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Synthesis and Luminescence Properties of Novel Europium and Terbium Complexes with Triblock Copolymer Ligand

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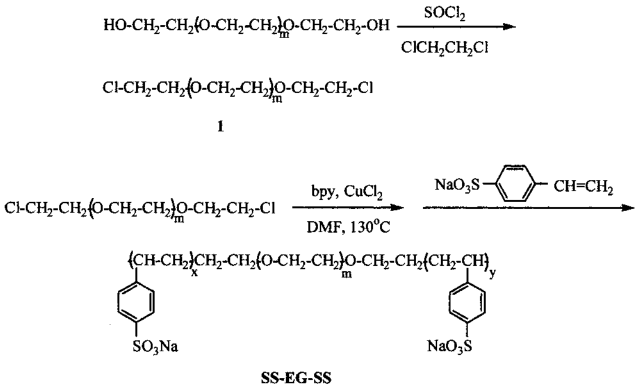
Rare earth complexes as fluorescent dyes have attracted attention not only from academic interest but also for their potential application, such as electroluminescence devices,[1,2] photoluminescence devices,[3,4] and laser systems.[5,6] The rare earth complexes based on organic low molecular weight ligands (organic low molecular weight rare earth complexes) have been investigated extensively. Since polymer is easy of processing, many reports focus on luminescence materials, which were prepared in recent years by blending organic low molecular weight rare earth complexes with a polymer matrix.[7−10] However, it is difficult to disperse the organic low molecular weight rare earth complexes in a polymer matrix. In addition, the effect of polymer matrix on the properties of organic low molecular weight rare earth complexes is still unclear now. Recently, although the study of luminescence materials prepared by direct binding rare earth ion to functional side chains of polymer has been receiving growing attention,[11] the comprehensive understanding is rather poor. In this paper, we address the aim of developing new luminescence materials based on rare earth (europium and terbium) complexes. We herein report the synthesis of a macromolecular ligand, sodium styrenesulfonate−ethylene glycol−sodium styrenesulfonate triblock copolymer (SS-EG-SS), and luminescence properties of trivalent ions Eu(III) and Tb(III) complexes based on the macromolecular ligand SS-EG-SS.

The macromolecular ligand SS-EG-SS was synthesized by atom transfer radical polymerization (ATRP). Our ATRP reaction was based on that described by Matyjaszewski's group.[12−14] The transition-metal catalyst was CuCl, and the ligand was 2,2′-bipyridine (bpy). The ATRP block copolymer preparation is described below (Scheme 1).

The macroinitiator **1** was prepared by the reaction of PEG2000 (20.0 g, 10.0 mmol) with thionyl chloride ($SOCl_2$) (5.0 g, 42.0 mmol) in 1,2-dichloroethane at refluxing temperature for 17 h under a nitrogen atmosphere. **1** was purified by precipitation from hexane to give a white wax solid (yield 43%). ^{1}H NMR spectroscopy and infrared (IR) absorption spectroscopy identified the formation of the expected macroinitiator **1**. The number-averaged molecular weight (M_n) of macroinitiator **1** was 2100 as determined by GPC using PEG standards.

Block polymerization was carried out in a baked three-necked round-bottomed flask equipped with a magnetic stirring bar. The flask was charged with dimethylformamide (DMF, refluxed and distilled), macroinitiator **1** (2.0 g, 1.0 mmol), CuCl (0.2 g, 2.0 mmol), and bpy ligand (0.47 g, 3.0 mmol). A degassed solution of the sodium styrenesulfonate monomer (7.0 g, 33.9 mmol) in DMF was added, and the reaction solution was degassed three times and then heated at 130 °C under nitrogen. The solution became dark brown, indicating the onset of polymerization. After 8 h, the solution was cooled by ice, and a white precipitate was observed. Exposure of the reaction solution to air caused the solution to turn from dark brown to blue, indicating termination of the reaction. The reaction solution was then filtered. To remove the copper catalyst, the resulting white crude product was dipped in DMF overnight and then filtered again. The white polymer was vacuum-dried at room temperature.

Scheme 1



The structure of the obtained triblock copolymer, SS-EG-SS, was then analyzed with ^{1}H NMR spectroscopy (Bruker DPX400, solvent: D_2O). ^{1}H NMR spectra showed that the polymer contained both ethylene glycol units and sodium styrenesulfonate units.

The SS-EG-SS was characterized by gel permeation chromatography (GPC, Waters 2410) at 25 °C with a RI detector using aqueous solution of 0.1 M Na_2SO_4 as the eluent. GPC analysis showed that the number-average molecular weight (M_n) was 8800, and the molecular weight distribution index (M_w/M_n) was 2.1.

The starting materials for preparation of the trivalent ions Eu(III) and Tb(III) complexes are the macromolecule ligand SS-EG-SS and $EuCl_3$ (or $TbCl_3$). In a typical run, SS-EG-SS and $EuCl_3$ (or $TbCl_3$) (1:3 in molar ratio) were dissolved in degassed water. The reaction solution was stirred at room temperature for several hours and evaporated under vacuum overnight to obtained solid complexes. The complexes were usually characterized by infrared (IR) spectra.[15,16] Comparison of IR spectra of the macromolecule ligand SS-EG-SS with Eu(III) and Tb(III) complexes showed that the strong stretching vibration of S−O in SS-EG-SS originally at 1129 cm^{-1} and the deforming vibration at 677 and 581 cm^{-1} shifted to 1121, 674, and 578 cm^{-1} for the Eu(III) complex and to 1120, 674, and 578 cm^{-1} for the Tb(III) complex. These shift changes indicate that the SS-EG-SS can be used as a macromolecular ligand because the oxygen atom of the sulfonic group can coordinate with Eu(III) and Tb(III) to form complexes.

