



EVA film doped with β -diketones macromolecular lanthanide complexes: Preparation, characterization and application



Penghui Chen^a, Jingsong Shi^a, Yalan Zhang^b, Kemin Wang^{a,*}, Jun Nie^{c,*}

^a School of Materials Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, PR China

^b School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu 213164, PR China

^c School of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

In this study, the β -diketones groups functionalized polymer D-HEA-C was first synthesized by chemically attaching D-HEA to the side chains of polycaprolactone and then coordinated with Eu(III) to form β -diketones macromolecular complexes. ¹H NMR, FT-IR, GPC, ICP-AES, ultraviolet absorption and fluorescence emission were used to characterize the polymeric rare earth complex materials composed of D-HEA-C and Eu³⁺ ion. The synthesized β -diketones macromolecular complexes were doped into EVA film to test the energy conversion efficiency. TGA, Transmittance, UV absorption spectra, fluorescence emission and SEM were used to study the properties of the doped EVA film. The macromolecular complexes could not only limit the coordination of small molecules to effectively avoid the fluorescence quenching, but also enhance the fluorescence intensity of the complex. Moreover, the β -diketones macromolecular complexes have good compatibility with the EVA matrix, and could increase the photovoltaic conversion efficiency and service life of EVA film. Therefore, the β -diketones macromolecular complexes could act as efficient light conversion molecular devices, and have a broad prospect in the solar packaging film.

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1. Introduction

Luminescent rare earth complexes have attracted considerable attentions in display devices, fluorescent probes, biological labels, polyvinyl chloride polymer (PVC) heat stabilizers and agricultural film light conversion fields due to their outstanding luminescent characteristics, such as high luminous intensity, long luminous lifetime and extremely sharp emission band during electronic transitions to 4f energy levels [1–7]. Europium itself has a very low molar absorptivity; however, it has been shown that certain ligand can absorb ultraviolet radiation and transfer this energy to bound lanthanide ion, from which available light is emitted [8,9]. Usually, organic small-molecule rare earth complexes

are used to dope into matrixes, while there are some limitations in practical applications, such as poor mechanical property, poor physicochemical stability and harsh processability as well as the incompatibility with the matrixes. Besides, organic small-molecule rare earth complexes contain inner-coordinated water molecules, resulting in low emission quantum efficiency due to the non-radiative dissipation of energy which is caused by the high energy vibration of –OH group [4,10]. In contrast, polymeric rare earth complex materials, in which lanthanide ions are directly linked to polymers via coordinating bond between the functional pendant groups of polymers and lanthanide ions, not only possess unique fluorescence properties of the rare earth ions and good mechanical toughness, chemical stability. Polymers can also shield the metal centers from water and solvent molecules and lend excellent processability to the luminescent materials [11,12]

* Corresponding authors.

E-mail addresses: wangkm61@gmail.com (K. Wang), niejun@mail.buct.edu.cn (J. Nie).

Recently, polymeric rare earth complexes have drawn many attentions for their potential applications. At present, there are two main methods to prepare polymer–rare earth complexes: (1) Small-molecule rare earth complexes containing polymerizable double bond as monomer are polymerized or copolymerized with other monomers resulting in polymeric rare earth complex materials; (2) Rare earth ions coordinate with the side groups of polymer chains to form polymeric rare earth complex materials [11,13]. In general, the latter method is more feasible because the small-molecule rare earth complexes containing polymerizable double bond are difficult to obtain. In this paper we used the latter method.

At present, most literatures have focused on the carboxylic acids based macromolecular lanthanide complexes, only a few reports studied on β -diketones macromolecular lanthanide complexes [2,10,11,13]. Due to the high UV absorption coefficient and well complex ability of dibenzoylmethane (DBM) and its derivatives, it could be used as lanthanide organic complexes. The plastic or film under illustrated, as we all know, is easy to be aged; however, it will be stable rather than exhausted if doped with the ultraviolet absorbing agent of dibenzoylmethane (DBM) or its derivatives. Therefore, the β -diketones macromolecular lanthanide complexes doped plastic or film has broad prospects.

