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Eu-PEG로 구성된 상변환 발광재료의 합성 및 물성에 대한 연구

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Study of Synthesis and Property of Eu-PEG Phase Change Luminescent Materials

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Abstract : A novel TPC-PEG-TPC with active end-groups was obtained from the end-groups of polyethylene glycol (PEG) modified by terephthaloyl chloride (TPC). These active end-groups can link up with a rare earth ion, which is a luminescent center of a rare earth fluorescent complex. Complexes of Eu-PEG with novel ligands (TPC-PEG-PTC) were synthesized by the coordination of the active reactant (as the first ligand) and phenanthroline (as the second ligand) with Eu^{3+}. IR, ^{1}H-NMR, element analysis, DSC, WAXD, fluorescent spectroscopy, TGA, and SEM were used to characterize the structure and properties of these complexes. The results showed that this type of complex is a heat storage material with the phase change character of polyethylene glycol (PEG) and the luminescent properties of europium. There was no thermal decomposition of the complex of Eu-PEG until 300 ℃. SEM showed that the complex of Eu-PEG can be dispersed in PE.

Keywords : polyethylene glycol (PEG), terephthaloyl chloride (TPC), phase change energy storage, rare earth, luminescence.

Introduction

Phase change materials (PCMs) are a series of compound materials with storing and releasing energy properties. PCMs can store thermal energy and adjust temperature through storing and releasing energy during phase change process.[1-3] PCMs have been widely studied and early applications in the field of outer space. PCMs can store solar energy that can be used for heating and keeping temperature constant. This technology was firstly used by national aeronautics and space administration (NASA) from the end of 70's to early 80's in the 20th century. PCMs have attracted much attention for a long time in the foreign countries. Up to the end of 20th century, breakthrough development has been attained in the field of exploration and application of PCMs.[4-7] However, it still takes a fairly long period of time to manage to mass production in industry.[8-11]

PCMs have lots of advantages, such as high storage density, constant temperature during phase change process and easily being processed. Therefore, PCMs can play a very important role on alleviating energy supply crisis and making best use of energy. Especially, the high molecule weigh PCMs

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have increasingly attracted more and more attentions. In recent years, the polymeric PCMs have become the research focus due to their excellent performances, for example, easy processing into expected shape, high storing capacity per unit volume, being applied conveniently, even being used as a series of materials directly.[12-15]

In the field of organic PCMs, PEGs with obvious phase change property have been widely used in pharmaceutics, biomedicine and other fields. However, PEG is a classical solid-liquid phase change material, which must be packaged in specially sealing containers to prevent its leakage in the melting state. In order to overcome these shortcomings, PEG solid-solid phase change materials have been researched via graft or block polymerization ways. In these PEG solid-solid PCMs, the transition enthalpy decreased as other constituents increased. So, it is important to control the percent of other constituents in PEG solid-solid PCMs. However, this is difficult in graft and block polymerization.[16-18]

There is a long history for the researches of luminescent materials. In particular, in previous decades, luminescent materials containing rare earth ions have been attracted much attention due to their long fluorescence lifetimes and strong fluorescence emission. Rare earth ions as an efficient luminescent center have a wide utilization in organic and inorganic materials, because of the high coordination property of rare earth ions. Especially, the rare earth ions coordinate with the carboxyl groups. If we synthesize a PEG compound with carboxyl groups via the end-groups modification of PEG, the novel polymeric PEG phase change material will be prepared through the coordination of the carboxyl groups and rare earth ions.

Based on the idea, we synthesized a PEG functional compound with double carboxyl groups. At the same time, making use of the functional compound, a novel polymeric PEG phase change material has been prepared. The analyzed results show that, one rare earth ion can coordinate with four PEG functional compounds with double carboxyl groups in the molecular structure of the novel polymeric PEG phase change material prepared, using the high coordination property of rare earth ion. In this kind of phase change material, the percent of phase change unit is much bigger; the phase change enthalpy of the phase change material is higher. So, through the coordination of carboxyl group and rare earth ion, the excellent PEG solid-solid phase change materials can be prepared. These research results provide a new way to produce novel PEG solid-solid phase change materials.[19-21]

In order to extend the application fields of the novel polymeric PEG phase change material, the phenanthroline (phen) was also introduced. This makes the novel polymeric PEG phase change material showing luminescent property.

