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### Control of Luminescence Intensity from Rare Earth Ion ( $\text{Eu}^{3+}$ , $\text{Tb}^{3+}$ )-DOPED POLYIMIDE NANOPARTICLES BY UV-IRRADIATION AND THERMAL TREATMENT

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## CONTROL OF LUMINESCENCE INTENSITY FROM RARE EARTH ION ( $\text{Eu}^{3+}$ , $\text{Tb}^{3+}$ )-DOPED POLYIMIDE NANOPARTICLES BY UV-IRRADIATION AND THERMAL TREATMENT

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*The control of luminescence intensity from rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped polyimide (PI) nanoparticle film by UV-irradiation and thermal treatment is reported. In the system, it was observed that luminescence intensity assigned to rare earth ion increased with increase of UV-irradiation time, whereas the intensity decreased with elevation of thermal treatment temperature. It was estimated that the mechanism of the above phenomena is based on a reversible change in an energy transfer probability from PI to rare earth ion by the UV-irradiation and the thermal treatment.*

**Keywords:** energy transfer; luminescence; polyimide; rare earth ion

## INTRODUCTION

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., laser, display 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 cost. However, there are few studies about rare earth ion-doped polymer materials [10]. The reason

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may be as follows. Polymer hosts having high phonon energy must lead to a high phonon relaxation probability, and a low dispersity of rare earth ion in polymer matrices would cause clustering of rare earth ion and a cross relaxation. Therefore, the luminescence intensity is considered to be weak. Moreover, ordinary polymers have lower stability against heat and light as compared with inorganic materials. Based on the above considerations, we reached conclusion that polyimide (PI) must be a very promising polymer to make rare earth ion doped material and draw strong luminescence. PI can be fabricated through a cyclodehydration reaction of polyamic acid (PAA). Generally, it is well known that rare earth ion makes complex with diketone, carboxylic acid and ether. Therefore, the dispersibility of rare earth ion would be improved by the coordination with the carboxylic groups in PAA. And then, PI is so stable against heat and light that suits to a host for such optical materials. In fact, in this paper, we describe that the rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PI nanoparticles with controlled size could be fabricated by our reprecipitation method, and their interesting luminescence properties, i.e., UV-induced enhancement and thermal elimination of luminescence from rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PI nanoparticles were observed.

## EXPERIMENTAL

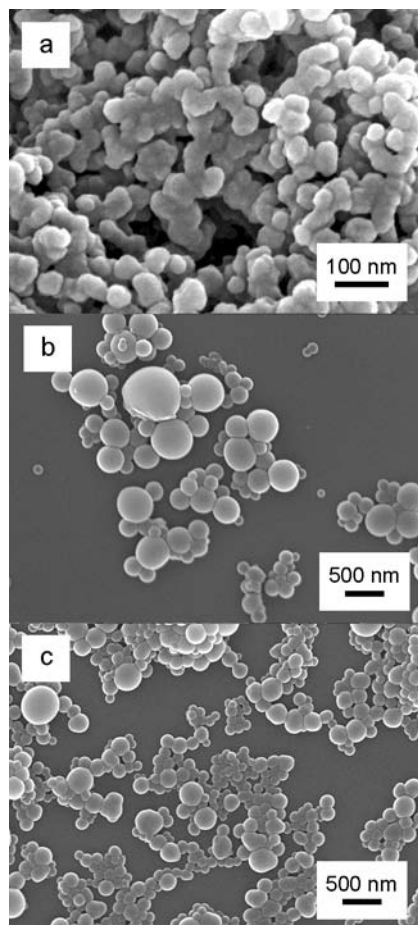
PAA used as the precursor polymer of PI was produced by polyaddition reaction of 4,4'-oxydianiline (ODA) and 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in *N*-methyl-2-pyrrolidinone (NMP), and the average molecular weight was ca. 120,000. All solvents and rare earth nitrate were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PAA nanoparticles were prepared by the conventional reprecipitation method [11–13]. Preparation method of non-doped PI particles has been already reported [14,15]. PAA and rare earth nitrate were dissolved in acetone or NMP (good solvent). Weight ratio of PAA to Acetone or NMP was 0.007 and rare earth ion to PAA was 0.05. This solution (100  $\mu\text{l}$ ) was rapidly injected using a microsyringe into 10 ml of cyclohexane (poor solvent) stirred vigorously. A small amount of the dispersing agent, Acrylic A-1381 (Dainippon Ink And Chemicals), was added into cyclohexane in order to suppress the aggregation of fine particles. Rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PAA nanoparticles were immediately fabricated after injection as white dispersion in cyclohexane. Rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PI nanoparticles could be obtained through the “two-steps imidization”, i.e., the rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PAA nanoparticles were chemically imidized, thereafter thermally imidized up to quantitative conversion.

