

Preparation of Photoluminescence Films Containing Rare Earth Complexes by UV Photograft Polymerization

Jian-Yu Li,¹ Yu-Mei Sun,¹ Hong Zeng,² Wei-Xing Xue,¹ Yang Xiao,¹ Qun Yu¹

¹College of Chemical Engineering, Beijing Technology and Business University, Beijing 100037, China

²Beijing Mineral and Metal Research General Institute, Beijing 100044, China

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ABSTRACT: To avoid the fluorescence quenching resulting from the uneven dispersion of fluorescent rare earth complexes in photoluminescence films, which were prepared by blending until recently, photoluminescence films were prepared in which the chemical bond combination occurs between the fluorescent rare earth complexes and the macromolecular material. Acrylic acid (AA) was grafted onto polyethylene (PE) film through liquid-phase UV photograft polymerization. Then the grafted films (PAA-g-PE) were reacted with a solution of Eu^{3+} and thenoyltrifluoroacetone (TTA) in alcohol–water and with a solution of Tb^{3+} and acetylacetone (AcAc) in chloroform–water, respectively. Thus, red (Eu^{3+} -TTA-PAA-g-PE) and green (Tb^{3+} -ACAC-PAA-g-PE) photoluminescence films were obtained. The fluorescence and infrared spectra of the photoluminescence

films were recorded. Compared with their corresponding solid fluorescent complexes, both the excitation and emission wavelengths of the photoluminescence films prepared in this way had been changed remarkably, indicating that the fluorescent rare earth complexes had been chemically bonded onto the PE film. Moreover, the effects of the conditions (including pH value, reaction time, and temperature) of the reaction of the grafted film with the solution containing Eu^{3+} and TTA on the fluorescence intensity of the red photoluminescence film were investigated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 662–667, 2003

Key words: polyethylene; films; metal–polymer complexes; photopolymerization; fluorescence

INTRODUCTION

In recent years photoluminescence films containing fluorescent rare earth complexes have attracted a great deal of interest for research because of the prospect of their wide application.¹ Because they are prepared by blending, however, difference in structure causes an uneven dispersion of the rare earth complexes in the macromolecular materials. This leads to the quenching effect between the fluorescent molecules, which results in a decrease of the ratio of effective fluorescent molecules, a decrease of fluorescence intensity, and the shortening of fluorescence lifetime.² Their application is therefore limited. The ideal improvement to avoid the above phenomenon and to try to bring each fluorescent molecule into play would be to make a chemical bond combination occur between the fluorescent rare earth complexes and the macromolecular film. The present study was carried out with the aim of preparing photoluminescence films meeting this demand by the method of liquid-phase UV photografting polymerization. First, acrylic acid (AA) was photografted onto polyethylene (PE) film. Then the grafted films (PAA-g-PE) were reacted with a solution

of Eu^{3+} and thenoyltrifluoroacetone (TTA) in alcohol–water or with a solution of Tb^{3+} and acetyl acetone (AcAc) in chloroform–water, which resulted in a red fluorescent film (Eu^{3+} -TTA-PAA-g-PE) and a green fluorescent film (Tb^{3+} -ACAC-PAA-g-PE), respectively. The basic reaction scheme is described in Figure 1.

The reaction of the grafted film with a solution of rare earth ions and β -diketone actually includes two processes; one is the coordination of the β -diketone to the rare earth ion, and the other is the bonding of the rare earth ion to the polymer film. Obviously, the grafted film can be considered as a polyelectrolyte with weak acidity. The interaction of a polyelectrolyte with metal ions has been studied previously.^{3,4} It was anticipated that the carboxyl groups of the acrylic acid grafted, where H^+ can be displaced by metal ions, would react with the rare earth ions that would also react in the meantime with the β -diketone ligands in the solution. This property of the grafted film provided a new type of photoluminescence film, in which rare earth complexes are chemically bonded onto the polymer matrix. (Photoluminescence film is essentially a ternary complex of rare earth ions with β -diketone ligands and macromolecular film grafted with acrylic acid.) In this article the preparation, characterization, and fluorescence properties of the photoluminescence films obtained in this way are reported. In

Correspondence to: J.-Y. Li.

