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Synthesis and Optical Properties of Transparent Resins Containing Rare Earth Compounds

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Abstract: Three kinds of transparent resins were prepared by three different synthesis methods. Sample 1 is transparent resins formed by RE(MA)₃ salt polymerizing, Sample 2 is transparent resins containing rare earth (RE) complexes by doping method, and Sample 3 is transparent resins containing rare earth complexes by in situ composite method. The transparent resins were characterized by TGA, impact energy, UV-Vis, FT-IR, ¹H-NMR and fluorescence spectra. The fluorescence data indicated that the optical resins display intense and narrow-band emission, highly visible transparency, and good mechanics performance in Sample 2 and Sample 3. The photoluminescence intensity enhanced and lifetime is raised in doping or in situ method after introducing RE complexes into copolymer system, by comparing with RE complexes powder. The fluorescence data revealed that the fluorescence intensity of Sample 3, which synthesized by in situ method, is the strongest among the three samples. It was revealed that the in situ synthesis method, as a novel method, can be quickly and simply employed to synthesize transparent optical resins. Comparing with the resins by doping method, these composite resins possess better luminescent property at the same RE concentration.

Key words: transparent resin; rare earth; fluorescent property; composite materials

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1 Introduction

Lanthanide elements are well known for uniquely optical properties^[1], so composite materials of RE doped polymers are a series of functional materials with many excellent properties of both the luminescence characteristics of lanthanide ions and the excellent mechanics properties of plastics, such as light weight, good transparency, impact resistance, low temperature processability and dyeability^[2], leading to great application in optics, electricity, magnetics, laser, catalysis, and analysis *etc.* Therefore, the deve-

lopment of the function materials displays an attractive prospect.

Now, the method of preparing the composite materials with RE doped polymers are divided into two classes: doping-type method and bonding-type method.

In doping-type RE polymers, the RE compounds were uniformly dispersed into monomers and polymers as a sort of dopant, this is the earliest method. The kinds of dopant include: lanthanide alloys, lanthanide inorganic compounds, lanthanide complexes. In this method, lanthanide inorganic compounds and

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thermosetting or thermoplastic resin polymers have widely been used. The PS/PMMA-RE composite with definite shielding neutron action was reported by Ida^[3]. The rare earth/nature rubber (RE/NR) and rare earth/thermoplastic polyurethane (RE/TPU) were studied by Liu^[4]. The two kinds of composites show outstanding neutron absorbing ability and can be used to make soft materials such as radiation protection coats in medical aspect. This doping method is simple and easy as synthesis technique and method. However, RE inorganic compounds have poor compatibility with polymer matrix, making the transmittance and mechanical strength of polymer material reduce^[5,6], so a good interface is hard to obtain. The doping content of RE compound is limited, leading to the property of the rare earth/polymer composite being affected. Although adding organic compounds can improve the RE content, but the problem is not completely achieved.

In attempting to resolve doping-type method problems, some research groups have done much work^[7,8]. However, there are still some problems in the composites of low molecular weight lanthanide complexes in polymer materials. Firstly, the most composites were prepared by direct reaction of the polymer ligands with lanthanide ions, the polymer luminophor usually exhibited serious emission concentration quenching due to the occurrence of ionic aggregates even at low lanthanide ion content, and the microenvironment of lanthanide ion is very complicated, which made the elucidation of the luminescent properties difficult. Secondly, the solubility of most lanthanide complexes in polymer systems is poor, which made it difficult to prepare a uniform thin film of high content lanthanide complexes or solid polymer material.

Our group has extended these efforts towards making transparent optical resins containing lanthanide compounds and complexes since 1995, and there are some research results on synthesis and properties of these transparent resins in our group^[9-13].

In this paper, we prepared three kinds of trans-

parent resins by different methods. The three samples display different fluorescence intensity. According to the fluorescence data, it was found that the fluorescent intensity of Sample 3 is the best one among the three kinds of resins prepared by different synthesis method. It was also verified the in situ synthesis method can be quickly and simply employed for synthesizing optical function resins.