Chemical imidization was performed by adding 500  $\mu\text{l}$  of pyridine/acetic anhydride mixture (1:1) into the rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PAA nanoparticles dispersion liquid and keeping at ambient temperature for 3 h. And then, rare earth ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ )-doped PI nanoparticles in the resultant liquid were centrifuged at 12,000 rpm, washed with cyclohexane for removal of the residual pyridine and acetic anhydride, and redispersed into cyclohexane. The nanoparticles were electro-deposited onto ITO substrates in the dispersion liquid, and the nanoparticle films attained were further cured at 270°C for 1 hour. Scanning electron microscope (SEM) photographs were taken by a JSM-6700F (JEOL). UV-irradiation was performed by a battery operated UV lamp (Spectroline EF-160C/J, 254 nm, 6 W). Luminescence and excitation spectra were recorded on a Hitachi F-2500 fluorescence spectrometer.

## RESULTS AND DISCUSSION

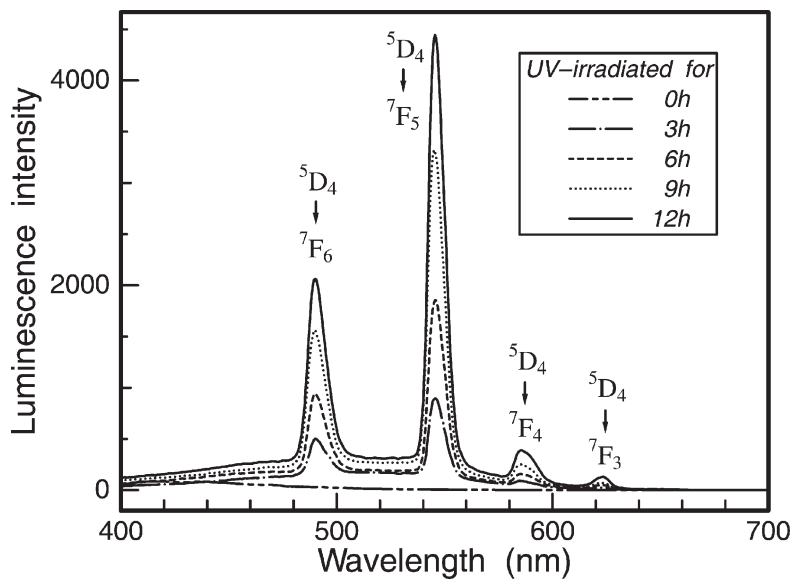
Figure 1 shows SEM photographs of  $\text{Eu}^{3+}$ -doped PI nanoparticles size-controlled prepared by the reprecipitation method. Rare earth ion-doped PI particles with various sizes were prepared under various experimental conditions. The particles (a) with average size of 30 nm and (b) with average size of 300 nm were prepared under poor solvent temperature of 20°C and using acetone and NMP as good solvent, respectively. About 100 nm-sized particles (c) were prepared using NMP and under temperature of 40°C. The results were similar to that of non-doped PI particle sizes prepared under various conditions [14,15]. The size of PAA particles fabricated in acetone system became decreasing compared with that in NMP system because the miscibility between acetone and cyclohexane is better than that between NMP and cyclohexane. On the other hand, the PAA particle size became smaller with elevation of poor solvent temperature in NMP system because the miscibility between NMP and cyclohexane became better with elevation of temperature. The author also reported that the particle size and its distribution were confirmed to be unchanged before and after chemical imidization [14,15]. In this study, the experimental condition of reprecipitation was also directly related to the size control of rare earth ion-doped PI particles.

