

# Luminescent Behavior of two Novel Thermo-Sensitive Poly(N-isopropylacrylamide) Hydrogels Incorporated with Rare Earth Complexes

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**Abstract** Two novel luminescent temperature-sensitive poly(N-isopropylacrylamide) hydrogels fabricated with rare earth (Eu, Tb) picolinic acid complexes were in-situ synthesized within the interpenetration networks. Fluorescence spectra indicate the two functional gels exhibit red for  $\text{Eu}^{3+}$  species and green emissions for  $\text{Tb}^{3+}$  ones, respectively, whose luminescence intensities are changed due to temperature increasing from 5 to 30°C until totally quenched at lower critical solution temperature (33°C). In addition, the decreasing luminescence behavior obeys the simple linear equations. The releasing experiment substantiates that there may be complexation between  $\text{O}=\text{C}-\text{NH}-$  moieties of P-NIPAA and  $\text{Eu}^{3+}$  ions for the prolonged released time.

**Keywords** Rare earth · Luminescence · Hybrid materials · Temperature-sensitive · Poly(N-isopropylacrylamide)

## Introduction

Temperature-sensitive hydrogels have been extensively studied and developed in the past decades [1, 2]. In particular, a typical thermal-sensitive polymer named as poly(N-isopropylacrylamide) (denoted as P-NIPAA) causes much

interest and it has a lower critical solution temperature (LCST) at around 33°C in an aqueous solution, indicating that P-NIPAA dissolves and gets swollen within water below LCST and can not dissolve, and becomes aggregated above LCST. As a result, this special phase transition property triggers lots of researches concerns designing drug delivery systems recently [2, 3]. In the meantime, lanthanide ( $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ ) containing materials especially rare earth complexes have been focused on their potential uses in photoluminescence or electroluminescence applications [4]. Since these polymers capabilities of showing high luminescent intensity are quite limited, it will be necessary to introduce fluorescent components into hydrogels so as to clarify the luminescence dependence on changing temperature [5]. On the grounds of our previous work [6, 7], carbonyl groups in the amide moieties can coordinate to rare earth ions and strong characteristic narrow emissions will be achieved due to the occurrence of efficient energy transfer from  $\text{O}=\text{C}-\text{NH}-$  part to rare earth ions. In this report, two binary Eu(Tb) –picolinic acid complexes were prepared and brought into the interpenetration network of P-NIPAA and non-temperature-sensitive poly(acrylamide) hydrogels (predicted graph was shown in Fig. 1). Their emissions properties and rare earth complexes release were discussed in detail.

## Experimental

### Starting materials

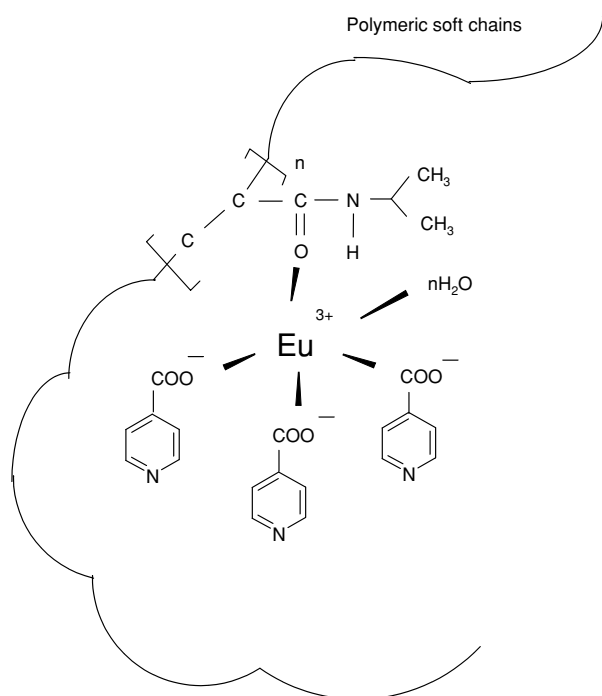
N-isopropylacrylamide (99% purity, Acros Co., Belgium), acrylamide, potassium persulfate (KPS), N, N, N', N' – tetramethyldiamine (TEMED) and picolinic acid were provided by (Shanghai chemical reagent, Analytically pure).  $\text{Tb}_4\text{O}_7$  and  $\text{Eu}_2\text{O}_3$  (99.9% purity) were purchased from

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**Fig. 1** Predicted picture of poly(N-isopropylacrylamide) hydrogels and Eu-picolinic acid complex

Shanghai Yuelong company. All the received reagents were used without further purification. All solutions applied in this experiment were deionized water.