2 Experimental Section

2.1 Materials

Tb₄O₇, Eu₂O₃, Y₂O₃, Gd₂O₃, Sm₂O₃, Nd₂O₃ and La₂O₃, (99.99%, Yuelong Chemical Co., Shanghai). EuCl₃, TbCl₃, GdCl₃, YCl₃ and LaCl₃ were obtained by dissolving lanthanide oxides Tb₄O₇, Eu₂O₃, Y₂O₃, Gd₂O₃, and La₂O₃ into hydrochloric acid. Styrene (St), *a*-methyl acrylic acid (MA), 2,2-azoisobutyronitrile (AIBN), octadecanic acid have been purified before using.

1,10-phenanthroline (phen), dibenzoyl-methane (DBM), 4,4,4-trifluoro-1-(2-thenyl) 1,3-butane-dione (TTA), 2,2'-dipyridine (Dipy), salicylic acid (Sal), acetylacetone (AA), and cetyl pyridinium bromide (CPB) are analytical grade.

Lanthanide complexes, such as Eu(TTA)₃phen, Eu(DBM)₃phen^[12], Eu(DBM)₄CPB, Tb(AA)₃phen, Tb(Sal)₃, Eu(phen)₂Cl₃ · 2H₂O, and Tb(phen)₂Cl₃ · 2H₂O, were synthesized and purified according to the publications^[13].

2.2 Experimental Procedures

2.2.1 The preparation of Sample 1

The RE methacrylic acid salt RE(MA)₃ were synthesized through the reaction of Sm₂O₃, Eu₂O₃, and Nd₂O₃ and methacrylic acid, and then the 0~3% salt were incorporated into methacrylic acid and styrene copolymer system, transparent resin (Sample 1) with the thickness of 1.5 mm were obtained^[7].

2.2.2 The preparation of Sample 2

After a certain amount of one of the lanthanide complexes was dissolved into the mixture of *a*-methyl acrylic acid (MA) and styrene (St) monomers,

0.5% AIBN was added as an initiator. The resulting mixture was pre-polymerized at 60 °C for 20 min. The content was cast and sealed into a mold consisting of two glass plates and a silicone rubber gasket. The sample was kept for 14 h at 57 °C. Afterwards, it was gradually heated to 110 °C with a speed of 20 °C/h and then kept for 2 h at 110 °C in order to polymerize completely. The obtained sheet (Sample 2) with the thickness of 3 mm is transparent.

2.2.3 The preparation of Sample 3

$TbCl_3 \cdot 6H_2O$ ($EuCl_3 \cdot 6H_2O$), the first organic ligands (DBM, TTA and Sal) and the second organic ligands (phen, Dipy and Sal) with the molar ratio of 1:3:2, were dissolved in the mixture solution of methyl-acrylic acid (MA) and styrene (St) (the molar ratio of binary complex is 1:3). The volume ratio of MA and St is 3:7 for Tb^{3+} , as well as the volume ratio of MA and St of 1:1 for Eu^{3+} . Then AIBN was added as initiator. The mixture has been polymerized for 20 min at 60 °C. The pre-polymerized product was cast and sealed into a mold consisting of two glass plates and a silicone rubber gasket and maintained at 57 °C for 14 h. Afterwards, it was gradually heated to 110 °C with 5 °C/15 min and further maintained for 2 h at 110 °C to polymerize completely. The obtained sheet (Sample 3) are transparent with the thickness of 3 mm.

2.3 The Main Characterization

The refractive index (η_D) of the composite resins was measured using an Abbe refractometer at 23 °C.

The polymer decomposition temperatures were measured by thermogravimetry analysis (TGA) with a Perkin-Elmer TGA-7 thermogravimetric analyzer. The TGA measurements are conducted with a heating rate of 10 °C/min in nitrogen, the temperature at 5% weight loss is regarded as the decomposition temperature.

Impact energy of the test sheet with no notch was evaluated using an XJ-40A Impact Testing Machine at room temperature, and the impact strength was calculated. Surface hardness was evaluated by

pencil hardness.

UV-Vis spectra and transmittance of samples were recorded on a Shimadzu 3100 UV-Vis-NIR spectrometer in the range of 200 ~ 800 nm. Visible light transmittance was recorded at 550 nm wavelength.

The FT-IR spectra were recorded on a Nicolet AVATAR360 FT-IR spectrometer in the 4 000 ~ 400 cm^{-1} regions.

