermal treatment, resulting in changes in the luminescence of Eu^{3+} due to the energy transfer from the matrix to Eu^{3+} .

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Keywords: Polyimide; Rare earth ion; Luminescence; UV-induced luminescence enhancement; Recording medium

1. Introduction

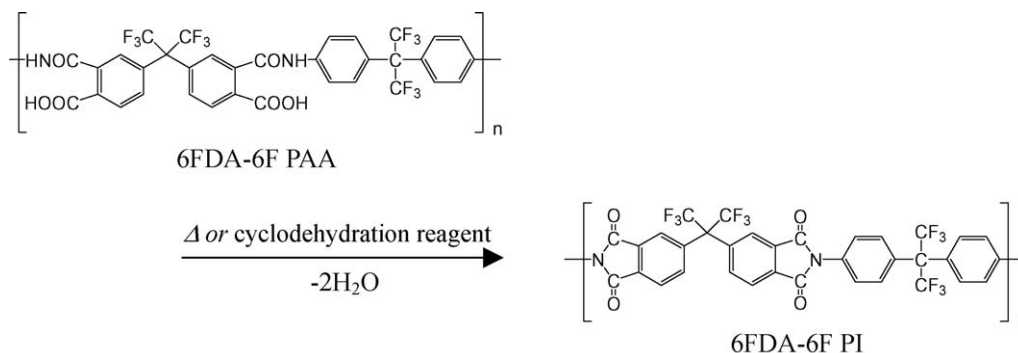
The optical properties of rare earth ion-doped glasses, crystals and rare earth ion complexes have been studied extensively for use in optical materials, e.g. lasers, displays and persistent spectral hole burning memory devices [1–9]. Polymers have good properties for optical materials, such as a transparency, easy processability, low density and low costs. However, there are few studies about rare earth ion-doped polymer materials [10]. Polymer hosts having high phonon energies gives high phonon relaxation probability, and low dispersibility of rare earth ions in polymer matrices cause clustering of rare earth ion and cross relaxation. Therefore, the luminescence intensity tends to be weak. Moreover, ordinary polymers have lower stability against heat and light as compared to inorganic materials. Polyimide (PI) is one of the most promising high-performance polymers possessing high thermal stability and good mechanical properties [11], and in particular, fluorinated PI has low phonon energy. Therefore, fluorinated PI is a suitable host for optical materials. We previously reported the fabrication of rare earth ion-doped PI nanoparticles and their unique luminescence properties [12,13]. In these previous papers, we indicated that the luminescence

intensity of rare earth ion-doped fluorinated PI (6FDA-ODA) nanoparticles increased with increases in the UV-irradiation time and decreased with elevation of the treatment temperature. The luminescence intensity assigned to Eu^{3+} was reversibly varied by the UV-irradiation and thermal treatment. There is no other report on these luminescence properties of Eu^{3+} . We thought that Eu^{3+} -doped polyimide may be suitable as a material for a high-density recordable and rewritable optical memory medium based on luminescence. In this study, we investigated the luminescence properties of Eu^{3+} -doped other fluorinated PAA and PI (6FDA-6F) films, i.e., dependences of UV-irradiation and thermal treatment.

2. Experimental

PAA, which was used as a precursor polymer, was produced by a polyaddition reaction of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 4,4'-(hexafluoroisopropylidene)dianiline (6F) in *N*-methyl-2-pyrrolidinone (NMP). The average molecular weight was ca. 60,000. NMP, acetone and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. An Eu^{3+} -doped PAA film was prepared by casting. An NMP solution of PAA was diluted with acetone, and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to this solution. The PAA concentration in the final

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Scheme 1.

solution was 1 wt.%, and the weight ratio of Eu to PAA was 0.05. Fifty microliter of this solution prepared was casted onto a glass plate (10 mm \times 20 mm \times 1 mm), and then the sample was dried under vacuum for 3 days. Finally, a transparent thin film was obtained. In general, PI was fabricated by thermally and chemically imidization of PAA as described in Scheme 1. An Eu³⁺-doped PI film was prepared by thermal imidization of an Eu³⁺-doped PAA film. The Eu³⁺-doped PAA film was heat-treated at 350 °C for 2 h. Finally, a yellow Eu³⁺-doped PI thin film was obtained. A UV-irradiation treatment was performed using a battery-operated UV lamp (Spectroline EF-160C/J, main peak: 254 nm, 6 W). A thermal treatment was carried out in a muffle furnace. Excitation and luminescence spectra were recorded on a Hitachi F-2500 fluorescence spectrometer.