Experimental

Reagents and Apparatus.

Reagents: Polyethylene glycol (MW=1000) and terephthaloyl chloride (TPC) were from China Medicine (Group) Shanghai Chemical Reagent Corporation. Eu_2O_3(99.99%) was provided by Shanghai Yuelong Nonferrous Metals Corporation. The other chemicals were AR reagent grade and also from China Medicine (Group) Shanghai Chemical Reagent Corporation.

Apparatus: The IR absorption spectra were recorded with a Nicollet NEXUS-670 infrared spectrophotometer. The KBr pressed disc technique was used. ^{1}H-NMR (DMSO) was measured on a Bruker Avance 400 NMR spectrometer. C, H, O, and N of the Eu-PEG phase change luminescence material were determined by Carbo-Eroa 1106 elemental analyzer, and Eu ions were analyzed by complexometric titration with EDTA. DSC curves were recorded using a 2920 TA differential scanning calorimeter. Samples (ca. 10 mg) were sealed in aluminum pans and the measurements were performed in nitrogen atmosphere at a heating rate of 10 ℃/min in the temperature range of −50 to 150 ℃. Wide-angle X-ray diffraction (WAXD) was carried out with a Philip PW 1710 at 30 kV and 20 mA. Bragg's angle 2 θ is from 10 to 500 at the rate of 30/min. TGA were carried out using TA Instruments Co., thermal analysis system (TGA2050, USA). About 10 mg sample dried was sealed in aluminum pan and the curves were recorded from 0 to 650 ℃ at a heating rate of 10 ℃/min. The excitation and emission spectra were taken on an F-4500 spectrophotometer equipped with a 150 W Xenon lamp as excitation source. The band pass for the luminescence spectrophotometer was set at 2 nm. SEM photos were observed by Field emission scanning Electron microscope, JEOL JSM-6330F. UV spectrum was tested with 760CRT UV spectrophotometer.

Synthesis of Phase Change Luminescent Material.

Synthesis of the PEG Functional Compound: The PEG functional compound was synthesized as following : A threenecked flask (250 mL) equipped with a condenser and a thermometer was immersed in oil bath. Threphthaloyl chloride (0.088 mol) and polyethylene glycol (M_W=1000, 0.04 mol) were added into the flask (ice water cold) containing chloroform (80 mL). The whole mixture was reacted under the conditions of reflux and nitrogen atmosphere for 6 h. The resulted solution was washed repeatedly with mixture solutions of deionized water and *N, N*-dimethylformamide (DMF), filtered and dried at 40 ℃ in vacuum oven. The synthetic route of the PEG functional compoundis shown in Figure 1.

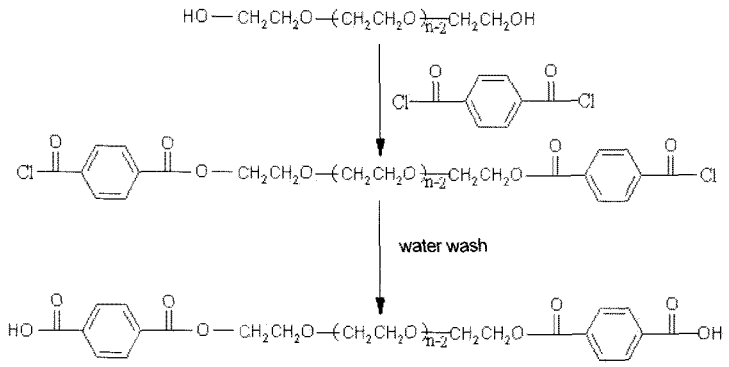

Figure 1. The synthetic route of the PEG functional compound.