The 1H -NMR spectra were obtained from a unity-400NMR in $CDCl_3$ solution using tetramethylsilane as an internal reference.

The far infrared spectra were recorded on a Magna 560 FT-IR spectrometer in the 600 ~ 0 cm^{-1} regions.

Excitation and emission spectra were measured on a RF-5301PC fluorescence spectrophotometer with a 450 W xenon lamp as excitation source. Fluorescence lifetime measurements were carried out on an SPEX 1934D phosphorimeter, adopting a 7 W xenon flash lamp as excitation source.

3 Results and Discussion

3.1 Sample 1

We prepared the transparent resin of methacrylic acid and styrene copolymer system containing $RE(MA)_3$ in order to study the polymer material with luminescence and magnetic properties.

The FT-IR spectra of $Eu(MA)_3$ are shown in Fig. 1. The other characteristics of $RE(MA)_3$ can't be obtained except for FT-IR spectra owing to the poor solubility in other solvents. The chemical shift

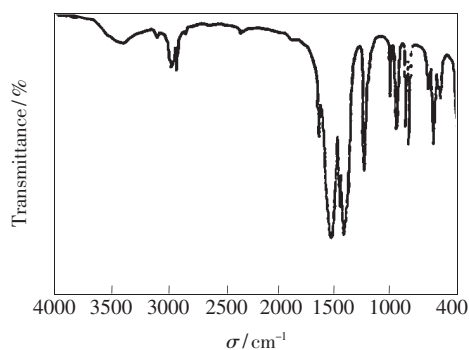


Fig. 1 The FTIR spectra of $Eu(MA)_3$

of $^1\text{H-NMR}$ and elemental analysis of other six kinds of $\text{RE}(\text{MA})_3$ are displayed in Table 1. The results indicate that the ratio of $a\text{H}:b\text{H}:c\text{H}$ is 1:1:3, due to the different effect from different metal ions to the chemical shift of H. The paramagnetism of Nd^{3+} and Sm^{3+} is strong, while the magnetic of La^{3+} and Sc^{3+} is absent. The transmittance of the resins is over 80%, and the refractive index is about 1.55. The

transparent resin containing $\text{RE}(\text{MA})_3$ is weak color. The presence of Sc^{3+} enhanced the luminescence of the Eu^{3+} in the transparent resins, when the ratio of Sc^{3+} and Eu^{3+} is 1:1. The luminescent intensity is doubled, demonstrating an important feature of energy transfer from scandium to europium in the transparent resins, whereas the emission of the resins containing Sm^{3+} , Ho^{3+} , Er^{3+} , and Y^{3+} can't be found.

Table 1 Chemical shift of $^1\text{H NMR}$ and elemental analysis of $\text{Re}(\text{MA})_3$

| $\text{Re}(\text{MA})_3$ | $^1\text{H NMR}(\delta, \text{ppm})$ | | | Elemental analysis(Theoretical) | |
|--------------------------|--------------------------------------|--|--|---------------------------------|------------|
| | $-\text{CH}_3^c$ | $\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COO} \\ \text{aH} \end{array}$ | $\begin{array}{c} \text{H} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{COO}^- \\ \text{bH} \end{array}$ | C(%) | H(%) |
| $\text{Er}(\text{MA})_3$ | 0.69 | 4.15 | 4.38 | 33.71(35.35) | 3.87(3.68) |
| $\text{La}(\text{MA})_3$ | 1.86 | 5.44 | 5.77 | 34.74(36.53) | 3.88(3.80) |
| $\text{Sc}(\text{MA})_3$ | 1.87 | 5.41 | 5.75 | 39.03(37.23) | 4.43(3.87) |
| $\text{Sm}(\text{MA})_3$ | 2.00 | 5.57 | 6.05 | 33.67(35.49) | 3.39(3.69) |
| $\text{Y}(\text{MA})_3$ | 2.71 | 6.20 | 7.14 | 41.15(41.83) | 3.87(4.35) |
| $\text{Nd}(\text{MA})_3$ | 2.92 | 6.52 | 7.45 | 34.55(36.04) | 3.71(3.75) |

3.2 Sample 2

The mechanical performance of these composite resins don't show obvious change compared with the PMA/St matrix materials when lanthanide complexes are added to the copolymer system(The concentration of the rare-earth complexes is 5.0×10^{-4} mol/L). The physical and mechanical performances of the composite resins containing lanthanide complex and PMA/St matrix are shown in Table 2. For the composite resins, the light transmittance is 80% ~ 89% and the refractive index is about 1.538 ~ 1.539.

