

Preparation and Properties of Rare Earth Polymer Complex Photoconversion Ecological Agricultural Film Materials

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Abstract

Rare earth polymer complexes not only have excellent luminescence properties of rare earth metals but also have excellent mechanical properties of polymers, which are widely used in photochemistry, electrochemistry, aerospace, material dyeing, agricultural planting, and other aspects. With the in-depth study of rare earth polymer complexes, people have tried a variety of synthetic processes with different advantages, such as the synthesis of single rare earth polymer, the synthesis of double rare earth polymer, and the synthesis of rare earth double ligand polymer. In this study, the polymeric intermediate PBS(HDI)-DAC was prepared by doping β -diketol hydroxyl molecules and butanediol succinic acid esters with extended chain synthesis, and then the rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC was synthesized by hydrothermal method with rare earth element ion Eu^{3+} . Finally, rare earth polymeric complex film Eu^{3+} -PBS(HDI)-DAC was prepared by the light transfer agent. The rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC was characterized by FTIR, UV absorption, and fluorescence emission. The film was prepared by volatilization of solution and its mechanical properties were tested. Rare earth polymer complexes have good mechanical properties and have certain shielding and conversion abilities to ultraviolet light.

Keywords

Rare earth organic complex, β -diketol, PBS, Fluorescence excitation and emission

Introduction

Rare earth light-transfer film, also known as rare earth luminescent material, is a light-emitting material using the principle of photoluminescence. It is widely used in the optical industry and can be used as the top wrapping material for various optical devices [1-3]. Rare earth luminescent materials have good photoluminescence properties and high luminous intensity and can emit specific wavelengths under the irradiation of UVA and some short-wavelength light [4-8]. The rare earth element europium (Eu) is a rare earth element with 6 electron components, which is located in the fifth place of rare earth elements, belonging to the light rare earth element, and is an important red-orange luminous material [9-11].

In this study, the polymeric intermediate PBS(HDI)-DAC was prepared by doping β -diketol hydroxyl molecules and butanediol succinic acid esters with extended chain synthesis, and then the rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC was synthesized by hydrothermal method with rare earth element ion Eu^{3+} . Finally, rare earth polymeric complex film Eu^{3+} -PBS(HDI)-DAC was prepared by the light transfer agent. The rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC was characterized by infrared spectroscopy, ultraviolet absorption, and fluorescence spectroscopy. The film was prepared by volatilization of solution and its mechanical properties were tested.

1. Experimental part

1.1 Reagents and drugs used

Butenediol (HAC, analytical pure, Sinopharm Group chemical reagent); Dibenzoylmethane (DBM, analytically pure, Sinopharm Group chemical reagent); Commercially available PBS (Analytical Pure, Sinopharm Group Chemical Reagents Co., LTD.); N, N-dimethylformamide (analytical pure, Taicang Hu Reagent Co., LTD.); Europium chloride (EuCl₃, Analytically pure, Sinopod Chemical Reagent Co., LTD.); Hexylene diisocyanate (HDI, Analytical pure, Sinopharm Group Chemical Reagent Co., LTD.); Triethylamine (TEA, Analytical Pure, Sinopharm Group Chemical Reagent Co., LTD.); ε-caprolactone (analytical pure, Sinopharm Group Chemical Reagent Co., LTD.); Stannous caprylate (analytical pure, Sinopsin Group chemical reagent); Dichloromethane (analytical pure, Taicang Hu Reagent Co., LTD.); Ferric chloride hexahydrate (analytical purity, Tianjin Damao Chemical Reagent Factory)

1.2 Experimental content

1.2.1 Synthesis of DAC

An appropriate amount of dibenzoylmethane (DBM) was dissolved in 60ml of dichloromethane, and then 0.135mol of butenediol (HAC) and 0.0216gFeCl₃·6H₂O were dissolved in 40ml of dichloromethane. When it reaches 60°C, the HAC is added to DBM at a constant rate, and the reaction is stirred for 7.5 hours. After the reaction is over, wash the reaction liquid with distilled water 1-2 times. Then, use anhydrous potassium sulfate and let it stand for 8 hours to dry the residual water. After drying, the product solution was spun dry by a gyroscope to obtain the product solution DAC.