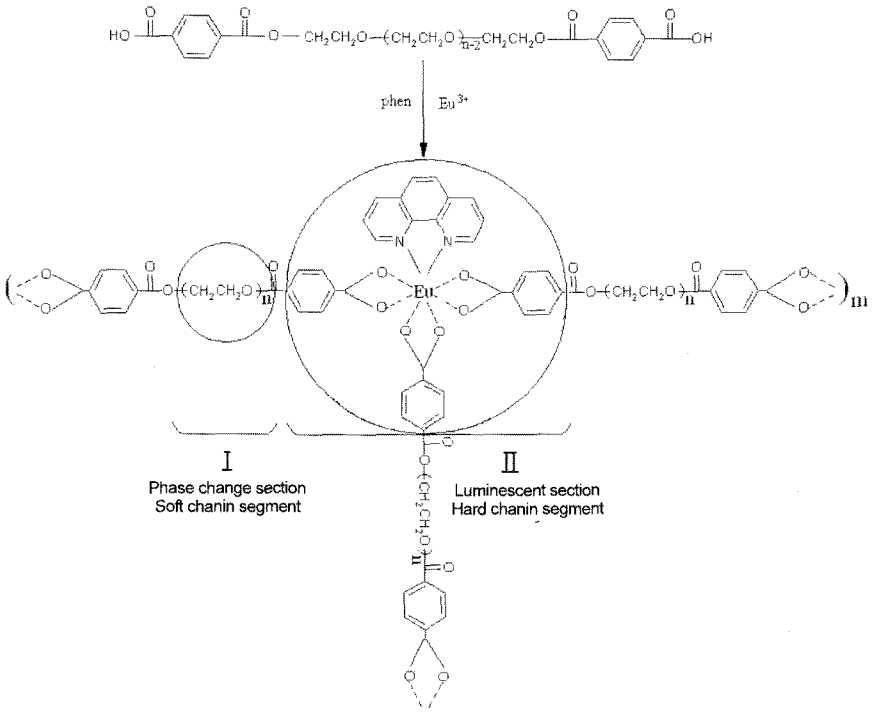

Figure 2. The synthetic route of Eu-PEG phase change luminescence material.

Synthesis of Eu-PEG Phase Change Luminescent Material. $EuCl_3$ (0.2 mmol) and phenanthroline (0.2 mmol) were dissolved in anhydrous ethanol (solution 1). The PEG functional compound (0.3 mmol) was dissolved in dimethyl sulphoxide (20 mL), which was stirred at 30 ℃ until it became transparent (solution 2). Solution 1 and solution 2 were stirred at 30 ℃ for 3 h, and then the mixture solution was delaminated. After 48 h, the mixture solution resulted was filtered, then solid powder product was obtained. The synthetic route of Eu-PEG phase change luminescence material was shown in Figure 2.

Results and Discussion

Characterization of the Composition and Structure for the PEG Functionalized Compound. Figures 3 and 4 show the IR and ^{1}H-NMR spectra of the PEG functional compound. In Figure 3 the carbonyl group stretching vibration peaks of the ester group is appearing at 1719 cm^{-1}. The characteristic peak of νCOOH is appearing at 1690 cm^{-1}. The peaks lie in 3060, 1600, 1580, 1519 and 1430 cm^{-1} are the characteristic peaks of benzene ring. The absorption peaks of νC-O are at 1280 and 1100 cm^{-1}. The characteristic peak of the νC-H for PEG lies in 2870 cm^{-1}.

In Figure 4, the chemical shift (δ) of ^{1}H in the ^{1}H-NMR spectrum of the PEG functional compound correspond to the ^{1}H in the molecular structure of the PEG functional compound. The results of IR and ^{1}H-NMR for the PEG functional compound verify that PEG functional compound with

double carboxyl has been synthesized.