The impact strength is about 4.78 ~ 4.82 ($\text{kgf} \cdot \text{cm}/\text{cm}^2$) and the density is 1.25 ~ 1.278 (g/cm^3). The surface hardness is HB. The composite resins possess the advantages of low density and good impact resistance, compared with the inorganic materials.

Trans. stands for the visible light transmittance at wavelength 550 nm. CTE shows the changing temperature that was measured by thermomechanical analysis. TGA shows the polymer decomposition temperature.

Table 2 The physical performances of optical resins containing rare earth complex

| Complexes | Trans (%) | Refractive index | Abbe number | Impact strength ($\text{kgf} \cdot \text{cm}/\text{cm}^2$) | UVs (nm) | Density (g/cm^3) | CTE ($^{\circ}\text{C}$) | TGA ($^{\circ}\text{C}$) | Surface hardness |
|--|-----------|------------------|-------------|--|----------|------------------------------------|----------------------------|----------------------------|------------------|
| No complex | 89 | 1.538 | 37.7 | 4.8 | 306 | 1.273 | 119.0 | 320.1 | HB |
| $\text{Tb}(\text{AA})_3$ phen | 77 | 1.539 | 34.5 | 4.8 | 350 | 1.289 | 119.0 | 320.1 | HB |
| $\text{Tb}(\text{phen})_2$ | 78 | 1.539 | 34.6 | 4.82 | 352 | 1.288 | 119.2 | 320.3 | HB |
| $\text{Eu}(\text{DBM})_3(\text{TPB})_2$ | 76 | 1.538 | 34.2 | 4.78 | 350 | 1.279 | 119.0 | 320.0 | HB |
| $\text{Eu}(\text{TTA})_3(\text{phen})_2$ | 75 | 1.538 | 34.3 | 4.79 | 351 | 1.278 | 119.1 | 320.1 | HB |
| $\text{Eu}(\text{phen})_2$ | 89 | 1.538 | 37.7 | 4.8 | 306 | 1.273 | 119.0 | 320.1 | HB |

Fig. 2 and Fig. 3 shows the excitation and emission spectra of the composite resin containing Tb(phen)₂(0.31%) and Eu(TTA)₃phen (0.31%), respectively. The fluorescence emission spectra of the composite resins are similar to that of corresponding lanthanide complexes (Eu³⁺ and Tb³⁺), and the full width at half maximum (FWHM) of the strongest bands are less than 10 nm. It is indicated that the composite optical resins exhibit high fluorescence intensity and color purity.

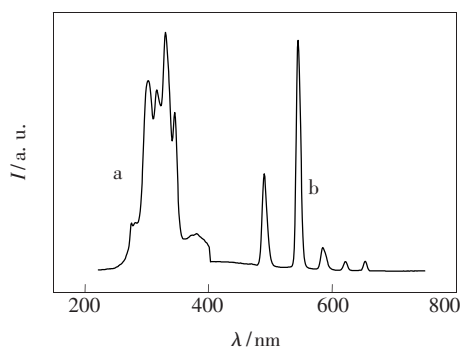


Fig. 2 Excitation and emission spectra of the optical resin doped with Tb(phen)₂, (a) Excitation ($\lambda_{em} = 544$ nm) (b) Emission ($\lambda_{ex} = 329$ nm).

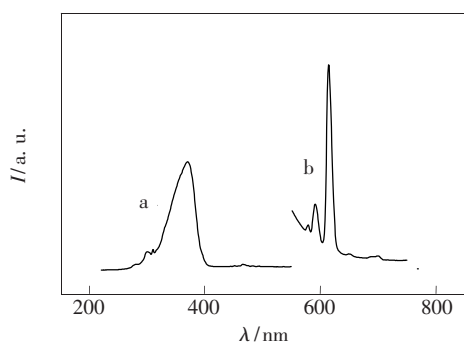


Fig. 3 Excitation and emission spectra of optical resin doped with Eu(TTA)₃(phen)₂, (a) Excitation ($\lambda_{em} = 613$ nm), (b) Emission ($\lambda_{ex} = 368$ nm).

