Polym. Bull. (2009) 62:337–344
DOI 10.1007/s00289-008-0017-8

ORIGINAL PAPER

Study on interaction between Eu(III) and thermosensitive microsphere

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Received: 27 May 2008 / Revised: 15 October 2008 / Accepted: 2 November 2008 /

Abstract Based on the synthesis of poly(*N*-isopropylacrylamide)-grafted poly(*N*-isopropylacrylamide-co-styrene) (PNNS) microsphere, Eu(III) was chosen to coordinate with PNNS. The interaction between Eu(III) and PNNS was characterized by using X-ray photoelectron spectroscopy, Fourier transform infrared, ultraviolet–visual and fluorescence spectroscopy. The results from experiments indicated that the Eu(III) is mainly bonded to O of the carbonyl groups of PNNS and formed the complex of PNNS–Eu(III). After forming the PNNS–Eu(III) complex, the emission fluorescence intensity of Eu(III) in the complex is significantly enhanced because the effective intramolecular energy-transfer from PNNS to Eu(III). Especially, the maximum emission intensity of the PNNS–Eu(III) complex at 614 nm is enhanced about 33 times comparing to that of the pure Eu(III). The intramolecular energy-transfer efficiency from PNNS to Eu(III) reaches 55%.

Keywords *N*-Isopropylacrylamide · Thermosensitive · Spectroscopy · Fluorescence · Energy transfer

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Introduction

Much attention has been directed in recent years at environmentally responsive hydrogels due to their potential applications in numerous field, including drug delivery, bioseparation, chemical transducer, enzyme and cell immobilization [1–4]. Poly(*N*-isopropylacylamide) (PNIPAM) has been extensively studied because its lower critical solution temperature (LCST, ~32 °C) [5] is very close to room temperature and its related gels can undergo a volume change as large as 100 times upon an infinitesimal environmental change. Until now, many studies were focused on the temperature-induced transition [6, 7]. Only few reports were related to the optical property of PNIPAM. In order to extend the application of PNIPAM, further functionalization of these thermosensitive materials is needed.

In this article, on the basis of our previous work [8], to further endow microspheres with useful properties, we present the preparation of multistimuli-responsive microspheres that possesses important temperature-responsive and fluorescence properties. A complex of PNNS and Eu(III) [PNNS–Eu(III)] has been synthesized and characterized with different techniques. The complexes have important temperature-responsive and fluorescence properties, in which the properties have been used for developing new applications in fluorescence and biomedical field.

Experimental sections

N-Isopropylacrylamide (NIPAM)(Aldrich Chemical Co., Inc. 99%) was used without further purification. Potassium peroxydisulfate was recrystallized twice from water. Styrene (St) was distilled under the reduced pressure and then stored in the refrigerator before use. $EuCl_3$ was prepared according to the method described in the literature [9]. Other reagents were of analytical grade and purchased from Shanghai Chemical Co. All the solutions were prepared with the deionized water purified with the Milli-Q SP/UF system (Millipore).

The P(NIPAM-co-St) core was synthesized using a surfactant-free emulsion polymerization, based on NIPAM as a monomer, and St as a comonomer. Nine grams of St and 1 g of NIPAM were dissolved in 175 mL deionized water. Nitrogen was bubbled into the mixture solution with stirring for 30 min to remove oxygen dissolved in the mixture solution. The polymerization was initiated by adding 10 mL of the aqueous solution with 0.3 g of potassium peroxydisulfate at 70 °C. After the reaction was allowed to proceed for 6 h at 70 °C under stirring, the P(NIPAM-co-St) suspension was obtained. Then, the PNIPAM shell layers were prepared using the above-prepared P(NIPAM-co-St) core as the seeds by a seed polymerization method. 1 g of NIPAM, 0.02 g of *N*,*N*′-Methylenebisa-crylamide and 0.01 g of potassium peroxydisulfate was dissolved in 15 mL mixture solution of organic solvent and deionized water and then added into the above-prepared P(NIPAM-co-St) suspension. After 2 h under intermittent microwave irradiation, the product was obtained. After the product was dialyzed and purified by repetitive centrifugation, decantation, and redispersion, it was freeze–dried. The PNIPAM would be grafted on the surface of P(NIPAM-co-St) core, forming the shell layers. Thus, the product possesses the core-shell structure and is denoted as PNNS.

The preparation procedure of the PNNS–Eu(III) complex is as follows. The certain amount of PNNS was mixed with the ethanol solution of $EuCl_3$. The mixture was stirred for 24 h at 25 °C. After the purification as mentioned above, the PNNS–Eu(III) complex was obtained.