Characterization of the Composition and Structure for the Eu-PEG Phase Change Luminescent Material. Figures 5 and 6 present the IR spectra of phen and the Eu-PEG phase change luminescent material. In Figure 6, the characteristic peak of νCOOH for the PEG functional compound (1690 cm^{-1})

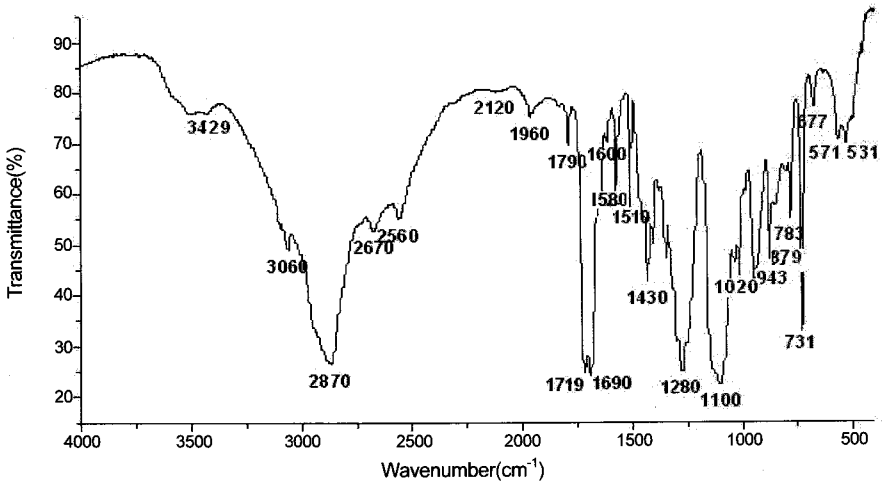

Figure 3. IR spectrum of the PEG functional compound.

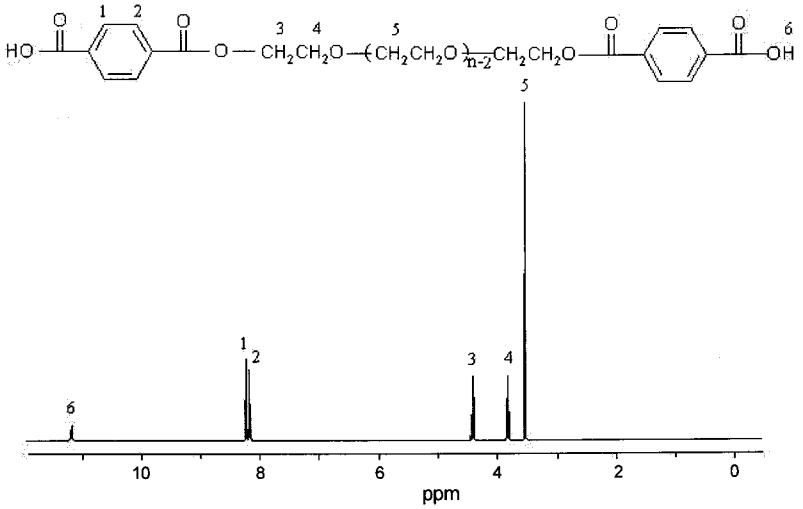

Figure 4. ^{1}H-NMR spectrum of the PEG functional compound.

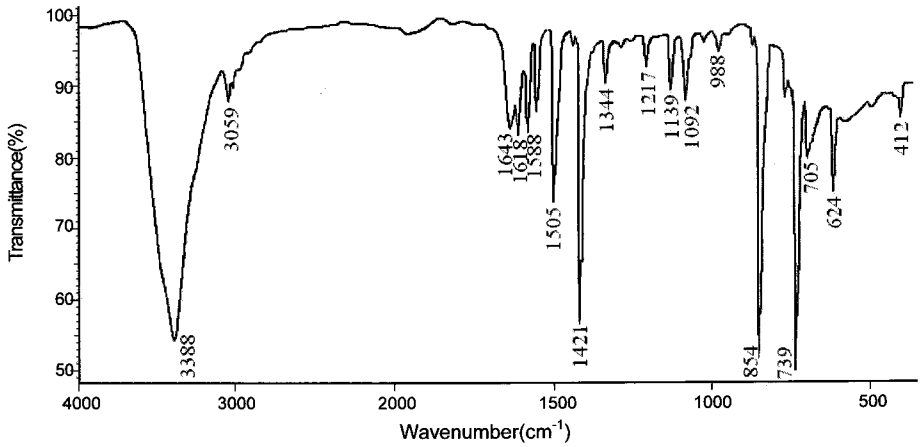

Figure 5. IR absorption spectrum of phen.