It is also compared the luminous property of the lanthanide complexes in powder with composite resins (Table 3). There is no obvious shift of the emission peaks. Some transition variations in intensity show that the maximum excitation peak position depending on the coordinative environment (Table 2). The influences of the matrix resin on the coordinative environment of the lanthanide ions change the energy transfer probabilities of the electric dipole transitions corresponding to the increases in luminescent intensity of 614 nm and 544 nm peaks of Eu³⁺ and Tb³⁺ complexes, respectively. In MA/St polymer-based, α -methyl acrylic acid acts as both a solubilizer and a ligand coordinating with lanthanide ions. By a copolymerization process, stable lanthanide-polymer-organic ligand complexes were formed in the resin matrix. The lanthanide ions are surrounded with a cage-like polymer network, which decreases non-radiative transition and increases the emission of central lanthanide ion. This result explains why the composite resins containing lanthanide complexes possess higher luminescence efficiency and why the composite resins may act as a good composite matrix of these lanthanide complexes.

For the content of rare earth complexes in resin is 0.31%, the fluorescence lifetimes of lanthanide complexes in composite resins and in ethanol solution are listed in Table 4. It shows that the fluorescence lifetime of lanthanide complexes is longer in the composite resins than that in ethanol solution. It is well known that luminescence lifetime is related to the vibration of the nearby ligands. The vibration of the ligands, which decreased the lifetime of the

Table 3 The luminescences properties of the rare earth complex powder and in optical resin

| Rare earth complex | λ_{ex}/nm | | λ_{em}/nm | | Intensity/a. u. | |
|--|--------------------------|----------|--------------------------|----------|-----------------|----------|
| | Powder | In resin | Powder | In resin | Powder | In resin |
| Tb(Sal) ₃ | 331 | 309 | 543 | 544 | 33 | 815 |
| Tb(AA) ₃ Phen | 397 | 327 | 545 | 545 | 1 629 | 1 060 |
| Tb(phen) ₂ | 328 | 328 | 543 | 548 | 35 | 514 |
| TbCl ₃ | 370 | 357 | 541 | 541 | 115 | 50 |
| Eu(TTA) ₃ (phen) ₂ | 380 | 384 | 611 | 613 | 667 | 613 |
| Eu(DBM) ₃ (phen) ₂ | 397 | 394 | 610 | 614 | 178 | 171 |

lanthanide ions, can make nonradiation probability of the lanthanide ions increased.

The difference on the fluorescence lifetime of lanthanide complex in different matrixes can be interpreted as follows: In the absolute ethanol solution, the movement and the rotation of the complex molecules are free relatively. After lanthanide complexes being introduced into the matrix resins, the molecular motion is restricted. Therefore, the stretching and bond vibration are weakened, ascribed to the polymer matrix, both of which decreases the non-radiative transition. As a result, the lifetime of lanthanide complexes in the matrix resins is longer than that in ethanol solution. It is shown that the composite resins can provide a relatively stable environment for lanthanide complexes, and improve the luminous properties.

Table 4 The fluorescence lifetimes of rare earth complexes in luminescence optical resin and in ethanol solution

| Rare earth complexes | Fluorescence lifetime/ms | |
|------------------------------|--------------------------|------------------|
| | In ethanol solution | In optical resin |
| Eu(DBM) ₃ phen | 0.156 | 1.006 |
| Eu(TTA) ₃ phen | 0.655 | 0.832 |
| Eu(o-MOBA) ₃ phen | 0.458 | 1.167 |
| Eu(DBM) ₄ CPB | 0.150 | 0.532 |
| Tb(AA) ₃ phen | 0.596 | 1.158 |
| Tb(Sal) ₃ | 1.241 | 1.456 |

3.3 Sample 3

However, lanthanide complexes of organic ligands, especially complexes of Eu^{3+} or Tb^{3+} with excellent luminescence characteristics, are dissolved poorly in most solvents, which made it difficult to prepare a uniform thin film of high content lanthanide complexes or solid polymer material. Accordingly, the application of these complexes is restricted. In attempting to resolve the problem, we have prepared the transparent resins containing rare-earth complex by in situ composite method. The lanthanide complexes were synthesized in the polymerization process^[29].