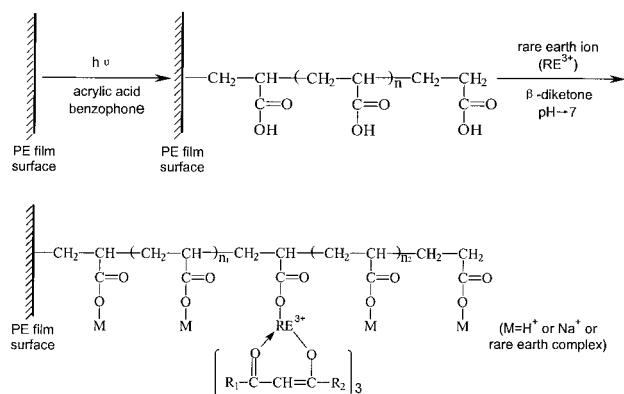


Figure 1 Reaction scheme for the preparation of photoluminescence films.

addition, the effects of the conditions of the reaction of the grafted film with the solution of Eu^{3+} and TTA, such as pH value, reaction time, and temperature, on the fluorescence intensity of the red photoluminescence film are discussed.

EXPERIMENTAL

Materials

Low-density polyethylene film (75 μm thick) was prepared in our laboratory. Eu_2O_3 and Tb_4O_7 (purity > 99.9%, purchased from Shanghai Yao Long Chemical Factory) were dissolved with diluted HCl to prepare a 0.3 mol L^{-1} solution of EuCl_3 and TbCl_3 , respectively. Acrylic acid (AA), benzophenone (BP), acetone, thenoyltrifluoroacetone (TTA), acetyl acetone (AcAc), alcohol, and chloroform. were all reagent grade. The solid complexes, $\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2$ and $\text{Tb}(\text{AcAc})_3(\text{H}_2\text{O})_2$, to be used for comparing the fluorescence spectra with the photoluminescence films were synthesized according to a method described in the literature,⁵ and fine powder samples were prepared for the measurement.

Apparatus

The IR spectra were measured on a Shimadzu IR-440 spectrophotometer. The fluorescence spectra were recorded with a Shimadzu RF-540 spectrofluorimeter.

The liquid-phase photografting device was self-made. The ultraviolet light source used was a 500W high-pressure mercury lamp. A filter that absorbs ultraviolet radiation with a wavelength shorter than 300 nm was fixed at the bottom of the reactor as an irradiation window. The reactor was placed in a temperature-controlled water bath.

Preparation of grafted film

All the PE films to be grafted were preextracted with acetone to remove greasy dirt. A film was placed on

the bottom of the reactor containing a solution of 2 mol L^{-1} of monomer AA and 0.2 mol L^{-1} of initiator BP in acetone. After placing a piece of glass onto the sample, the reactor was purged with nitrogen for 15 min, heated in a water bath at a constant temperature of 50°C, and then irradiated through the filter window for 10 min. After irradiation, the grafted film was extracted with acetone in a Soxhlet extractor to remove unreacted monomer, initiator, and homopolymer formed during grafting. The samples grafted with AA were washed with hot water for 2 h. After that the grafted samples were washed with distilled water, and then dried at room temperature.

The photografting reaction was performed by a procedure described in the literature.⁶ The reaction conditions described therein were confirmed or further optimized through our experiments. Grafting yield was determined according to the contact angle measurement, also with reference to the above literature, based on the fact that film grafted with AA is hydrophilic. For the grafted film samples, a contact angle of about 10° was obtained (on a CA-D contact angle goniometer at ambient humidity and temperature).

Preparation of photoluminescence films

The above grafted film, PAA-g-PE (4 cm^2 in size), was pretreated in 100 mL of 0.1 mol L^{-1} NaOH solution with stirring for 2 h and taken out. Then 1.0 g of TTA was dissolved in 100 mL of 95% alcohol, and the pretreated grafted film was placed into it. After that, 5 mL of a solution composed of 0.3 mol L^{-1} of EuCl_3 [at the molar ratio of $n(\text{TTA}):n(\text{Eu}^{3+}) = 3:1$, which is the optimum molar ratio of β -diketone ligand to rare earth ion at maximum fluorescence intensity⁷] was added dropwise with stirring. In the meantime, the pH of the mixture solution was adjusted to a given value (between 4.5 and 7.0) by dripping a NaOH solution (because the EuCl_3 solution used was prepared with dilute HCl). After adding, the mixed system was continually stirred at a constant temperature (from 20°C to 50°C) for a certain period of time (from 1 to 10 h). It is noteworthy that the amount of organic solvent in the reaction system should be enough to prevent the complex of Eu^{3+} with TTA from appearing as precipitation. To avoid the solvent volatilizing when headed, the reaction was performed in a vessel with condenser.