#### Synthesis of the hydrogels

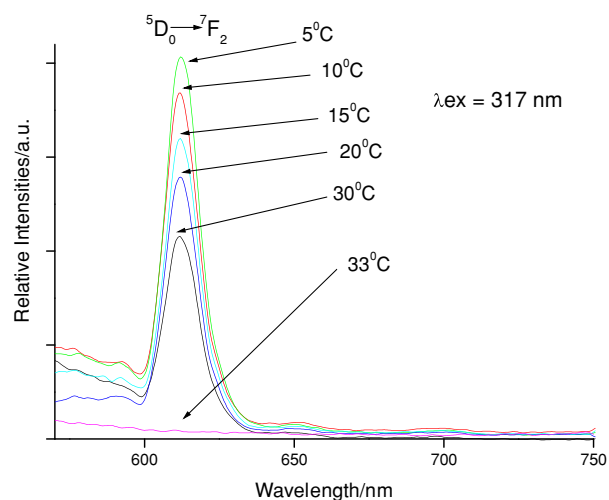
Rare earth nitrate were obtained by dissolving  $Tb_4O_7$  and  $Eu_2O_3$  in concentrated nitric acid. The preparation of P-NIPAA and poly(acrylamide) hydrogels were according to reference [8]. After vacuum drying process, P-NIPAA gels were incubated in water and picolinic acid was dissolved in water and a stoichiometric amount of NaOH solution was added to adjust pH to around 6–7. Then  $Eu(NO_3)_3 \cdot 6H_2O$  (or  $Tb(NO_3)_3 \cdot 6H_2O$ ) was added in this solution with stirring for 2 h. For fluorescence measurements, the water temperature range was recorded at 5°C, 10°C, 15°C, 20°C, 30°C and 33°C, respectively. Molar ratios of P-NIPAA/ $Eu(NO_3)_3 \cdot 6H_2O$ /picolinic acid were 10: 1: 3. The starting hydrogels in released experiment was furnished as follows: firstly, luminescent P-NIPAA gels containing Eu binary complex were in-situation synthesized the same as the above procedure and the gels were allowed to swell to equilibrium in deionized water at 20°C at least 72 h. Secondly, the obtained hydrogels were used for releasing measurement after vacuum drying treatment. The absorbance changes of released complex were recorded under the same conditions at regular time intervals using Agilent 8453 ultra-violet spectrophotometer.

#### Physical measurements

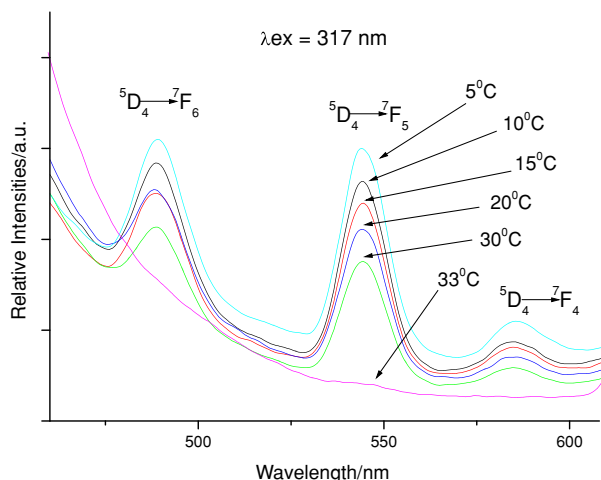
Ultraviolet absorption spectra were recorded with an Agilent 8453 spectrophotometer. Fluorescence excitation and emission spectrums were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation.