The structure of the transparent resin containing RE complex is confirmed by FT-IR spectra (Fig. 4).

According to the data, it is demonstrated that the Tb^{3+} , MA and phen are combined by the coordinate link action in resins of Sample 2 and Sample 3.

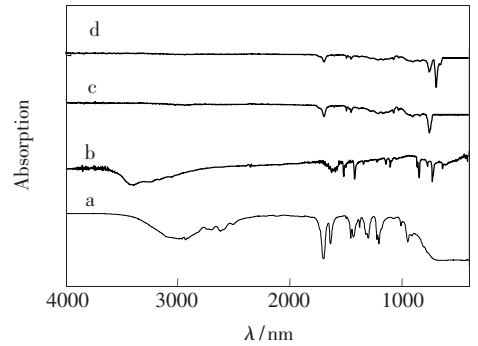


Fig. 4 FTIR spectra of the pre-polymerized liquid containing $\text{Tb}(\text{phen})_2\text{-MA/St}$ (a), $\text{Tb}(\text{phen})_2$ powder (b), the resin containing $\text{Tb}(\text{phen})_2$ (c), and the resin containing $\text{Tb}(\text{phen})_2\text{-MA/St}$ (d).

Fig. 5 shows the excitation and emission spectrum of the composite resin containing $\text{Tb}(\text{phen})_2\text{-MA/St}$ (0.31%). The emission spectrum of the composite resins are similar to that of corresponding lanthanide complexes (Tb^{3+}). FWHM of the strongest bands are less than 10 nm, which indicate that the optical composite resin exhibits high fluorescence intensity and color purity.

In order to observe the influence between the luminescent property and the different organic ligand in Eu^{3+} (Tb^{3+}) and MA/St copolymer system, the composite resin containing Eu^{3+} -single ligand, Eu^{3+} -double ligands, and the composite resin containing Tb^{3+} -single ligand, Tb^{3+} -double ligands were obtained. The luminescent data of these composite

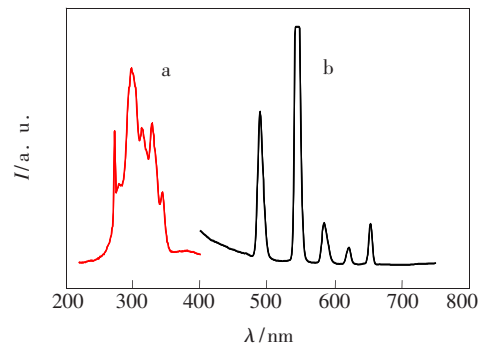


Fig. 5 Excitation and emission spectra of optical resin containing $\text{Tb}(\text{phen})_2$, (a) Excitation ($\lambda_{\text{em}} = 545 \text{ nm}$) and (b) Emission ($\lambda_{\text{ex}} = 297 \text{ nm}$).

resins are listed in Table 5. For the Eu^{3+} , the luminescent intensity of the composite resin containing $\text{Eu}^{3+}(\text{TTA})_3$ is the strongest in the composite resin containing Eu^{3+} -single ligand. The luminescent intensity of the composite resin containing $\text{Eu}^{3+}(\text{TTA})_3(\text{phen})_2$ and the composite resin containing $\text{Eu}^{3+}(\text{TTA})_3(\text{Bipy})_2$ are the strongest in the composite resins containing Eu^{3+} -double ligand. It is revealed that Eu^{3+} and organic ligand TTA, Bipy and phen may match well, leading to the composite resin emitting intense Eu^{3+} characteristic luminescence. For the Tb^{3+} , the luminescent intensity of the composite resins containing $\text{Tb}^{3+}(\text{Bipy})_3$ is the strongest in the composite resins containing Tb^{3+} -single ligand, and the luminescent intensity of the composite resin containing $\text{Tb}^{3+}(\text{Sal})_3(\text{Bipy})_2$ is the strongest in the composite resins containing Tb^{3+} -double ligand. It is suggested that Tb^{3+} and organic ligand Sal and Bipy may match well, resulting in the composite resin emitting intense Tb^{3+} characteristic luminescence.