After reaction, the film was placed in a beaker containing 100 mL of alcohol with stirring to wash the complexes of Eu^{3+} with TTA adsorbed physically on the film surface. The alcohol was replaced every 12 h. This process was continued for 5 days. The washed film was dried at room temperature. When the film, which was represented by $\text{Eu}^{3+}\text{-TTA-PAA-g-PE}$, was placed under a 365-nm ultraviolet lamp, bright red fluorescence was observed.

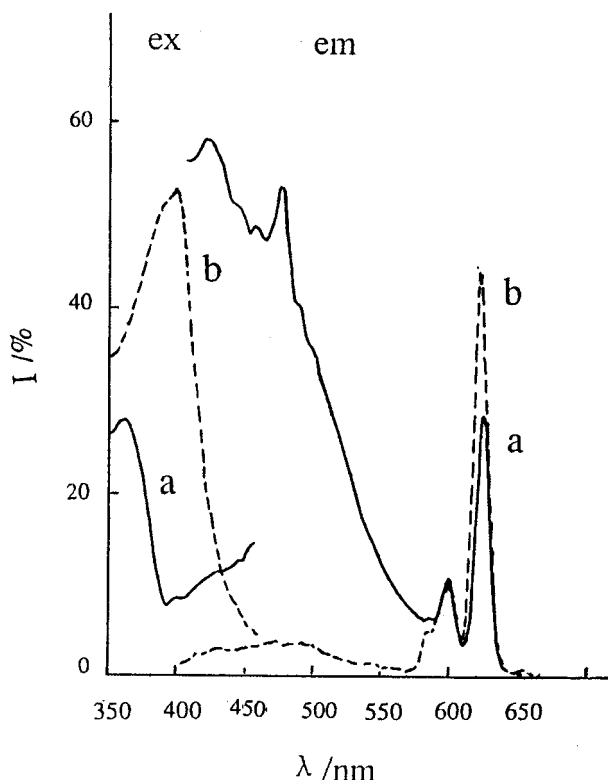


Figure 2 Fluorescence spectra of (a) Eu^{3+} -TTA-PAA-g-PE film and (b) $\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2$ solid complex (b).

The green fluorescent film (Tb^{3+} -AcAc-PAA-g-PE) was prepared in a similar way, but the reaction solvent was chloroform-water. Its luminescence was weaker than that of the red fluorescent film.

RESULTS AND DISCUSSION

Characterization

Fluorescence spectra

To confirm that a chemical bond combination, not physical adsorption, occurred between the fluorescent rare earth complexes and the macromolecular film, the fluorescence spectra of both the Eu^{3+} -TTA-PAA-g-PE film and its corresponding solid complex, $\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2$, and the fluorescence spectra of both the Tb^{3+} -AcAc-PAA-g-PE film and its corresponding solid complex, $\text{Tb}(\text{AcAc})_3(\text{H}_2\text{O})_2$, were recorded (see Figs. 2 and 3, respectively). For easy comparison of the spectra of the fluorescent film and its corresponding solid complex, their excitation spectra were measured with the same emission wavelength, and their emission spectra were measured with the same excitation wavelength.

The excitation and emission spectra of the photoluminescence films and the corresponding solid complex samples were found to be different under the same conditions. The data of the fluorescence spectra

are listed in Tables I and II, respectively. It can be seen that both the excitation and emission wavelengths of the fluorescent films, compared with their corresponding solid complexes, show remarkable differences. It has long been known that the fluorescence of rare earth complexes results from the intramolecular energy transfer from organic ligands to rare earth ions—that is, the ligands absorb excitation energy, and the rare earth ions exhibit fluorescence when they are excited with the ultraviolet light absorbed by ligands. The said differences show that the coordination environment of the rare earth ions has been changed in the fluorescent films compared with the corresponding solid complexes. The above is sufficient to indicate that chemical bond combination, instead of simple physical adsorption, has occurred between the fluorescent rare earth complexes and the grafted films.

Moreover, in the emission spectrum of the green fluorescent film, Tb^{3+} -AcAc-PAA-g-PE [Fig. 3(a)], the intensity of the peak at 492.5 nm originating from the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition of Tb^{3+} was much higher than that of the peak at 547.6 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition. This is remarkably different from the emission spectrum of the solid complex $\text{Tb}(\text{AcAc})_3(\text{H}_2\text{O})_2$ [Fig. 3(b)], in which the peak at 551.1 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition is the maximum emission.