disappears, when the Eu-PEG phase change luminescent material is formed. The asymmetric and symmetric stretching vibrations of carboxylic group are appearing at 1610 and 1520 cm^{-1} in the Eu-PEG phase change luminescent material. These data prove that the coordinate bonds are formed between oxygen atom in carboxylic group and the rare earth ion. On the other hand, the benzene ring νC-H bending vibration peaks of phen in high frequency region appearing at 854 and 739 cm^{-1} (shown in Figure 5) are shifted to 847 and 733 cm^{-1}, indicating that the chemical bonds are formed between rare earth ion and nitrogen atoms of phen. Finally, the absorption peak at about 423 cm^{-1} can be assigned to the Eu-O vibration absorption band. According to the analysis of the IR spectra of the Eu-PEG phase change luminescent material and phen, the Eu-PEG phase change luminescent material has been formed.

The elemental analytical data of the Eu-PEG phase change luminescence material is recorded in Table 1, and these are in agreement with calculated values for the proposed structure (shown in Figure 2).

Phase Change Property Analysis of the Eu-PEG Phase Change Luminescent Material. Figure 7 shows the DSC curves of pure PEG and the Eu-PEG phase change luminescent material, and the data of their phase change temperature and enthalpy are summarized in Table 2. It indicates that there is a melting peak at about 39.2 ℃ in the heating scan of the DSC curve of pure PEG and the latent heat of fusion is 164.2 J/g. While in the heating scanning DSC curve of the Eu-PEG phase

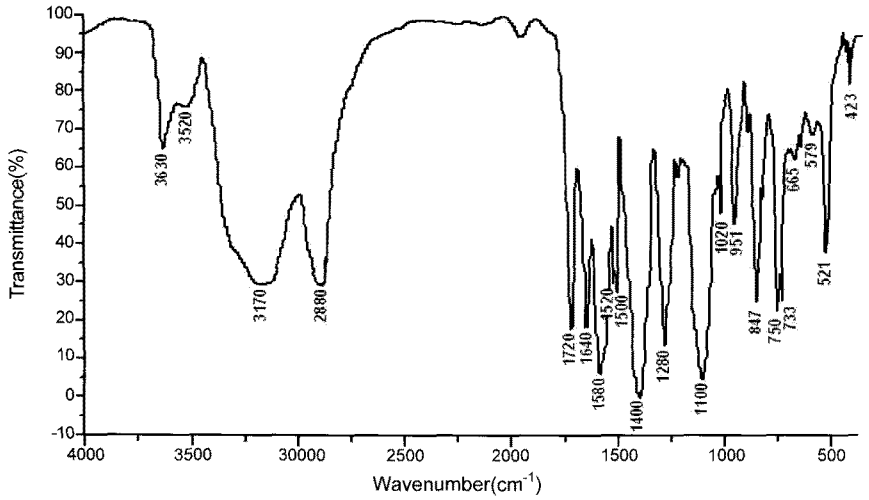

Figure 6. IR spectrum of the Eu-PEG PSSPCLM.

Table 1. The Elemental Analytical Data of the Eu-PEG Phase Change Luminescence Material

Sample		C%	H%	O%	N%	Eu%
The Eu-PEG phase change luminescence material	Test value	69.93	9.51	15.05	0.86	4.65
	Calculate value	69.91	9.48	15.03	0.85	4.66