3. Results and discussion

Strong red-colored luminescence from the Eu³⁺-doped PAA film as-prepared could be seen with the naked eye. Fig. 1 shows luminescence spectra of the Eu³⁺-doped PAA film before and after the UV-irradiation treatment. Luminescence peaks assigned to Eu³⁺ were observed at 579 (⁵D₀ \rightarrow ⁷F₀), 593 (⁵D₀ \rightarrow ⁷F₁) and 616 nm (⁵D₀ \rightarrow ⁷F₂). Luminescence peaks ascribed to the transitions from D₀ to ⁷F₃ and ⁷F₄ level could

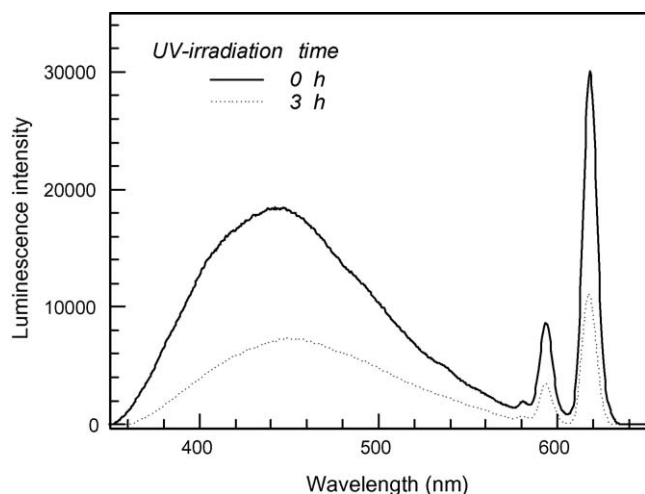


Fig. 1. Luminescence spectra of Eu³⁺-doped PAA film before and after the UV-irradiation treatment. Excitation wavelength was 280 nm.

not be measured because the wavelength was out of the range of our equipment. A broad luminescence band ascribed to the matrix was also measured. Eu³⁺ has been used to study the local environment of rare earth ions [14,15]. The ⁵D₀ \rightarrow ⁷F₂ emission band is hypersensitive and the intensity can vary by orders of magnitude, depending on the local environment. If Eu³⁺ occupies a spherically symmetric site, the intensity is zero but increases with increasing asymmetry of the site. The ⁵D₀ \rightarrow ⁷F₁ transition is a magnetic transition that can be used as a reference because its intensity is not sensitive to environment. Hence, the ⁵D₀ \rightarrow ⁷F₂/⁵D₀ \rightarrow ⁷F₁ luminescence ratio can be used as a measure of the site symmetry of Eu³⁺. In our case, the electric dipole transition (⁵D₀ \rightarrow ⁷F₂) was the most intense, indicating that Eu³⁺ ions were not dispersed as a crystalline state in the PAA matrix. The observation that there were no X-ray diffraction (XRD) peaks also supported this result. It is known that carboxyl anions coordinate to rare earth ions and complexes are created. Because PAA has carboxyl groups and NMP acts as Brønsted base, a PAA-Eu³⁺ complex was formed. Furthermore, Eu³⁺ ions were homogeneously dispersed in the PAA matrix and although Eu³⁺ shows only very weak luminescence in organic matrices, its luminescence is enhanced due to the energy transfer from PAA to Eu³⁺. The luminescence intensities assigned to the matrix and Eu³⁺ drastically decreased after the UV-irradiation treatment. Eu³⁺ cannot absorb the UV-light from the lamp because absorption peaks assigned to Eu³⁺ were not observed in this spectral region. On the contrary, a strong absorption band (\sim 300 nm) attributed to the matrix was measured. Therefore, it is considered that photolysis of PAA occurred. The luminescence ratios (⁵D₀ \rightarrow ⁷F₂/⁵D₀ \rightarrow ⁷F₁) did not change before and after the UV-irradiation treatment. This result indicates that the number of luminescent centers decreased during UV-irradiation, i.e., the photolysis of a moiety including carboxyl groups was caused by UV-light. Excitation spectra of Eu³⁺-doped PAA films are shown in Fig. 2. A broad excitation band was observed, indicating energy transfer from the matrix to the Eu³⁺.