Under the experimental conditions described above, for enhancing the luminescence intensities of these optical resins, the inert lanthanide ion such as yttrium(III) lanthanum(III) and gadolinium(III) are added into copolymer system. The molar ratio of Eu^{3+} (or Tb^{3+}) to inert lanthanide ion is 2:1, and the luminescent data of these optical resins are listed in Table 6. According to the data, it is easily observed that the luminescence intensities of these

optical resins containing Eu^{3+} (or Tb^{3+}) is decreased by adding inert lanthanide ion lanthanum(III) or gadolinium(III) into the copolymer system. On the contrary, the luminescent intensity of optical resins containing Tb^{3+} isn't decreased. It is also discovered that the luminescence intensity of the optical resin containing $\text{Tb}^{3+}(\text{Sal})_3(\text{Bipy})_2$ is the same as that of the resin without yttrium(III). For the optical resin containing $\text{Tb}^{3+}(\text{Bipy})_3$, the luminescence intensity of the resin is decreased from 1 015.658 to 760.383, owing to the concentration of center luminous Tb ion being decreased (it is only primary 2/3). As a result, the luminescent intensity of the optical resins containing Tb^{3+} isn't decreased. For those optical resins containing Eu^{3+} , the luminescent intensity of the resins is also decreased. The phenomenon could be interpreted as that the added inert ion Y^{3+} (La^{3+} or Gd^{3+}), with whole unoccupied or whole replete state atomic orbit, can form mono-core complex, so the excited state energy level of these complexes is higher than the triplet state energy level of ligand, the intramolecular energy transfer can't achieve. The inert lanthanide ion can form complexes easily, compared with luminous lanthanide ion, and they is surround by Eu^{3+} (Tb^{3+}) complex, making center luminous lanthanide ion reduced. If the triplet state energy level of inert lanthanide ion and that of center luminous lanthanide ion is suited, the intermolecular energy transfer will appear. As a result, the luminescent intensity will be enhanced,

Table 5 The luminescence properties of optical resin containing Eu^{3+} and Tb^{3+} complex by in situ composite method

| Ion [Re^{3+}] | Ligand 3 [Re^{3+}] | Second ligand 2 [Re^{3+}] | $\lambda_{\text{ex}}/\text{nm}$ | $\lambda_{\text{em}}/\text{nm}$ | I/a. u | Slit |
|--------------------------|----------------------------------|---|---------------------------------|---------------------------------|------------|---------|
| Eu^{3+} | TTA | 0 | 354 | 614 | 523.962 | 1.5,1.5 |
| Eu^{3+} | TTA | Phen | 366 | 613 | >1 015.658 | 1.5,1.5 |
| Eu^{3+} | TTA | Bipy | 356 | 613 | 865.815 | 1.5,1.5 |
| Eu^{3+} | TTA | Sal | 353 | 613 | 182.109 | 1.5,1.5 |
| Eu^{3+} | DBM | TTA | 390 | 614 | 86.901 | 1.5,1.5 |
| Tb^{3+} | TTA | 0 | 348 | 544 | 257.188 | 1.5,1.5 |
| Tb^{3+} | Bipy | 0 | 314 | 543 | >1 015.658 | 1.5,1.5 |
| Tb^{3+} | Sal | Bipy | 311 | 544 | >1 015.658 | 1.5,1.5 |
| Tb^{3+} | Bipy | Phen | 330 | 544 | 261.981 | 1.5,1.5 |
| Tb^{3+} | Phen | Bipy | 298 | 543 | 236.422 | 1.5,1.5 |

Table 6 The luminescence properties of optical resin containing rare earth complex Tb³⁺, Eu³⁺ and inert lanthanide ion such as yttrium(III) lanthanum(III) and gadolinium(III) by in situ composite method