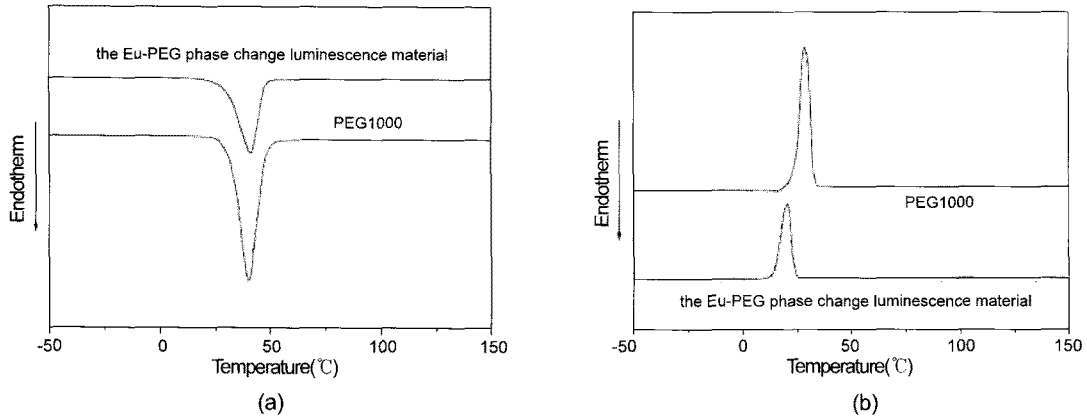

Figure 7. DSC curves of pure PEG and the Eu-PEG phase change luminescence material: (a) heating traces and (b) cooling traces.

Table 2. DSC Analysis Data of the Eu-PEG Phase Change Luminescence Material

Samples	Phase transition	ΔH_m(J/g)	T_m(℃)	ΔH_c(J/g)	T_c(℃)
PEG 1000	Solid-liquid	164.20	39.20	129.50	28.4
The Eu-PEG phase change luminescence material	Solid-solid	118.26	42.60	98.26	22.38

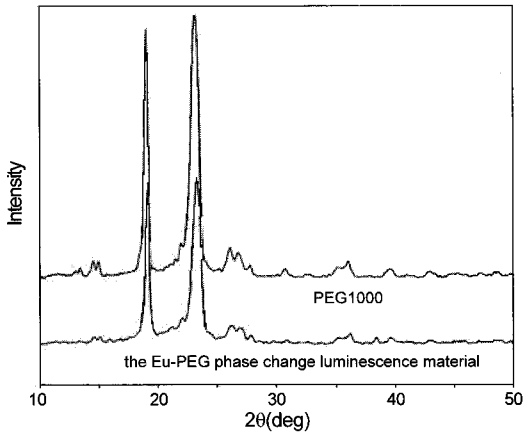

Figure 8. WAXD patterns of the pure PEG1000 and the Eu-PEG phase change luminescence material.

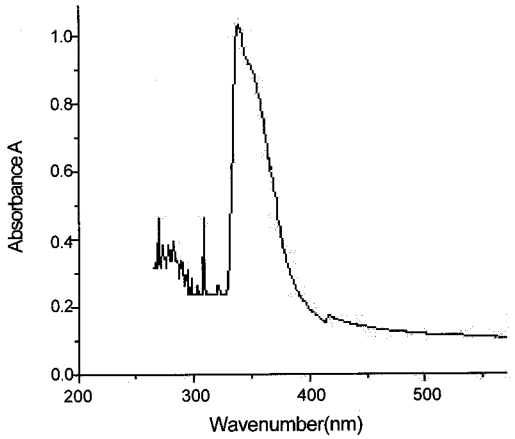

Figure 9. UV spectrum of the Eu-PEG phase change lumenescence material.

change luminescent material, it also shows a melting peak at 42.6 ℃, and the enthalpy is 118.5 J/g. This indicates that the phase change unit is PEG chain segments in the Eu-PEG phase change luminescent material. Both pure PEG and the Eu-PEG phase change luminescent material undergo phase transition with high transition enthalpy, but their phase change types are quite different. The type of the phase change of pure PEG is a process from solid to liquid. When some pure PEG were heated, it can be seen that it starts to change from a white crystal solid to a transparent liquid as heated to about 50 ℃; while, when the Eu-PEG phase change luminescent material is heated directly, it remains solid, and no liquid is observed in the complete heating process, even if the temperature is raised to 100 ℃ or higher. It indicates that the phase change of the Eu-PEG phase change luminescent material is a solid-solid phase transition.

In order to further study phase change property of the Eu-PEG phase change luminescent material, the WAXD patterns of the pure PEG1000 and the Eu-PEG phase change luminescent material were investigated (shown in Figure 8). It is obvious that pure PEG and the Eu-PEG phase change luminescent material show similar diffraction curves with respect to diffraction curve and angle and crystal plane distance are nearly the same. The analyzed results of DSC and WAXD indicate that the phase change unit of the Eu-PEG phase change luminescent material is PEG chain segment, the phase change type is solid-solid phase change, and the phase change enthalpy is higher.