The complex film was prepared by drop casting on a glass substrate. Figure 2 shows the emission spectra of Eu(III) complex film excited at 394 nm. The assignments of emission bands for the Eu(III) complex and

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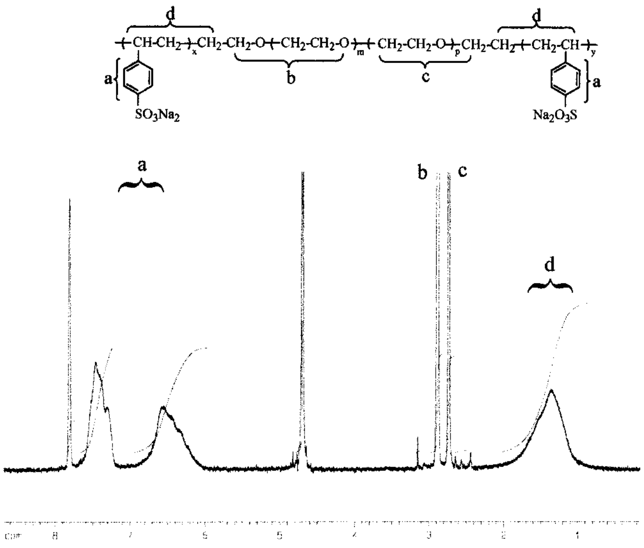

Figure 1. ^{1}H NMR spectrum of SS-EG-SS.

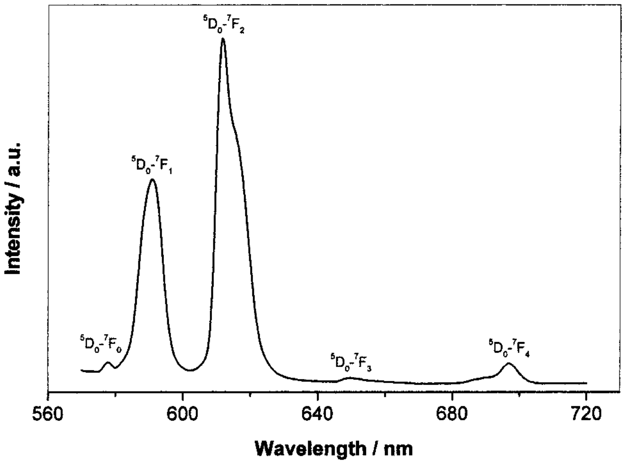

Figure 2. Emission spectra of Eu(III) complex film.

the Tb(III) complex are carried out according to the results in the literature.[17,18] The emission spectra region displayed overlaps with the Eu(III) transition from the $^5D_0$ state to $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ terms in the ground-state manifold. The five peaks were observed at 578 nm ($^5D_0$−$^7F_0$), 591 nm ($^5D_0$−$^7F_1$), 612 nm ($^5D_0$−$^7F_2$), 649 nm ($^5D_0$−$^7F_3$), and 697 nm ($^5D_0$−$^7F_4$). Figure 3 depicts the emission spectra of Tb(III) complex film excited at 230 nm. The emission spectra exhibit typical ligand-sensitized emission of the Tb(III) ion. Four luminescence bands centered at 489, 543, 584, and 619 nm are attributed to the $^5D_4$−$^7F_6$, $^5D_4$−$^7F_5$, $^5D_4$−$^7F_4$, and $^5D_4$−$^7F_3$ transitions, respectively.

The excitation spectra of the SS-EG-SS coordinated Eu(III) and Tb(III) complexes show the similar bands to the macromolecular ligand SS-EG-SS. Therefore, the excitation energy is absorbed by the macromolecular ligand SS-EG-SS, resulting the energy transfer from its excited single state to its triplet state. This energy, in turn, transfers from the macromolecular ligand SS-EG-SS to Eu(III) and Tb(III) ions without radiation. The luminescence of Eu(III) and Tb(III) ions in the SS-EG-SS coordinated complex films indicates that the rare earth ions are efficiently excited by this absorbed energy from excitation of the macromolecular ligand. In other words, the energy-transfer chain is successfully completed from excitation of the macromolecular ligand to emission of the coordinated Eu(III) and Tb(III) ions.

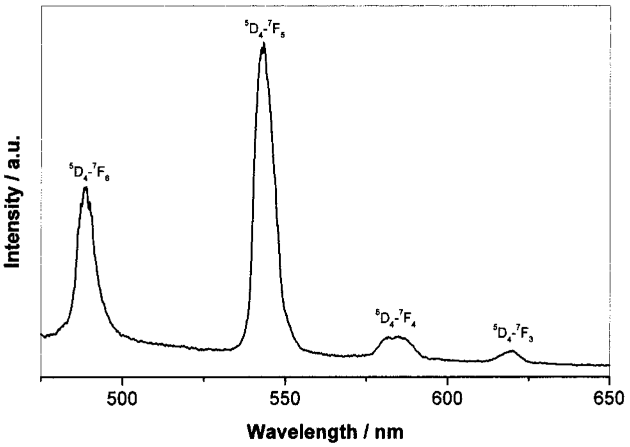

Figure 3. Emission spectra of Tb(III) complex film.

In summary, a macromolecular ligand, sodium styrenesulfonate−ethylene glycol−sodium styrenesulfonate triblock copolymer (SS-EG-SS), was synthesized with ATRP. Eu(III) and Tb(III) complexes film based on this macromolecule ligand SS-EG-SS exhibit ligand-sensitized emission typical of Eu(III) and Tb(III) ions.

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