Eu³⁺ showed the strong luminescence in the PAA film, and its luminescence intensity decreased after UV-irradiation treatment. On the other hand, the luminescence property of the Eu³⁺ was different in the PI film as described in the following paragraphs. Fig. 3 shows luminescence spectra of an Eu³⁺-doped PI film UV-irradiated for various times. The luminescence intensity of the Eu³⁺ drastically decreased after it was thermally imidized,

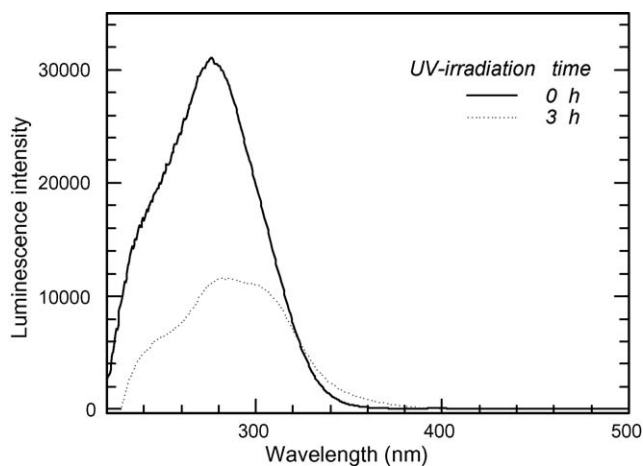


Fig. 2. Excitation spectra of Eu^{3+} -doped PAA film before and after the UV-irradiation treatment. Monitored wavelength was 618 nm.

and a luminescence band of the matrix was also observed. In the imidization process, the carboxyl groups of PAA are consumed by a cyclodehydration reaction. Therefore, the luminescence of Eu^{3+} became weak due to the disappearance of the energy transfer path. However, these luminescence intensities increased with increases in the UV-irradiation time, i.e., UV-induced luminescence enhancement was observed. The luminescence intensity of UV-irradiated sample was kept for several months in the dark at room temperature. Fig. 4 shows the excitation spectra of an Eu^{3+} -doped PI film after UV-irradiation for various times. Two broad bands at 240 and 280 nm and two shoulders at approximately 307 and 340 nm were observed. It is considered that these bands, which were different from that of Eu^{3+} -doped PAA, derive from the PI matrix. Thus, Eu^{3+} -doped PI could memorize the UV-irradiation time (amount) as the luminescence intensity.

The luminescence could be also decreased and eliminated by heat-treatment. Fig. 5 shows luminescence spectra of an Eu^{3+} -doped PI film, first at the saturation level with UV-irradiation at room temperature and subsequently heat-treated at various temperatures for 30 min. After heat-treatment, the samples were

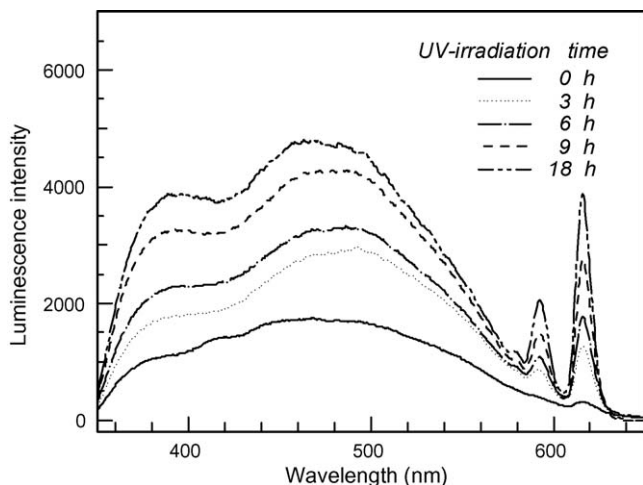


Fig. 3. Luminescence spectra of an Eu^{3+} -doped PI film UV-irradiated for various times. Excitation wavelength was 280 nm.

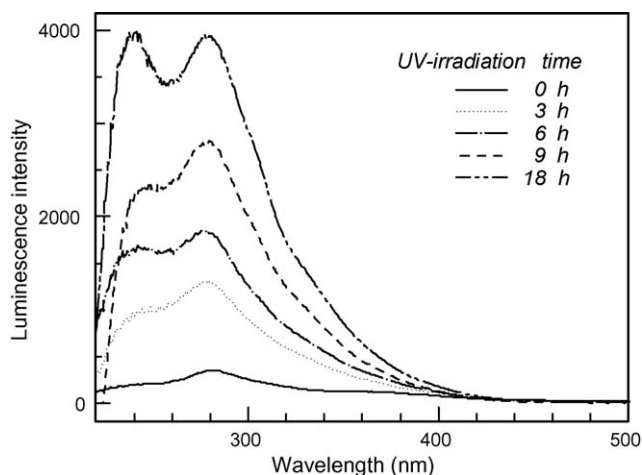


Fig. 4. Excitation spectra of an Eu^{3+} -doped PI film UV-irradiated for various times. Monitoring wavelength was 618 nm.