The XPS spectra were recorded with a VG Scientific ESCALAB spectrometer with an MgK radiator. A German Nicolet FT-IR Nexus-670 spectrophotometer was used to measure the FT-IR spectra in the range of 400–4,000 cm^{-1} with the KBr flake. The UV-Vis absorption spectra were recorded on a Perkin-Elmer lambda 17 UV-Vis absorption spectrophotometer. A German Perkin-Elmer model Ls50B fluorescence spectrophotometer was used to measure the fluorescence spectra of PNNS and the PNNS–Eu(III) complexes. Both the widths of the excitation and emission slits were 5 nm with a scanning speed of 600 nm/min.

Results and discussion

XPS measurement

The XPS measurement has become a powerful tool for providing the precise information concerning the core-level binding energies and the valence electronic structure of macromolecules [10]. The XPS spectra of $Eu_{4d5/2}$ (A), O_{1s} (B) and N_{1s} (C) are shown in Fig. 1. It was reported that the binding energy of N_{1s} for the C–N bonds is at about 400 eV and the binding energy of O_{1s} for the C–O bonds is at about 531 eV [11]. It was clearly observed from Fig. 1 that the average binding energies of N_{1s} and O_{1s} of the PNNS–Eu(III) complex were increased about 0.28 and 1.12 eV, respectively, comparing with that of PNNS, thus indicating a decrease in the electron density of N_{1s} and O_{1s} atoms in the PNNS–Eu(III) complex. Meanwhile, the average binding energy of Eu($4d_{5/2}$) was decreased about 4.82 eV, thus indicating an increase in the electron density of Eu(III) in the PNNS–Eu(III) complex. Therefore, the results from the experiment mentioned above further demonstrated that the PNNS–Eu(III) complexes may be formed with the coordination between Eu(III) and O of the carbonyl group [12]. After the electron density of O is decreased due to the coordination with Eu(III), the electron cloud of N would be shifted to O due to the inducement effects, leading the decrease in the electron density of N and increase in the average binding energy of N [13].

FT-IR measurement

The FT-IR spectra of PNNS and the PNNS–Eu(III) complex are shown in Fig. 2. It can be observed from Fig. 2 (curve a) that the main absorption bands are located at 3,061, 3,026, 2,972, 2,930, 2,875, 1,652 and 1,544 cm^{-1}. The bands at 3,061 and 3,026 cm^{-1} are assigned to the stretching vibration ($\nu_{C\text{–}H}$) of phenyl groups, respectively. The bands at 2,972 and 2,875 cm^{-1} are ascribed to the asymmetric and symmetric ($\nu_{C\text{–}H}$) of the methyl groups of *N*-isopropyl groups. The band at

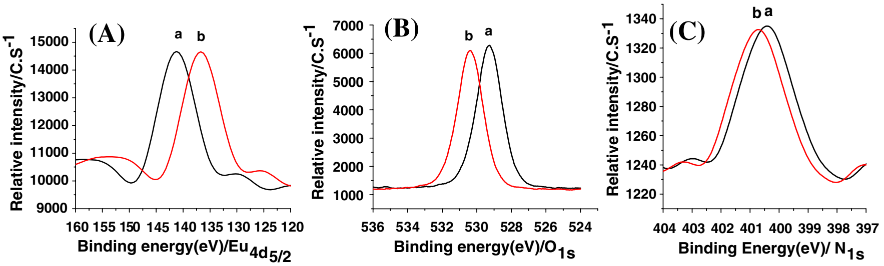
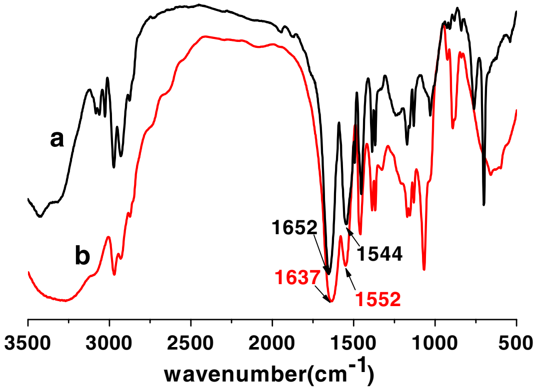


Fig. 1 **a** The Eu$_{4d5/2}$ XPS spectra of EuCl3 in the absence (*a*) and in the presence of PNNS (*b*). O1$_s$ (**b**) and N$_{1s}$ (**c**) of the PNNS (*a*) and the PNNS–Eu(III) complex with the weight ratio of 0.08:1 (*b*)