Fluorescent Characterization of the Eu-PEG Phase Change Luminescent Material. Figure 9 shows the UV spectrum of the Eu-PEG phase change luminescent material. From the UV spectra, it can be seen that the UV absorption range is 330-380 nm; the strongest absorption peak is 340 nm. The fact proves that the Eu-PEG phase change luminescent material possess good UV absorption property.

Figure 10(a),(b) show the fluorescent spectra of the Eu-PEG phase change luminescent material. In the excitation spectra of the Eu-PEG phase change luminescent material, the strong and smooth bands observed (330-348 nm) could be assigned to the efficient $\pi \rightarrow \pi^*$ transition based on the conjugated double bands of the PEG functional compound and phen. The most intense absorption wavelength is 340 nm. The results agree with the analysis results of UV spectra of the Eu-PEG phase change luminescent material.

The emission peaks of the complex with Eu^{3+} are all from $^5D_0 \rightarrow {}^7F_{J(0-4)}$ transition of Eu^{3+}.[22,23] In the emission spectra of the Eu-PEG phase change luminescent material, the corresponding emission peaks base on $^5D_0 \rightarrow 7F^1$ (603 nm), $^5D_0 \rightarrow {}^7F_2$ (625 nm), $^5D_0 \rightarrow {}^7F_3$ (660 nm) and $^5D_0 \rightarrow {}^7F_4$ (707 nm) transitions. The strongest emission peak is 625 nm. It belongs to $^5D_0 \rightarrow {}^7F_2$ transition. These facts indicate that the Eu-PEG phase change luminescent material process the characteristic emission spectra of Eu^{3+}, and can produce good fluorescence.

Thermal Stability of the Eu-PEG Phase Change Luminescent Material: Figure 11 presents the TGA curve of

the Eu-PEG phase change luminescent material. It is observed that the Eu-PEG phase change luminescent material begins to lose weight at 300 ℃. The losing weight becomes obviously at 356.3 ℃ and completes at 420 ℃. The rate of losing weight reaches maximum at 396 ℃. Therefore, we can conclude that the Eu-PEG phase change luminescent material has an outstanding thermal stability and there is no thermal decomposition below 300 ℃.

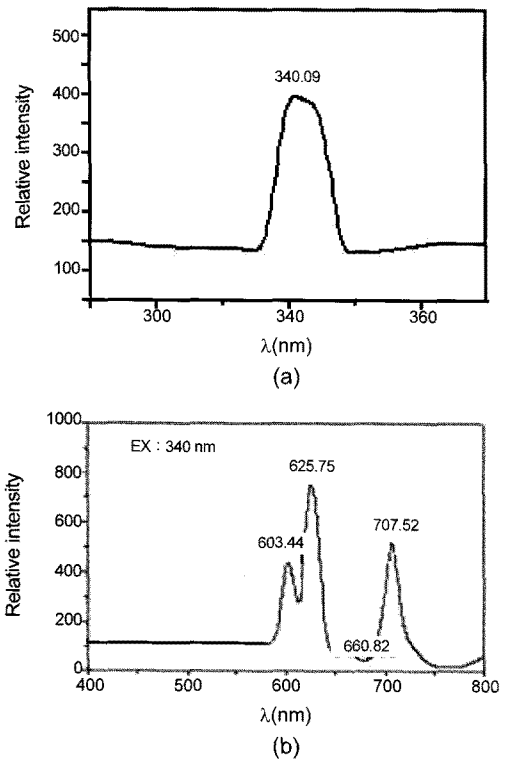

Figure 10. Fluorescent spectra of the Eu-PEG phase change luminescence material.

The Dispersion of the Eu-PEG Phase Change Luminescence Material in PE. Figure12 presents the SEM photos of the Eu-PEG phase change luminescent material (1%) in matrix of PE. When the amount of the Eu-PEG phase change luminescent material is 1%, the SEM results show that the Eu-PEG phase change luminescent material is well dispersed in the PE and not agglomerated.