kept at room temperature for 5 min, and luminescence intensity was measured. The luminescence intensity ascribed to Eu^{3+} and the matrix decreased with increasing treatment temperature and almost disappeared at approximately 220°C . Moreover, after the luminescence vanished, the luminescence intensity increased again upon UV-irradiation treatment. Thus, the luminescence intensity of Eu^{3+} -doped PI film could be controlled by the UV-irradiation and thermal treatment.

Although there have been no reports on these phenomena as regards rare earth ion-doped inorganic crystals, glasses, polymers and rare earth complexes, there have been a few reports on a luminescence enhancement of 6FDA based PI in dimethylformamide (DMF) caused by UV-irradiation [16,17]. Hoyle et al. has reported that upon photodegradation using polyimides by irradiation using unfiltered light from a medium-pressure mercury lamp. They found that hexafluoroisopropylidene (6F) hinge groups are the most unstable and photolysis of the 6F hinge group did not occur in an inert atmosphere. Moreover, they observed that 6FDA based polyimides in DMF showed an enhancement of the luminescence at around 490 nm caused

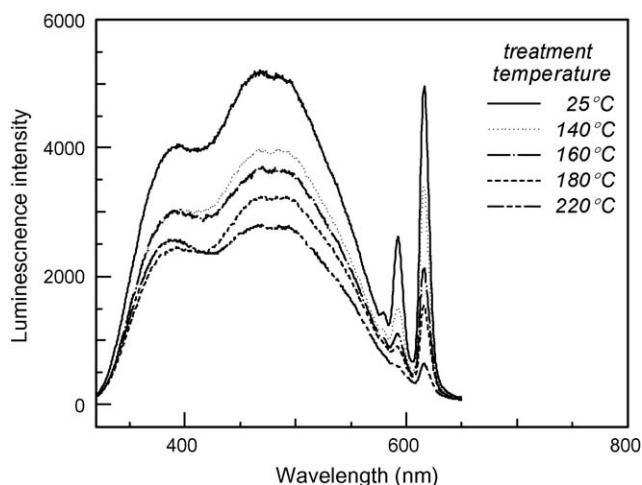
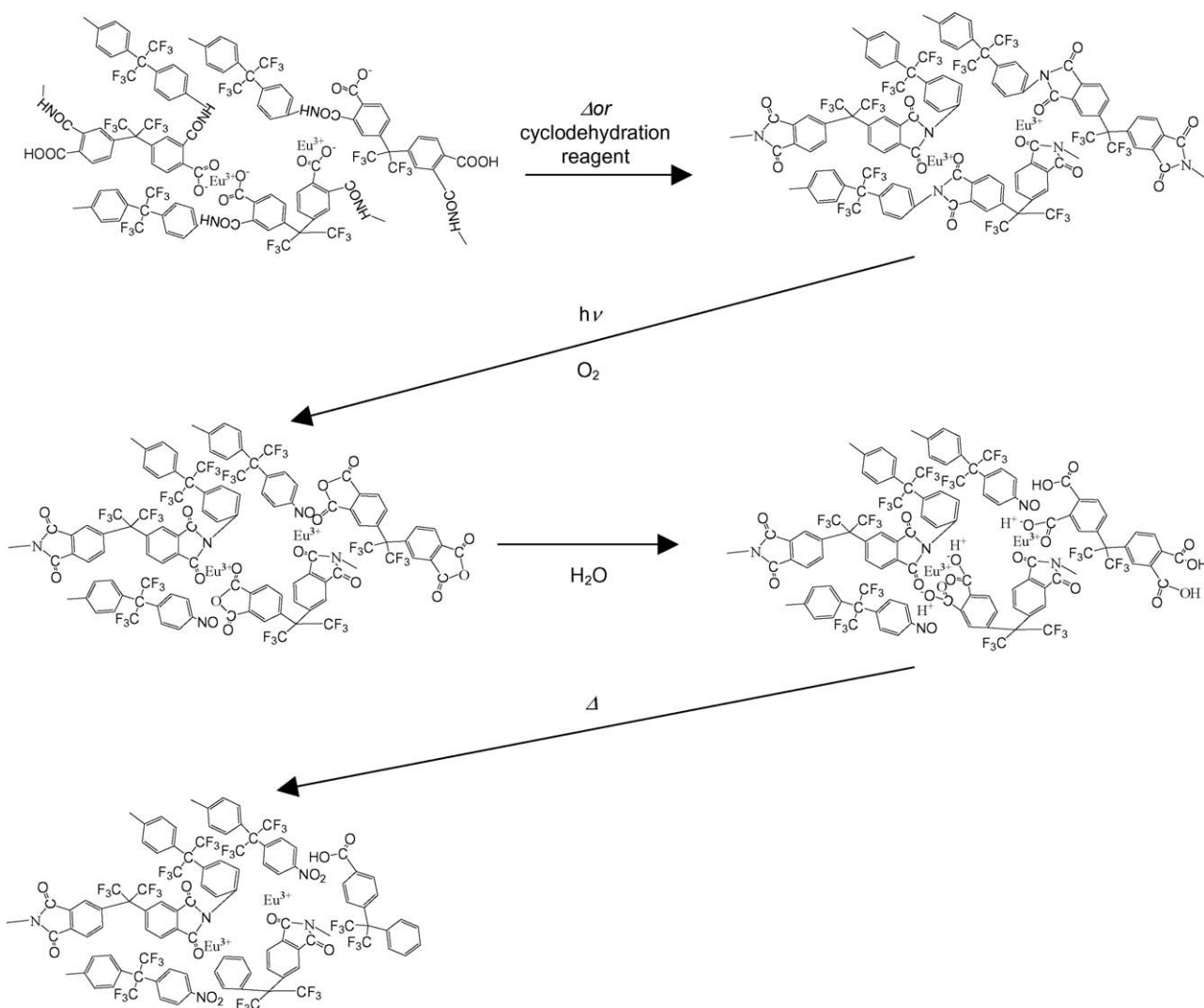