1.2.2 Chain extension synthesis of PBS(HDI)

Take an appropriate amount of succinic acid and butaneol (molar ratio 1:1.3), heat to 80°C to melt the reactant, then heat up to 110°C, pass nitrogen three times, and then add 0.1mol tetrabutyl titanate to it, vacuum reaction for 2.5 hours. Temperature rises to 220°C, vacuum reaction for 2 hours, when there is no water in the reaction container, you can get PBS products. The PBS was dissolved in dichloromethane at a temperature of 110°C. After the PBS was dissolved, 0.012mol of hexylene diisocyanate was added to the PBS, nitrogen was fed three times, N₂ atmosphere was reacted for 2 hours, and then the solvent was extracted by vacuum pump to obtain PBS(HDI).

1.2.3 Synthesis of polymer intermediate PBS(HDI)-DAC

An appropriate amount of the expanded PBS(HDI) and DAC were dissolved in 50ml of dichloromethane (molar ratio of reactant 1:2), heated to 60°C for 2 hours, and the solvent dichloromethane was extracted by vacuum pump to obtain the brown gel product PBS(HDI)-DAC.

1.2.4 Synthesis of rare earth polymer complex films Eu³⁺-PBS(HDI)-DAC

EuCl₃·6H₂O was added into PBS(HDI)-DAC solution, stirred at 65°C for 24 hours, and β-dikeyl reacted with Eu³⁺ for 24 hours (note: nEu³⁺: Nβ-dikeyl = 1:3). After the reaction, the crude product was precipitated in 100ml methanol, the mixture was centrifuged, the supernatant was poured out, the remaining solid was washed with methanol, and the washed product was dried in a vacuum drying oven for more than 24 hours to obtain the Eu³⁺-PBS(HDI)-DAC powder solid. The solid powder was dissolved in an appropriate amount of methylene chloride, poured into the petri dish, stood in the volatile solvent, and then placed in a vacuum drying oven at 60°C for 24 hours to prepare the complex film Eu³⁺-PBS(HDI)-DAC.

1.2.5 Structural characterization

- (1) The sample PBS(HDI) and Eu³⁺-PBS(HDI)-DAC were characterized by the WQF-510 Fourier transform spectrometer of Thermo Field by potassium bromide salt compression method, with a scanning range of 4000 cm⁻¹-400 cm⁻¹.
- (2) The sample DAC and Eu³⁺-PBS(HDI)-DAC were characterized with N, N-dimethylformyl (DMF) amine as solvent using Agilent's ultraviolet spectrophotometer. The measurement range was 200nm-400nm.
- (3) The sample Eu³⁺-PBS(HDI)-DAC was measured with the fluorescence spectrophotometer of Agilent Company of Australia, N, n-dimethylformyl (DMF) amine as solvent, and the wavelength and intensity changes of excitation and emission were observed. The width of the excitation and emission slit was 5 and 10, and the scanning range was 200-800nm. The scanning speed keeps the signal strength in the ideal range for measurement.
- (4) Scanning electron microscopy (JSM-7610F, Japan Electronics) was used to characterize the morphology of Eu³⁺-H-DBC light-transfer films and observe their morphology. Since the tested sample is not conductive, the sample is plated with a conductive metal film, and then the Eu³⁺-PBS(HDI)-DAC film is tested and analyzed.
- (5) The mechanical elongation and break elongation of Eu³⁺-PBS(HDI)-DAC films were measured by tension meter.

2. Results and discussion

2.1 Infrared spectrum analysis

As shown in Figure 1, infrared spectral analysis of small molecule DAC and polymerization product Eu^{3+} -PBS(HDI)-DAC shows that both products have specific absorption peaks at wave number 4000-500 cm^{-1} .

According to the spectral analysis of the sample Eu^{3+} -PBS(HDI)-DAC, the stretching vibration of O-H in the hydroxyl group was shortened at 3500 cm^{-1} , and the specific stretching vibration of N-H in the amino group appeared at 3100 cm^{-1} . A strong absorption peak appeared at 1650 cm^{-1} . The stretching vibration of phenyl cyclomethylene at 2940 cm^{-1} and 2864 cm^{-1} was strengthened. The C=O stretching vibration peaks at 1671 cm^{-1} and 1694 cm^{-1} did not disappear, and the C=O stretching vibration intensity weakened, indicating that the diketo group participated in the coordination reaction. The appearance of the new peak of 560 cm^{-1} is due to the coordination bond generated by Eu^{3+} . The results indicate that Eu^{3+} -PBS(HDI)-DAC has been synthesized.