Ethylene vinyl acetate (EVA) plays an important role in photovoltaic module manufacturing. It is used to encapsulate solar cells in a lamination process. Solar cell modules utilize EVA as a sealant due to its excellent light transmission ability, moisture resistance, and good adhesion to glass. The deterioration of EVA during its service life is impacted by heat, moisture absorption, and oxygen, especially ultraviolet radiation from sunlight [14–16]. Hence, β -diketones macromolecular lanthanide complexes were doped into EVA film in our research which could not only limit the coordination of small molecules to effectively avoid the fluorescence quenching [17–19], but also enhance the fluorescence intensity of the complex to a certain extent. Moreover, the β -diketones macromolecular complexes have good compatibility with the EVA matrix, and could increase the photovoltaic conversion efficiency and service life of EVA film.

In this study, the β -diketones group functionalized polymer D-HEA-C was first synthesized by chemically attaching D-HEA to the side chains of polycaprolactone and then coordinated with Eu(III) to form β -diketones macromolecular complexes. FT-IR, ^1H NMR, GPC, ICP-AES, ultraviolet absorption and fluorescence emission were used to characterize the polymeric rare earth complex materials composed of D-HEA-C and Eu^{3+} ion. Then the β -diketones macromolecular complexes were doped into EVA film. TGA, Transmittance, UV absorption spectra, fluorescence emission and SEM were used to study the properties of the doped EVA film.

2. Materials and methods

2.1. Materials

ϵ -Caprolactone (aladin, dried over CaH_2 and distilled prior to use), dibenzoylmethane (purified by recrystallization

from ethanol), 2-hydroxyethyl acrylate (aladin HPLC grade), Eu_2O_3 (Europium content 99.9%), (R)-(–)-1, 1-Binaphthyl-2, 2-diyl-Hydrogen Phosphate (R-BNPH). Eu (DBM-d)₃(D-HEA and the reaction of acryloyl chloride, then made with rare earth europium), PAA–Eu (acrylic acid homopolymer formed macromolecules and then with the rare earth europium) and other reagents were used as received without further purification.

2.2. Preparation and characterization of D-HEA

DBM (14.2 g, 0.063 mol) was added into a three-necked flask which equipped with a magnetic stirrer, dissolving 80 ml of CH_2Cl_2 . HEA (14.3 g, 0.123 mol) and the catalyst $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.6 g) were dissolved in 100 ml of CH_2Cl_2 , then dripped them into the DMB solution gradually. After reaction at 60 °C for 8 h, washed the mixture by distilled water for four times first, and then washed by ethanol. Subsequently, dried the mixture over anhydrous sodium sulfate and kept it overnight. After that, the CH_2Cl_2 solvent was made to product of D-HEA by Rotary evaporation. The FT-IR spectra were carried out with Nicolet 5700 Fourier transform infrared spectrometer. ^1H NMR spectra were recorded on an AVANCE III instrument Bruker company in CDCl_3 . All signals of the various protons were observed.

2.3. Preparation and characterization of polymer D-HEA-C

A representative procedure was proposed. Added D-HEA (10.06 g) and caprolactone (16.9 g) to a dried flask (it needs to be pointed out that the molar ratio of D-HEA to caprolactone was 1:10). Filled nitrogen into the flask and added 25 ml solution of BNPH into it. Mixing all of them to be reactive under 80 °C for 24 h. Cooled down the reaction mixture, precipitated it with 300 ml cold MeOH as precipitators. The product was collected on a fine frit, and dissolved in 80 ml of CH_2Cl_2 . Washed the mixture with additional cold distilled ion, got the product of D-HEA-C as a red-brown viscous liquid by rotary evaporation.

2.4. Preparation and characterization of polymeric rare earth complexes D-HEA-C–Eu(III)

Eu_2O_3 (0.352 g) was dissolved in 100 ml of 20% HCl solution, and heated until transparent. Then, the solution was cooled down, and 25 ml of distilled water was added. After completely dissolving, the content was heated and concentrated until crystalline grains were produced and a lot of crystals were separated out. Then placed the crystals in a vacuum oven at 25 °C, obtained the crystals of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The modified D-HEA-C was dissolved in 80 ml of N, N-dimethyl formamide (DMF), and the pH value was adjusted to 6–7 by triethylamine. Subsequently, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was added, and the coordination reaction between β -diketones of D-HEA-C and the ligand Eu^{3+} ion was conducted for 24 h at 60 °C with stirring (it is to be noted here, the molar ratio of the β -diketone ligand D-HEA-C to Eu^{3+} ion was 3:1 in the above coordination system, so the coordination reaction could be carried out smoothly). After finishing the coordination reaction

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