Fig. 2 The FT-IR spectra of PNNS (*a*) and the PNNS–Eu(III) complex with the weight ratio of 0.08:1 (*b*) in the range of 500–3,500 cm^{-1}



2,930 cm^{-1} is assigned to the asymmetric ($\nu_{C\text{–}H}$) of the methylene groups of the polymer backbone. Since the amide chains are included in the PNNS structure, the band at 1,652 cm^{-1} is ascribed to amide I [mainly the carbonyl stretching vibration ($\nu_{C=O}$)] and the band at 1,544 cm^{-1} is ascribed to amide II (mainly the N–H bending vibration ($\delta_{N\text{–}H}$) (Fig. 2, curve a) [14]. It was observed from the FT-IR spectrum of PNNS–Eu(III) complex (Fig. 2, curve b) that the band of amide I and amide II was shifted to 1,637 and 1,552 cm^{-1}, respectively. Thus, it can be deduced that when Eu(III) was bonded to O of the carbonyl group in PNNS, the part of the lone electron pair of O transfers to the empty orbit in the outer layer of Eu(III). The decrease in the electron density weakens the σ covalent bond and double bond of C=O, leading the characteristic band of amide I shifts to the low frequency. In addition, the inducement effect leads to that the electron in N is shifted to O and thus the characteristic band of amide II also shifts to the high frequency [12].

UV–visual measurement

Figure 3 shows the UV–Vis absorption spectra of PNNS and the PNNS–Eu(III) (8 wt%) complex. It was found from Fig. 3, curve a that the maximum absorption band of PNNS is located at 202 and 250 nm corresponding to the π–π* transition of the C=O double bond and the phenyl group, respectively [15]. The absorption peak

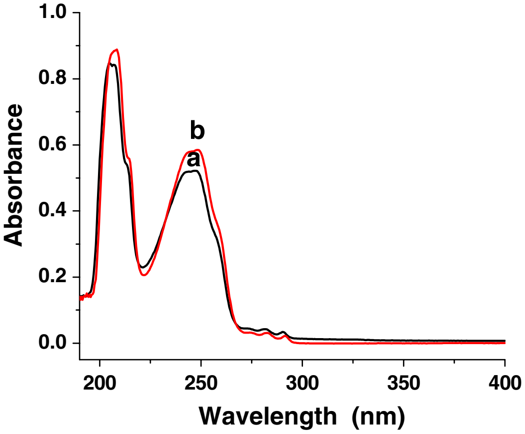


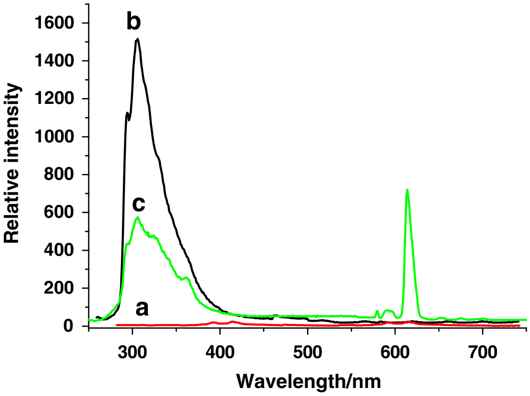
Fig. 3 UV–Visual absorption spectra of PNNS (*a*) and the PNNS–Eu(III) complex with the weight ratio of 0.08:1 (*b*)

of the carbonyl group shifts to 207 nm in the UV–Vis absorption spectrum of the PNNS–Eu(III) complex (Fig. 3, curve b). The absorbance of two peaks in the UV–Vis absorption spectrum of the PNNS–Eu(III) complex is increased. It illustrated that Eu(III) would coordinate with O atom of the carbonyl group, leading to the decrease in the electron density of the C=O bond and then the redshift of the absorption peak of the C=O bond.

Fluorescence measurement

The emission spectra of $EuCl_3$ (a), PNNS (b) and PNNS–Eu(III) (c) are shown in Fig. 4. The emission spectra were obtained under excitation at 270 nm, which was selected from the excitation spectrum of the PNNS–Eu(III). As shown in Fig. 4, curve a exhibits very weak characteristic emission peaks of Eu(III); curve b displays a broad band around 320 nm, which is assigned to polymer emission and curve c presents three narrow and strong characteristic emission peaks at 580, 592 and 614 nm, corresponding to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ electronic transition which occur from the excited state D to the multiplet F, and the most pronounced peak is situated at 614 nm ($^5D_0 \rightarrow {}^7F_2$). Owing to the shielding of 4f orbital from the environment by an outer shell of 5s and 5p orbital, the f–f absorption bands are very narrow [16]. This transition is responsible for the red color emitted by the complex. The maximum emission intensity of PNNS–Eu(III) at 614 nm is enhanced about 33 times compared with that of the corresponding Eu(III). The intramolecular energy-transfer efficiency for fluorescence peak at 614 nm can reach as high as 55%. According to the energy-transferring mechanism of the complexes [17], an organic ligand is necessary to improve the quantum yield of luminescent emission for the lanthanide ions since the absorption coefficients of the ligand are many orders of magnitude larger than the intrinsically low molar absorption coefficients of the trivalent Eu(III). In addition, the direct coordination of an organic ligand to a Eu(III) can further improve the energy-transfer rates by reducing the distance between the ligand and the Eu(III). The sensitization pathway in luminescent lanthanide complexes generally consists of an initial strong absorption of ultraviolet