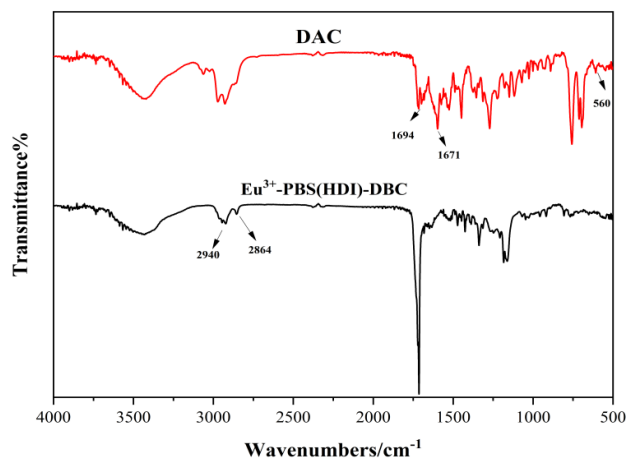


Figure 1. Infrared spectrum analysis of Eu^{3+} -PBS(HDI)-DAC.

2.2 Ultraviolet spectrum analysis

According to the absorption spectra of Eu^{3+} -PBS(HDI)-DAC, there are two strong absorption peaks at 274nm and 353nm, the former is the UV absorption of the diketone isomer of DBM, and the latter is the UV absorption of enol isomer, another isomer of DBM. At 300nm-350nm, the absorption phase is significantly shifted, and the absorption peak of Eu^{3+} -PBS(HDI)-DAC at 353nm is similar to that at 274nm. The introduction of rare earth metals will partially transform the diketone isomer into the enol isomer, while increasing the conjugation between ions, resulting in energy changes. The complex Eu^{3+} -PBS(HDI)-DAC has UV absorption in the UV region from 200nm to 380nm.

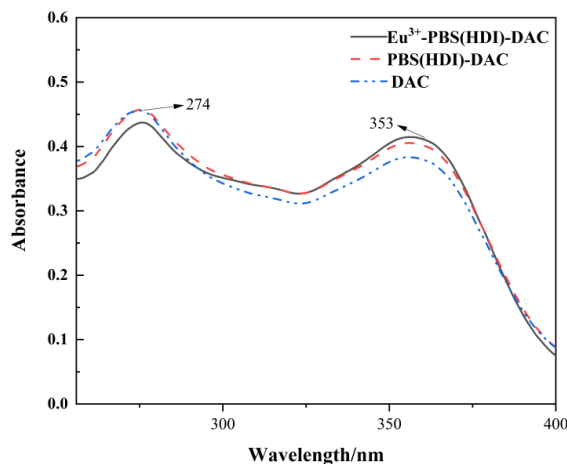


Figure 2. Ultraviolet absorption spectrum of rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC, solvent: DMF.

2.3 Fluorescence spectrum analysis

From the emission spectrum of rare earth complex Eu^{3+} -PBS(HDI)-DAC, it can be seen that the rare earth complex Eu^{3+} -PBS(HDI)-DAC is excited at the incident light wavelength of 350nm, 5D₀-7F₁ is located at 388nm, 5D₀-7F₂ is located at 600-650nm, and 5D₀-7F₃ is above 650nm. The main emission peak of the rare earth complex Eu^{3+} -PBS(HDI)-DAC is located in the orange light region between 600nm and 650nm, which indicates that the rare earth polymer complex can be excited by light in the ultraviolet region and emit orange light required by crops.

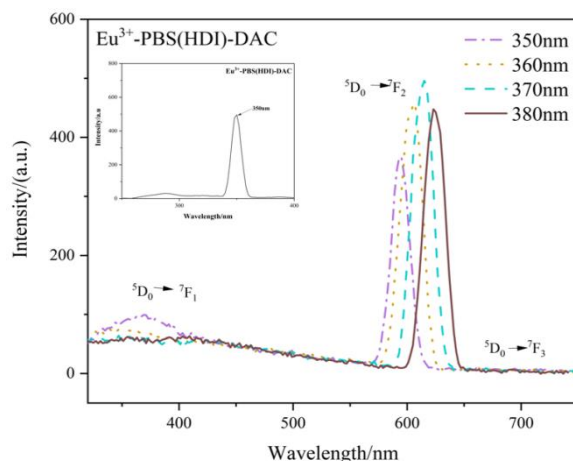


Figure 3. Fluorescence excitation and emission spectra of rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC, solvent: DMF.

2.4 Fluorescence stability experiment

As can be seen from Figure 4, the initial fluorescence intensity of the material was 515(a.u.), and the final fluorescence intensity was 515(a.u.), and the fluorescence intensity only changed by 1(a.u.) after 10 months of measurement. The above data show that the material has good fluorescence stability.