#### Results and discussion

In Fig. 2, it is noteworthy that characteristic emission of  $Eu^{3+}$  was located at around 612 nm under the excitation wavelength at 317 nm. This specific red narrow peak was ascribed to  ${}^5D_0 \rightarrow {}^7F_2$  transition jumping from excited state level to ground state of  $Eu^{3+}$  ions. Much weak magnetic dipole transition  ${}^5D_0 \rightarrow {}^7F_1$  at 590 nm was found, indicating coordination chemical environment around Eu(III) ions is in low symmetry due to the influence of soft coil like P-NIPAA networks. According to the temperature change from 5 to 33°C, it was observed emission had been reduced along with the increase of temperature, until 33°C, the luminescence was sharply quenched. Two possible reasons may account for such phenomenon, firstly is high temperature would make relaxed excited state return to the ground state in a nonradiative manner (thermal quenching of luminescence); secondly, when phase separation takes place (reaching LCST), the delicate hydrophilic/hydrophobic balance within P-NIPAA backbones is affected and dehydration in the P-NIPAA net appears, that may accelerate the aggregation of P-NIPAA chains and large volume shrinkage. Consequently, the drastic difference concerns coordination chemical environment broke the unstable complex formation between  $O=C-NH-$  groups of P-NIPAA and  $Eu^{3+}$  ions and a large amount of released water molecules act as efficient



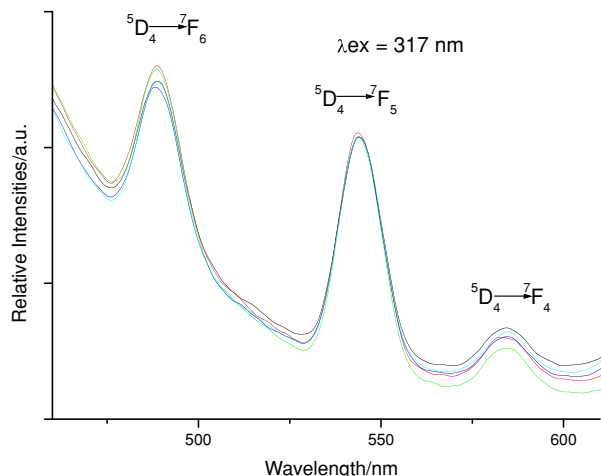
**Fig. 2** Emission spectra of Eu containing P-NIPAA hydrogels under different temperature



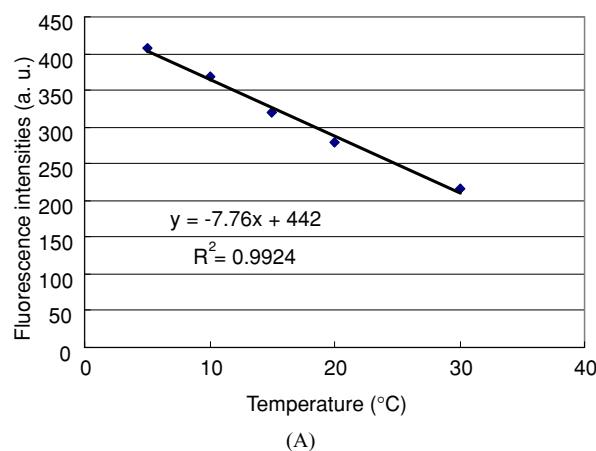
**Fig. 3** Emission spectra of Tb containing P-NIPAA hydrogels under different temperature

quenchers of emissions. From Fig. 3, likewise, under the excitation wavelength at 317 nm, three characteristic emission bands of Tb<sup>3+</sup> ions were observed and they were assigned to the transitions from the <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> (J = 6, 5, 4) transitions at 490, 544, 587 nm respectively. Among the above peaks, <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition was quite strong and located at green region. With the increasing temperature, the fluorescence relative intensities exhibit similar results as Eu containing hydrogels and also disappeared exactly at LCST which may substantiate the predicted explanations. In Fig. 4, no corresponding intensity differences were observed in the non thermo-sensitive poly(acrylamide) hydrogels that also bear amide groups, pointing out that conformational change of P-NIPAA chains is considered to be a prevalent factor determining fluorescence quenching.