Fig. 4 The emission fluorescence spectra of $EuCl_3$ (*a*), PNNS (*b*) and the PNNS–Eu(III) complex with the weight ratio of 0.08:1 (*c*). Excitation wavelength: 270 nm



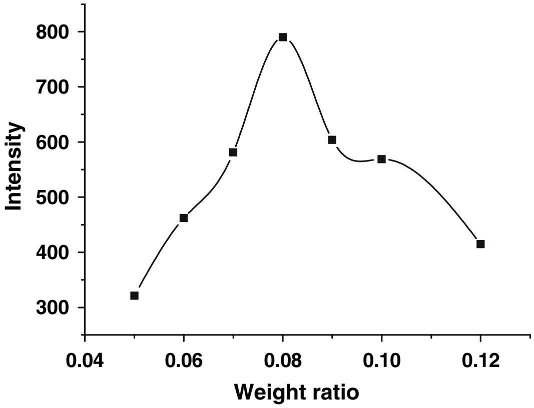
energy that excites the ligand to the excited singlet (S_1) state, followed by an energy migration via intersystem crossing from the S_1 state to a ligand triplet (T) state. The energy is then nonradiatively transferred from the lowest triplet state of the ligand to a resonance state of a coordinated Eu(III), which in turn undergoes a multiphoton relaxation and subsequent emission in the visible region. The intramolecular energy migration efficiency from organic ligands to the central Eu(III) is the most important factor influencing the luminescent properties of the Eu(III) complexes. If the triplet energy is low, back-transfer from the Eu(III) to the ligand occurs. The absorption coefficient of Eu(III) is small at the ultraviolet region, while PNNS has a strong absorption in the range of ultraviolet and it emits a strong red luminescence, suggesting that PNNS transfers its energy to Eu(III) after absorbing energy of photon, then the excited Eu(III) generates enhanced fluorescence [18].

The relationship between the $^5D_0 \rightarrow {}^7F_2$ fluorescence emission intensity of Eu(III) at 614 nm and the weight ratio of Eu(III) in PNNS–Eu(III) complex was also investigated in Fig. 5. In the PNNS–Eu(III) complexes, the characteristic emission intensities show a linear increase with increasing content of Eu(III) ion until the weight ratio of Eu(III) to PNNS–Eu(III) is 8wt%, and decreased with the further increase in the content of Eu(III). The decrease in the fluorescence intensity of the PNNS–Eu(III) complex when the amount of Eu(III) increases can be explained by the fact that the formation of ion aggregates in which rare earth (RE) ions lie in close proximity to one another causes the nonradiative energy transfer from the triplet state to the single ground state, and the exchange mechanism is predominately responsible for the emission quenching under this condition [19].

Conclusions

From the above experimental results, it can be concluded that when Eu(III) interacts with PNNS, Eu(III) mainly bonds to O of the carbonyl group of PNNS forming the PNNS–Eu(III) complex. After forming the PNNS–Eu(III) complex, the emission fluorescence intensity of Eu(III) in the PNNS–Eu(III) complex is significantly enhanced. Especially, the emission intensity of the fluorescence peak at 614 nm can

Fig. 5 Relationship between the fluorescence emission of Eu(III) and the weight ratio of Eu(III) ion in PNNS–Eu(III)



be increased as high as 33 times comparing with that of the pure Eu(III) because of the effective intramolecular energy transfer from PNNS to Eu(III). The intramolecular energy transfer efficiency for fluorescence peak at 614 nm can reach as high as 55%. The fluorescence intensity is related to the weight ratio of Eu(III) and PNNS in the PNNS–Eu(III) complex. When the weight ratio is 8 wt%, the maximum fluorescence enhancement can be obtained.

Acknowledgments The authors are grateful for the financial support of the National Natural Science Foundation of China (No. 20471030), the project of high and technology from Jiangsu province (BG2005040).

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