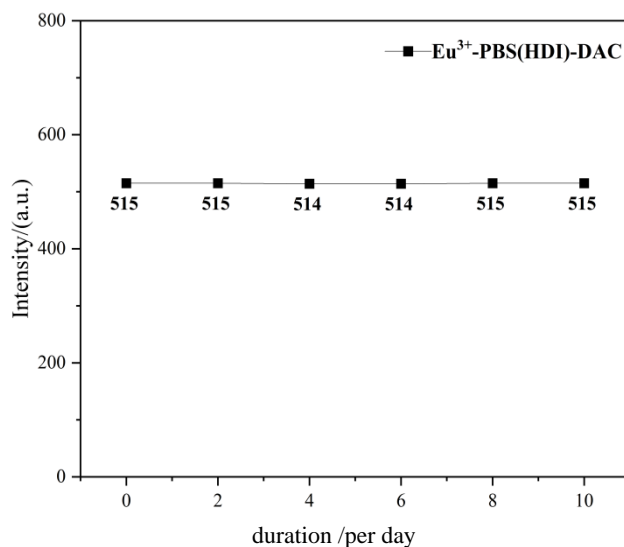


Figure 4. Fluorescence stability of Eu^{3+} -PBS(HDI)-DAC.

2.5 Elemental analysis

According to the EDS atlas, the material contains three elements, C, O, and Eu, and the unit content of Eu element is 3.21%, which further confirms that the polymer intermediate PBS(HDI)-DAC completes the coordination reaction with rare earth

element ion Eu^{3+} , and the coordination amount of rare earth metal is also very considerable.

2.6 Mechanical properties analysis

Figure 5 shows the tensile curve of the polymer film with the addition of an organic lightening agent, in which the tensile strength of PBS is $50.3 \pm 1.2 \text{ MPa}$ and the elongation at break is $564 \pm 25\%$. The tensile strength of Eu^{3+} -PBS(HDI)-DAC was $43.9 \pm 1.6 \text{ MPa}$ and the elongation at break was $483 \pm 18\%$ when the amount of organic light transfer agent was 3%. The rigidity of the substrate PBS increased significantly after the chain extension reaction of the chain extender diisocyanate, and the amount of light transfer agent was 3%, which did not affect the toughness of the material.

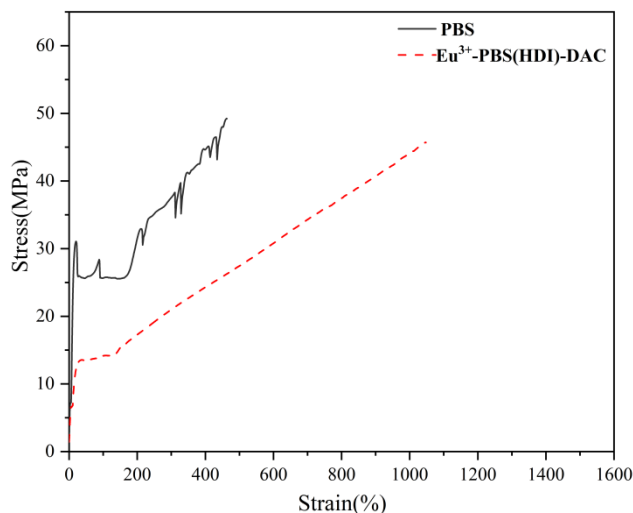


Figure 5. Determination of mechanical properties of Eu^{3+} -PBS(HDI)-DAC polymer films.

3. Conclusion

The method adopted in this study was to synthesize hydroxyl small molecule DAC by McKel-addition of enol (HAC) and dibenzoylmethane (DBM). The branched hydroxyl group of small molecule DAC was triggered by the reaction of the branched hydroxyl group of small molecule DAC with the expanded PBS cyanate group, and then the polymer PBS(HDI)-DAC was synthesized. The rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC was synthesized with the rare earth element ion Eu^{3+} . The fluorescence spectra of rare earth polymer complex Eu^{3+} -PBS(HDI)-DAC show that the ionic state of rare earth elements is an important condition for intramolecular energy conversion. After coordination reaction with organic ligand, rare earth elements can be excited by ultraviolet light to emit orange light, which proves that the material has good fluorescence properties and can maintain the original fluorescence intensity for more than 10 months. Therefore, the polymer complex Eu^{3+} -PBS(HDI)-DAC plays the role of light transfer agent, mechanical tensile proof that the content of organic light transfer agent should not exceed 3%. Therefore, rare earth polymer complexes containing β -diketol can be used as light conversion materials and can be used in agricultural production and life.