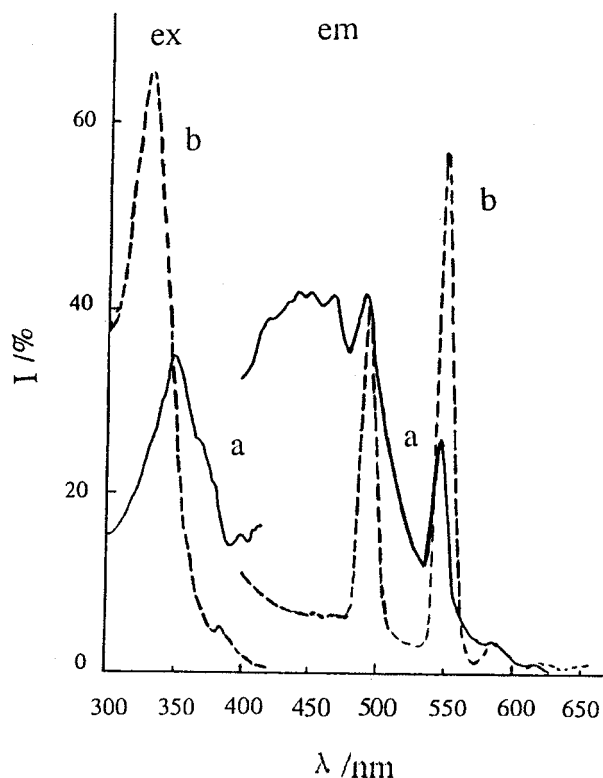


Figure 3 Fluorescence spectra (a) of Tb^{3+} -AcAc-PAA-g-PE film and (b) $\text{Tb}(\text{AcAc})_3(\text{H}_2\text{O})_2$ solid complex.

TABLE I
Fluorescence Spectrum Data of Eu³⁺-TTA-PAA-g-PE Film
and Eu(TTA)₃(H₂O)₂ Solid Complex

	λ ex/nm (λ em = 617.0 nm)	λ em/nm (λ ex = 365.0 nm)		
		⁵ D ₀ → ⁷ F ₀	⁵ D ₀ → ⁷ F ₁	⁵ D ₀ → ⁷ F ₂
Eu ³⁺ -TTA-PAA-g-PE	361.7	581.2	594.6	617.5
Eu(TTA) ₃ · (H ₂ O) ₂	398.0	582.1	596.3	610.0

Infrared spectra

The infrared spectra of the PE film, grafted film (PAA-g-PE), and red fluorescent film (Eu³⁺-TTA-PAA-g-PE) are shown in Figure 4(a-c), respectively. By comparison with the spectrum of the PE film [Fig. 4(a)], the characteristic peak of stretch vibration of the carbonyl group of acrylic acid appears at 1715 cm⁻¹ in the spectrum of the grafted film [Fig. 4(b)], which indicates that the acrylic acid has been photografted onto the PE film. Comparing the spectra of the grafted film [Fig. 4(b)] and the fluorescent film [Fig. 4(c)], a absorption band (centered at 1700 cm⁻¹) of the carbonyl group of β-diketone overlapping with the peak of the carbonyl group of acrylic acid can be observed in the spectrum of the fluorescent film [Fig. 4(b)]. The stretch vibration peak of unsaturated C=C bond of the enol form of the β-diketone is found at 1535 cm⁻¹ in the spectrum [Fig. 4(c)]. The peak at 470 cm⁻¹ in the spectrum [Fig. 4(c)] is the stretch vibration of the Eu—O.

The situation of the IR spectrum of the green fluorescent film, Tb³⁺-AcAc-PAA-g-PE is very similar to that of the red fluorescent film; therefore, further description is not necessary.

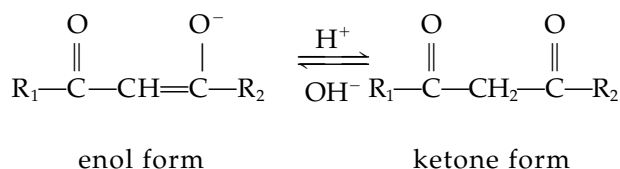
Factors affecting emission intensity of film

The photoluminescence films were prepared with the reaction of the grafted films with the solutions of rare earth ions and β-diketone ligands. The effects of the reaction conditions on the fluorescence intensity of the red photoluminescence film were investigated.