| Ion[Re ³⁺] | Ligand 3[Re ³⁺] | Second ligand 2[Re ³⁺] | λ_{ex} (nm) | λ_{em} (nm) | I (a. u) | Slit |
|---|---------------------------------|--|---------------------|---------------------|-------------|------------|
| Tb ³⁺ (2/3) La ³⁺ (1/3) | Bipy | 0 | 314 | 542 | 10. 83 | 1. 5, 1. 5 |
| Tb ³⁺ (2/3) Gd ³⁺ (1/3) | Bipy | 0 | 313 | 543 | 10. 674 | 1. 5, 1. 5 |
| Tb ³⁺ (2/3) Y ³⁺ (1/3) | Bipy | 0 | 312 | 543 | 760. 383 | 1. 5, 1. 5 |
| Tb ³⁺ | Bipy | 0 | 314 | 543 | >1 015. 658 | 1. 5, 1. 5 |
| Tb ³⁺ (2/3) La ³⁺ (1/3) | Sal | Bipy | 314 | 544 | 16. 025 | 1. 5, 1. 5 |
| Tb ³⁺ (2/3) Gd ³⁺ (1/3) | Sal | Bipy | 312 | 542 | 9. 218 | 1. 5, 1. 5 |
| Tb ³⁺ (2/3) Y ³⁺ (1/3) | Sal | Bipy | 312 | 543 | >1 015. 658 | 1. 5, 1. 5 |
| Tb ³⁺ | Sal | Bipy | 311 | 544 | >1 015. 658 | 1. 5, 1. 5 |
| Eu ³⁺ (2/3) La ³⁺ (1/3) | TTA | Phen | 329 | 614 | 60. 703 | 3, 3 |
| Eu ³⁺ (2/3) Gd ³⁺ (1/3) | TTA | Phen | 329 | 614 | 60. 703 | 3, 3 |
| Eu ³⁺ (2/3) Y ³⁺ (1/3) | TTA | Phen | 329 | 616 | 60. 703 | 3, 3 |
| Eu ³⁺ | TTA | Phen | 366 | 613 | >1 015. 658 | 1. 5, 1. 5 |
| Eu ³⁺ (2/3) La ³⁺ (1/3) | TTA | 0 | 360 | 614 | 87. 440 | 3, 3 |
| Eu ³⁺ (2/3) Gd ³⁺ (1/3) | TTA | 0 | 367 | 616 | 56. 784 | 3, 3 |
| Eu ³⁺ (2/3) Y ³⁺ (1/3) | TTA | 0 | 367 | 616 | 511. 182 | 3, 3 |
| Eu ³⁺ | TTA | 0 | 354 | 614 | 523. 962 | 1. 5, 1. 5 |

or else the concentration of center luminous lanthanide ion is decreased (it is only primary 2/3). Consequently, energy transfer is also inexistent, leading to reduce the luminescent intensities of the optical resins.

4 Conclusion

In a word, the research on the transparent resin containing RE compounds is carried out. RE salt and complexes are introduced into copolymer system consisting of methyl acrylic acid and styrene to prepare a series of transparent optical resins by doping method. The composite resins containing lanthanide complexes are prepared through bulk free radical copolymerization of EuCl₃ (or TbCl₃), organic ligands, MA and St by in situ composite method. According

to the study, it was revealed that transparent resins containing rare earth complex by doping method possess intense and narrow band emission, highly visible transparency and good mechanics performances. Comparing with the composite resin by doping method, these composite resins possess better luminescent property at the same concentration. The content of the components in the co-polymer system affects the luminescent intensity of the composite resins containing lanthanide complex. The composite resins embody a class of new materials that present the characteristics of the complexes, making them applicable in a wide range of new technologies, such as flexible large area displays and light-emitting devices.

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含稀土化合物透明树脂的合成与光学性质

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摘要: 我们采用三种不同方法制备了含稀土化合物的光学树脂。第一种是含稀土甲基丙烯酸盐的透明树脂, 第二种是采用直接掺杂法制备的含稀土配合物透明树脂, 第三种是采用原位复合法制备的含稀土配合物透明树脂。通过对三种透明树脂的热稳定性、抗冲击性、紫外-可见吸收光谱、红外光谱、荧光光谱及核磁等方面的表征, 结果表明获得的第二、第三种透明树脂具有非常好的透明性、发光性和相关物理机械性能, 进一步比较三种透明树脂的发光性质发现第三种采用原位复合法制备的含稀土配合物透明树脂最好, 这说明原位复合法是一种简便快捷合成透明荧光高分子材料的好方法。

关键词: 透明树脂; 稀土; 发光性质; 复合材料

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