References

- [1] Cardoso M A, Correia S F H, Frias A R, et al. Solar spectral conversion based on plastic films of lanthanide-doped ionosilicas for photovoltaics: down-shifting layers and luminescent solar concentrators [J]. *Journal of Rare Earths*, 2020, 38(5): 531-538.
- [2] Liu H, Chu T, Rao Z, et al. The Tunable White - Light and Multicolor Emission in An Electrodeposited Thin Film of Mixed Lanthanide Coordination Polymers [J]. *Advanced Optical Materials*, 2015, 3(11): 1545-1550.
- [3] Tang H, Pu Z, Wei J, et al. Fluorescence-color-tunable and transparent polyarylene ether nitrile films with high thermal stability and mechanical strength based on polymeric rare-earth complexes for roll-up displays [J]. *Materials Letters*, 2013, 91: 235-238.
- [4] Krishna Rao K S V, Liu H G, Lee Y I. Fluorescence spectroscopy of polymer systems doped with rare-earth metal ions and their complexes [J]. *Applied Spectroscopy Reviews*, 2010, 45(6): 409-446.
- [5] Chen Z, Yin G. Suitability of a rare earth organic light conversion agent of Eu (III) complex to improve ultraviolet protection properties

- of cotton fabrics [J]. *Textile Research Journal*, 2010, 80(18): 1982-1989.
- [6] Garcia-Torres J, Bosch-Jimenez P, Torralba-Calleja E, et al. Highly efficient luminescent materials: influence of the matrix on the photophysical properties of Eu (III) complex/polymer hybrids [J]. *Journal of Photochemistry and Photobiology A: Chemistry*, 2014, 283: 8-16.
- [7] Liu D, Yu H, Wang Z, et al. Synthesis and fluorescence properties of novel 1, 10-phenanthroline-functionalized polyaryletherketone and its rare earth complexes [J]. *Polymer International*, 2010, 59(7): 937-944.
- [8] Assunção I P, Costa I F, Santos P R S, et al. Luminescent analysis of Eu³⁺ and Tb³⁺ flufenamate complexes doped in PMMA polymer: Unexpected terbium green emission under sunlight exposure [J]. *ACS Applied Optical Materials*, 2022, 1(1): 354-366.
- [9] Zou Q, Chen F, Peng G, et al. Luminescent properties of Eu (III) complexes with carboxylate ligands and their light conversion films [J]. *Journal of Luminescence*, 2023, 264: 120194.
- [10] Znajdek K, Szczecińska N, Sibiński M, et al. Luminescent layers based on rare earth elements for thin-film flexible solar cells applications [J]. *Optik*, 2018, 165: 200-209.
- [11] Zhang D, Gao B, Li Y. Synthesis and luminescence properties of polymer-rare earth complexes containing salicylaldehyde-type bidentate Schiff base ligand [J]. *Luminescence*, 2017, 32(5): 855-865.
- [12] Zhang A, Xu W, Chen R, et al. Program controlling the emission color of blend polymer phosphors containing Eu (III), Tb (III), Be (II) ions for WLEDs [J]. *Optical Materials*, 2019, 89: 250-260.
- [13] Ding G, Tang F, Ding Z, et al. Synthesis and luminescent properties of Eu³⁺ organic complex PVA encapsulation film [J]. *Functional Materials Letters*, 2022, 15(02): 2251015.
- [14] Knyazev A A, Krupin A S, Galyametdinov Y G. Luminescence behavior of PMMA films doped with Tb (III) and Eu (III) complexes [J]. *Journal of Luminescence*, 2022, 242: 118609.
- [15] Shahi P K, Singh A K, Rai S B, et al. Lanthanide complexes for temperature sensing, UV light detection, and laser applications [J]. *Sensors and Actuators A: Physical*, 2015, 222: 255-261.
- [16] Li S, Zhou L, Zhang H. Investigation progresses of rare earth complexes as emitters or sensitizers in organic light-emitting diodes [J]. *Light: Science & Applications*, 2022, 11(1): 177.
- [17] He J, He Y, Zhuang J, et al. Luminescence properties of Eu³⁺/CDs/PVA composite applied in light conversion film [J]. *Optical Materials*, 2016, 62: 458-464.
- [18] Forster P, Lugao A, Brito H, et al. Calorimetric investigations of luminescent films polycarbonate (PC) doped with europium complex [Eu (TTA) 3 (H₂O) 2] [J]. *Journal of Thermal Analysis and Calorimetry*, 2009, 97(2): 497-502.