Conclusions

Through the end-group modification of PEG and the coordination reaction of the PEG functional compound and Eu^{3+}, the novel Eu-PEG phase change luminescent material has been prepared. The composition and structure of the PEG functional compound and the Eu-PEG phase change luminescent material have been investigated. IR and NMR spectra indicate that the Eu-PEG phase change luminescent material possesses good steady structure. The analytical results of the DSC and WAXD show that the Eu-PEG phase change luminescent material has excellent solid-solid phase change property. The luminescent property of the Eu-PEG phase change luminescent material has also been studied. The complexes exhibit characteristic emission peaks of Eu^{3+} ion and good luminescent intensity in the excitation spectrum. The thermal property was tested by TGA. The results indicate that the Eu-PEG phase change luminescent material possesses good heat stability, and there was no thermal decomposition until 300 ℃.

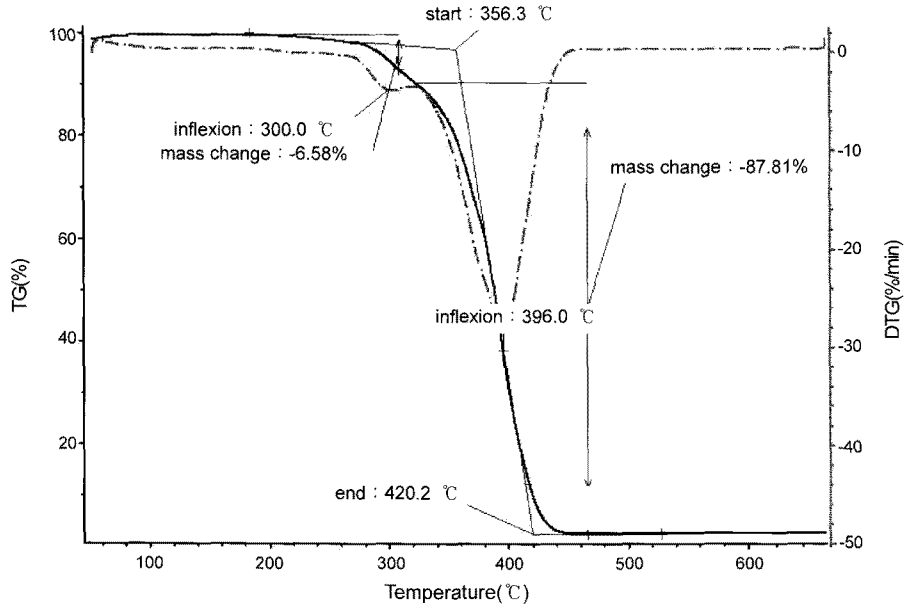

Figure 11. TGA curve of the Eu-PEG phase change luminescence material.

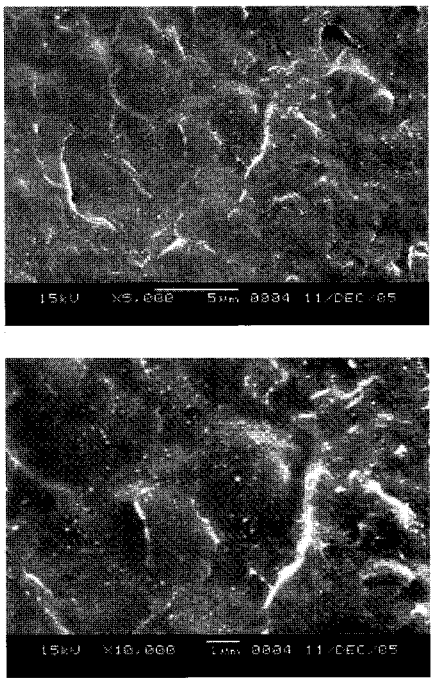

Figure 12. SEM photos of the Eu-PEG phase change luminescence material in the PE.

The dispersion of the Eu-PEG phase change luminescent material in PE was observed by SEM. It shows that the Eu-PEG phase change luminescent material was well dispersed in PE.

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