Effects of pH value

The pH value of the reaction system is of great importance to the fluorescence intensity of films prepared because both the coordination of the rare earth ions

with the β-diketone ligands in solution and the combination of the rare earth ions with the acrylic acid grafted onto PE film are highly dependent on the acidity of the medium. First, the β-diketone exists in the isomeric forms of both the ketone and the enol (enolic ion) as follows:



The fluorescence intensity of the rare earth-enolic ion complex is stronger than that of the rare earth-ketone complex.⁸ When the pH is higher, the balanced equation of the isomerization shifts to the enol form, and the enolic ions coordinate with rare earth ions more effectively. Second, the combination of the rare earth ions with the grafted film can be considered as the competition between the rare earth ions and the H⁺ in the carboxyl groups of grafted acrylic acid, which is the actual site of the reaction. When the pH of the solution is lower, the combination site is occupied by H⁺ more readily; on the other hand, the rare earth ions that have already been combined tend to be displaced by H⁺, which is more dominant in the solution. In other words, a higher pH value is favorable for increasing the fluorescence intensity of the film. Figure 5 shows the variation of the relative fluorescence intensity (I) of the red photoluminescence film (Eu³⁺-TTA-PAA-g-PE) when the pH of the solution is adjusted to different values. It can be seen that the fluorescence of film obtained is weak at a lower pH and that the emission intensity of film increases considerably with an increase in pH value. For the rare earth ions, however, hydrolysis occurs when the pH value of the solution is higher than 7.0, which results in the

TABLE II
Fluorescence Spectrum Data of Tb³⁺-AcAc-PAA-g-PE Film and Tb(AcAc)₃(H₂O)₂
Solid Complex

	λ ex/nm (λ em = 547.0 nm)	λ em/nm (λ ex = 365.0 nm)			
		⁵ D ₄ → ⁷ F ₆	⁵ D ₄ → ⁷ F ₅	⁵ D ₄ → ⁷ F ₄	⁵ D ₄ → ⁷ F ₃
Tb ³⁺ -AcAc-PAA-g-PE	351.4	492.5	547.6	584.4	616.1
Tb(AcAc) ₃ · (H ₂ O) ₂	332.3	494.2	551.1	585.4	623.2

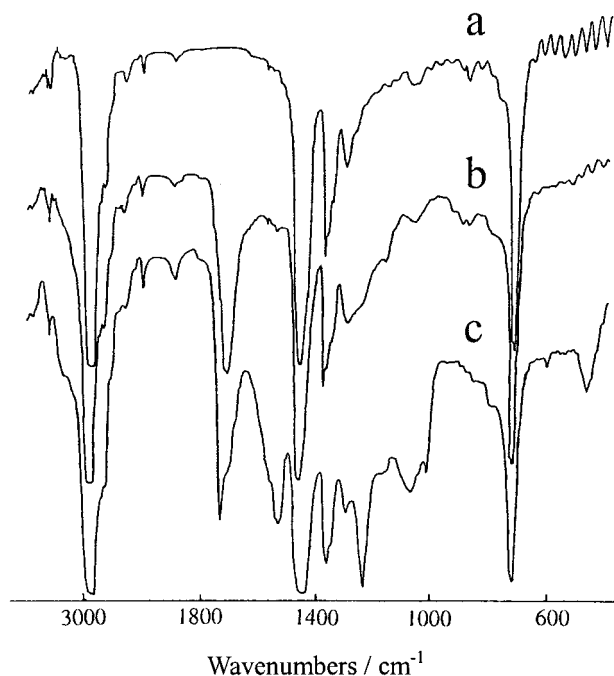


Figure 4 IR spectra of (a) PE film, (b) photografted film, and (c) red fluorescent film.

precipitation as hydroxide. For this reason, the investigation was limited to those pH values, at which precipitation was just prevented. We chose 6.5 as the appropriate pH value in the experiments.

Effect of reaction time

Figure 6 illustrates the effect of reaction time on the relative fluorescence intensity of the red photoluminescence film. The fluorescence intensity increased as the reaction time extends during the first 5 h; however, the curve leveled off after 5 h, indicating that in a period of about 5 h, the reaction was already close to completion. A longer reaction time had no evident effect on grafted film to react with more rare earth ions

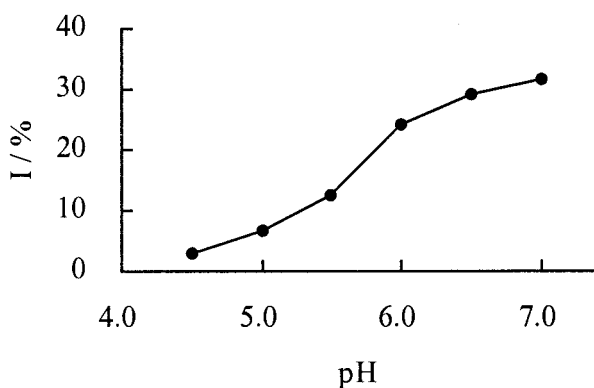


Figure 5 Influence of pH on emission intensity of red fluorescent film (temperature: 20°C; reaction time: 5 h).