Fig. 5. Luminescence spectra of an Eu^{3+} -doped PI film after heat-treatment at various temperatures.



Scheme 2.

by the UV-irradiation treatment, although no luminescence was observed before photolysis. In addition, they showed that photolysis of *N*-phenylphthalimide and *N*-arylphthalimide, model compound of PAA, in an air-saturated acetonitrile solution resulted in the formation of phthalic anhydride and nitrosobenzene moieties [18,19]. In our case, since a similar luminescence enhancement of the PI matrix was observed after the UV-irradiation treatment, analogical photolysis such as in Scheme 2 occurred. Furthermore, it is well known that phthalic anhydride is easily hydrolyzed and give phthalic acid. It is considered that the enhancement of the luminescence intensity of Eu³⁺ through the energy transfer results from a structural change, namely the formation of phthalic acid-Eu³⁺ complexes. This conclusion is supported by experimental results that show that the IR absorption assigned to the OH group increased with increases in the UV-irradiation time and the luminescence intensity did not increase upon UV-irradiation treatment in vacuum and although the luminescence intensity increased with increases in the UV-irradiation time, the ratios (⁵D₀ → ⁷F₂/⁵D₀ → ⁷F₁) did not change.

On the other hand, the luminescence assigned to the matrix and Eu³⁺ decreased with elevation of the treatment temperature. In addition, the absorption peak ascribed to the OH vibration decreased after the thermal treatment. A structural change in the matrix due to the thermal treatment, e.g. thermal decomposition of moieties containing carboxyl groups, must result in the decrease in luminescence intensity of the matrix, influencing luminescence intensity of Eu³⁺. To our knowledge, there is no report on these unique luminescence properties of Eu³⁺. Eu³⁺-doped 6FDA based PI may be a promising material for rewritable memories, image-recording devices and thermal sensors. Further investigations, e.g. TG, DSC, will be needed to describe the mechanism of these luminescence properties in greater detail.

4. Conclusion

We investigated the luminescence properties of Eu³⁺-doped 6FDA-6F PI films, and unique luminescence properties were observed. The luminescence intensity assigned to Eu³⁺ increased with increases in the UV-irradiation time. The

intensity decreased with increases in treatment temperature, and vanished at 220 °C. After the erasure of the luminescence, the intensity increased upon repeated UV-irradiation treatment. The luminescence of the matrix showed similar changes upon UV-irradiation and thermal treatment. It was considered that the structural change of the PI matrix upon UV-irradiation and thermal treatment led to the luminescence changes of the matrix, resulting in changes in the luminescence of the Eu^{3+} due to the energy transfer from the matrix to Eu^{3+} .

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