Luminescence spectra of  $\text{Tb}^{3+}$ -doped PI nanoparticle film after the UV-irradiation for various times are shown in Figure 2. Typical luminescence bands ascribed to  $\text{Tb}^{3+}$  ion were observed at 490 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ), 546 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ), 586 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_4$ ) and 623 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_3$ ). Luminescence intensity increased with increase in UV-irradiation time, i.e., UV-induced luminescence enhancement was observed. Its intensity was kept for several months in darkness and room temperature. Figure 3 shows luminescence

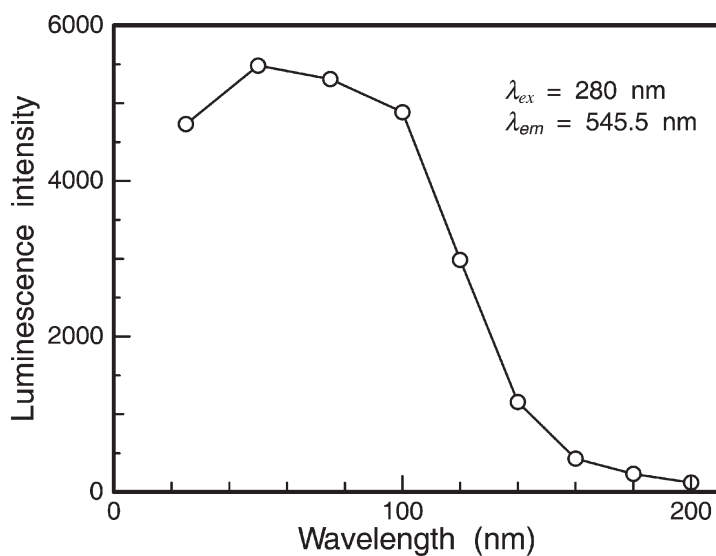


**FIGURE 1** SEM photograph of  $\text{Eu}^{3+}$ -doped PI nanoparticles prepared under various conditions. (a) poor solvent was acetone, temperature is  $20^\circ\text{C}$ , (b) poor solvent was NMP, temperature  $20^\circ\text{C}$ , (c) poor solvent was NMP, temperature  $40^\circ\text{C}$ .

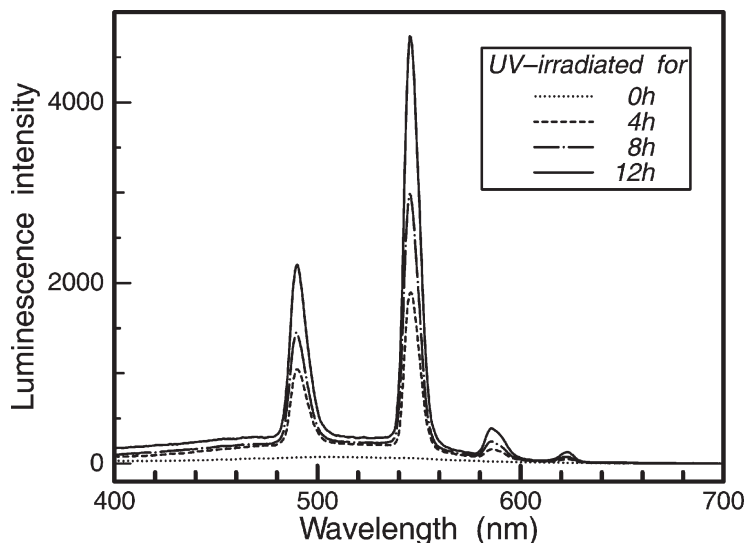
intensity of  $\text{Tu}^{3+}$ -doped PI nanoparticles heat-treated at various temperatures for 5 minutes after UV-irradiation for 12 h at room temperature. Luminescence intensity measurement was performed at room temperature. Excitation wavelength was 280 nm and monitored wavelength was 545.5 nm. Luminescence intensity decreased with elevation of treatment temperature and disappeared at about  $200^\circ\text{C}$ . Figure 4 shows luminescence intensity when UV-irradiation for various times again after the thermal elimination of luminescence. Luminescence intensity increased with increase of UV-irradiation times again and finally recovered to the intensity



**FIGURE 2** Luminescence spectra of  $\text{Tu}^{3+}$ -doped PI nanoparticle film after UV-irradiation for various times. Excitation wavelength was 280 nm.



**FIGURE 3** Change of luminescence intensity at 545.5 nm of  $\text{Tu}^{3+}$ -doped PI nanoparticle film after thermal treatment.