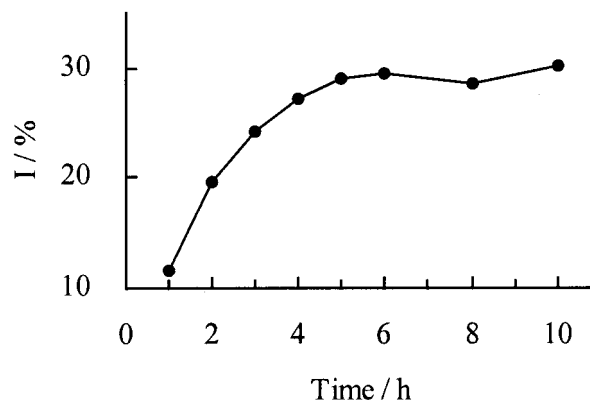


Figure 6 Relationship between emission intensity of red fluorescent film and reaction time (temperature: 20°C; pH: 6.5).

(or rare earth complexes). As a result, we chose 5 h as the optimum reaction time in the experiments.

Effect of reaction temperature

The reaction was conducted at different temperatures (from 20°C to 50°C). Figure 7 demonstrates the relationship between the relative fluorescence intensity of the red photoluminescence film and the reaction temperature. It may be seen that the reaction temperature had almost no effect on the emission intensity of the fluorescent film. Therefore, the reaction of the grafted films with the solution of rare earth ions and β -diketone ligands can be carried out at room temperature.

CONCLUSION

The foregoing work has shown that photoluminescence films in which the chemical bond combination occurs between fluorescent rare earth complexes and macromolecular material can be prepared by photografting acrylic acid onto PE film and treating the

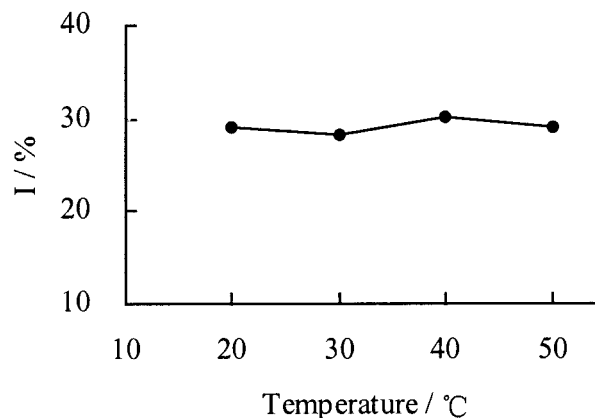


Figure 7 Effect of reaction temperature on emission intensity of red fluorescent film (reaction time: 5 h; pH: 6.5).

grafted film with a solution of rare earth ions and β -diketone. It is noteworthy that, compared with the corresponding solid complexes, both the excitation and emission spectra of the photoluminescence films were changed considerably, which is sufficient to confirm the expectation that chemical combination, not physical adsorption, occurred between the fluorescent rare earth complexes and the macromolecular material. In the reaction of the grafted film with a solution of rare earth ions and β -diketone, the pH value of the solution had a remarkable effect on the emission intensity of the fluorescence film. A higher pH value is favorable for increasing the emission intensity of the film prepared. However, a pH value higher than 7.0 will result in rare earth hydroxide precipitation; so the reaction should be conducted at a pH value lower than 7.0. The emission intensity of the red photoluminescence film increased as the reaction time extended over a period of about 5 h; however, the reaction was close to completion after 5 h. The reaction temperature had almost no effect on the fluorescence intensity of the film; hence, the reaction can be carried out at room temperature.

In addition, the fluorescence spectra of all the photoluminescence film samples were measured again after being kept under normal condition for about 10 months. The fluorescence intensities of the films were almost unchanged. This indicates that photoluminescence films are stable, which is because the fluorescent rare earth complexes were attached to the PE film through chemical bonding.

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