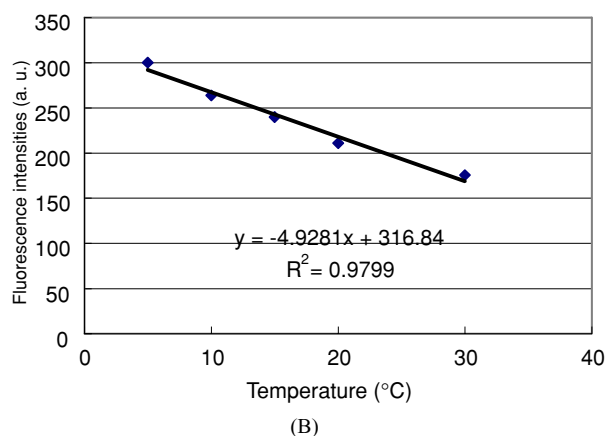
To investigate effects of changing temperature on fluorescence intensities quantitatively, it was found that this de-



**Fig. 4** Emission spectra of Dy containing P-NIPAA hydrogels under different temperature



(A)

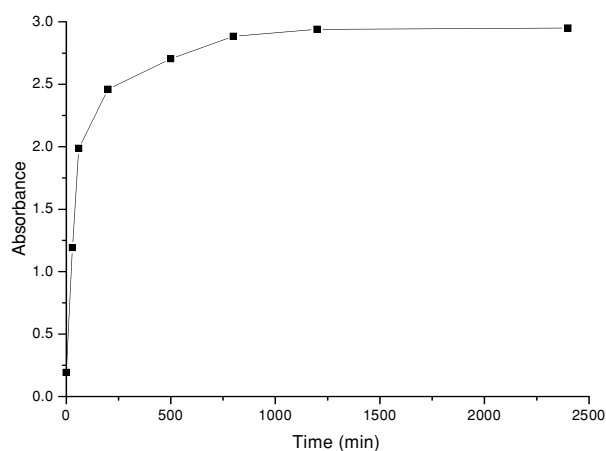


(B)

**Fig. 5** Effects of changing temperature on fluorescence intensities in Eu containing P-NIPAA hydrogel (A) and Tb containing P-NIPAA hydrogel (B)

creasing luminescence behavior follows the simple equation  $y = -7.76x + 442$  by linear least square fitting method and the correlation coefficient  $R^2 = 0.9924$  showing that the two variable are best fit with linear correlation (Fig. 5(A)). The mathematical expression of Tb containing hydrogels (Fig. 5(B)) is  $y = -4.9281x + 316.84$  with  $R^2 = 0.9799$ , representing a similar result of Eu. P-NIPAA segment presents solubility and thermo-sensitivity in water treated under low temperature, whereas aqueous solution of such polymer realizes a coil to globule transition at LCST. In regard to the temperature increasing, soft and extended coil chains transform into contracted cages step by step. Since rare earth line emissions are heavily depended on outside temperature for the temperature affects the surrounding environment of Ln<sup>3+</sup> in hydrogels, it seems that Eu<sup>3+</sup> ions probably coordinate to both picolinic acid and amide components simultaneously and the resulting rare earth complexes may be incorporated into the interface of hydrophobic polymer matrices but not exposed to surrounding water phase lonely.

In order to further study the usefulness of P-NIPAA in the rare earth complexes delivery and stabilization properties, Fig. 6 illustrates release rate (described as absorbance of Eu-



**Fig. 6** Release rate (expressed as absorbance of Eu-picolinic acid complexes) from the P-NIPAA hydrogels as a function of time

picolinic acid complexes) from the P-NIPAA hydrogels as a function of time (time intervals as 0.5, 30, 60, 200, 500, 800, 1200 and 2400 min) at 20°C. As exhibited in Fig. 6, a burst release of binary complex from gels in the first period and the maximum amount of the complex loading in the gels can be released out within 500 min. It is estimated that the rare earth complex molecules that are not introduced into polymeric networks just attached to the surface during the drying process, consequently, there is an extraordinary release when the dried complex loaded gels were immersed in solution. Furthermore, in terms of the inclusion complexation between O=C–NH– moieties of P-NIPAA and Eu<sup>3+</sup> ions, the exchange possibility among complex and water molecules decreased accordingly and lead to gradual release rate until the final balance on both sides.

## Conclusions

Two kinds of luminescent hydrogels composed of thermo-sensitive poly(N-isopropylacrylamide) and Eu(Tb)-picolinic

acid complexes were synthesized and their characteristic red or green narrow peaks were obtained. Along with the increasing temperature, the emission intensities reduced accordingly and conform to linear functions as  $y = kx + b$ . Furthermore, the slow release of rare earth complexes from hydrogels proves that complex formation and host-guest interactions may exist between polymeric backbones and phosphors.

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