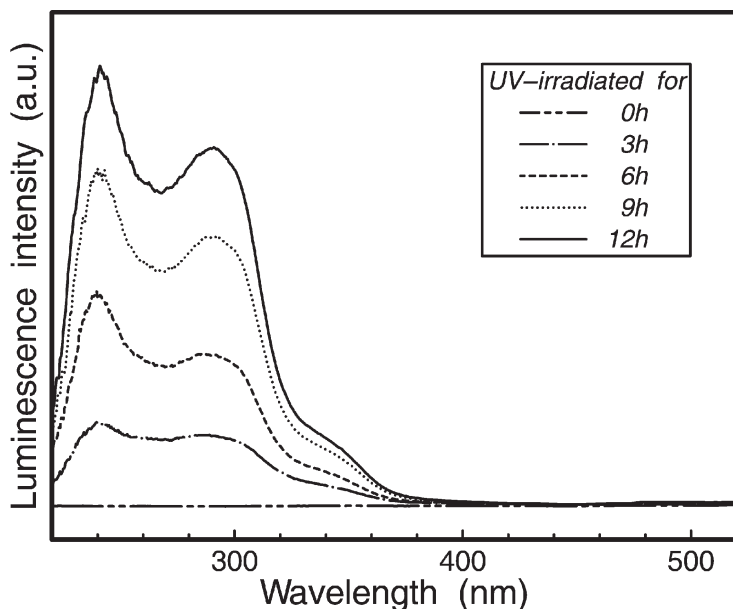
**FIGURE 4** Luminescence spectra of  $\text{Tu}^{3+}$ -doped PI nanoparticle film UV-irradiated for various times after thermal elimination.

UV-irradiated for 12 h before thermally erased. These phenomena above described was also observed in  $\text{Eu}^{3+}$ -doped PI particles. Thus, luminescence intensity of rare earth ion-doped PI particles could be controlled by UV-irradiation and thermal treatment.

Figure 5 shows excitation spectra of  $\text{Tu}^{3+}$ -doped PI particles, obtained by the luminescence at 545.5 nm, after the UV-irradiation with different time. Two broad bands at 240 nm and 296 nm and a shoulder around 346 nm were observed. The excitation spectra of  $\text{Tu}^{3+}$ -doped PI particles almost coincided with that of  $\text{Eu}^{3+}$ -doped PI particles, and the absorption bands were ascribed to PI. Therefore, an energy transfer from PI to rare earth ion was suggested.

Although there was no reports of these phenomena in regard to rare earth ion doped inorganic crystal, glass, polymer and rare earth complex, the researches about the luminescence enhancement of semiconductor particles in organic matrices by UV-irradiation were reported [16,17]. The mechanisms were explained as reduction of trap sites, which acted as luminescence killer centers, in polymers or semiconductor particle surfaces, or decrease in quenching at trap sites. However, no one has reported that the trap sites act as killer centers for luminescence of rare earth ion. The oxidation of rare earth ions ( $\text{Eu}^{2+}$ ,  $\text{Tu}^{3+}$ ,  $\text{Sm}^{2+}$ ) by UV-irradiation under existing of trap sites and the reduction of oxidized rare earth ions ( $\text{Eu}^{3+}$ ,  $\text{Tu}^{4+}$ ,  $\text{Sm}^{3+}$ ) through a release of the trapped electron by





**FIGURE 5** Excitation spectra of  $Tu^{3+}$ -doped PI nanoparticle film after UV-irradiation for various times.

a thermal energy are also known [18,19]. However, the change of charge number of rare earth ion did not occur in our system because luminescence assigned to  $Tu^{3+}$  was enhanced by UV-irradiation. The change of charge number is often examined by an EPR measurement [20].  $Eu^{3+}$ -doped PI particles were investigated by the EPR measurement. As a result, there was no change in EPR signals indicating that the oxidation-reduction of Eu ion occurred. Therefore, it was estimated that an energy transfer probability from PI to rare earth ion was changed reversibly by the UV-irradiation and the thermal treatment. Further analysis such as the estimation of the lifetime must be performed to clarify the detailed mechanism.

## CONCLUSION

We prepared size-controlled rare earth ion-doped PI particles by the reprecipitation method. The particles with various sizes were prepared under various reprecipitation conditions. The interesting luminescence properties were observed: luminescence intensity assigned to rare earth ion increased with increase of UV-irradiation time. The intensity decreased with elevation of treatment temperature, and vanished at  $200^{\circ}\text{C}$ . After the erase of

luminescence, the intensity increased under the UV-irradiation again. UV-induced luminescence enhancement, thermal luminescence elimination and UV-reinduced enhancement after elimination of rare earth ion have never been reported. Rare earth ion-doped PI particles may be promising material for a rewritable memory and image-recording devices.

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