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Synthesis and property study on Eu(III) complexes of modified poly(*N*-isopropylacrylamide)

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Abstract Poly(*N*-isopropylacrylamide) with aromatic end groups (Ar-PNIPAM) were synthesized by atom transfer radical polymerization of *N*-isopropylacrylamide in isopropanol using phenyl 2-chloropropionate, (4′-phenyl)phenyl 2-chloropropionate, and (2′,6′-diphenyl)phenyl 2-chloropropionate as initiators and CuCl/tris(2-dimethylaminoethyl)amine (Me_6TREN) as a catalytic system. The resulting polymers had narrow polydispersity index of 1.10–1.14 and molecular weights of 3700–4600 g mol^{-1}. Then, novel functional complexes of Ar-PNIPAM, Europium(III) (Eu(III)), and α-Thenoyltrifluoroacetone (TTA) (Ar-PNIPAM/Eu(III)/TTA) with thermosensitive and fluorescent properties were synthesized and characterized by Fourier transform infrared spectra and fluorescence spectroscopy. Metal Eu(III) was not only bonded to oxygen and nitrogen atoms of polymer chain in PNIPAM, but also bonded to TTA. The maximum emission intensity of the complexes at 613 nm was enhanced about 22, 27, 33 times compared with that of the corresponding Eu(III). The lower critical solution temperatures (LCSTs) of Ar-PNIPAM/Eu(III)/TTA were slightly greater compared with that of PNIPAM. Eu(III) complexes had excellent fluorescence performance, the fluorescence spectrum presented characteristic emission of Eu(III) at 613 nm.

Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known thermoresponsive polymer that changes its appearance in water from a clear solution to a turbid suspension at a relatively lower critical solution temperature (LCST) of ca. 32 °C [1]. This useful property can be exploited in many new applications, such as adsorption/desorption sheets for cell cultures [2, 3], drug delivery [4], tunable optical devices [5], and chromatographic separation [6]. The preparation of linear narrow-dispersed PNIPAM by reversible addition-fragmentation transfer (RAFT) polymerization has been reported [7–10]. Atom transfer radical polymerization (ATRP) [11, 12] has emerged as one of the most widely controlled/“living” free radical polymerization methods due to the facile experimental setup, the use of readily accessible and inexpensive initiators and catalysts. In addition, ATRP is especially attractive as it can provide good control over both polymer molecular weight and end groups [13], and the reaction is tolerant to water, which occurs in a conventional temperature range from the room temperature to 130 °C [14]. Our group recently studied end-functionalization of PNIPAM via ATRP [15, 16], and the thermoresponsive properties were also discussed.

Until now, many studies were focused on the temperature-induced transition of PNIPAM [17, 18]. However, there is little study about PNIPAM as a ligand [19, 20]. In order to extend the application of PNIPAM, further functionalization of these thermosensitive materials is needed. Eu^{3+} posses good luminescence characteristics based on the 4*f* electronic transitions, a variety of rare earth

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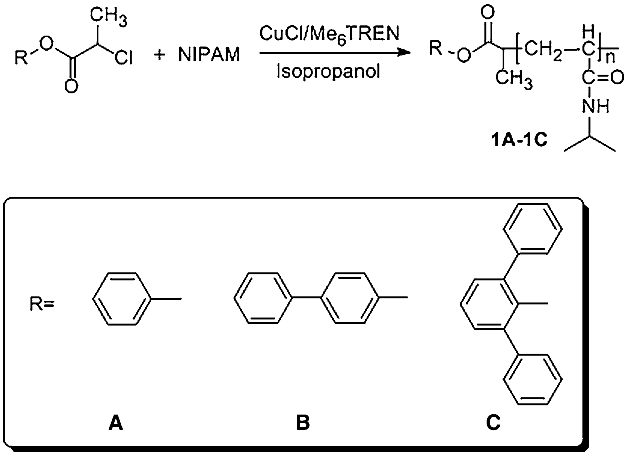
compounds activated by Eu^{3+} have been studied for practical applications [21]. Photoactive lanthanide organic coordination compounds usually exhibit extensive luminescence, owing to the strong absorption of the ligands in the ultraviolet region and efficient energy transfer from the ligands to the central rare earth ions.

In this article, luminescent europium PNIPAM complexes, Poly(*N*-isopropylacrylamide) with aromatic end groups/Europium/Thenoyltrifluoroacetone (Ar-PNIPAM/Eu(III)/TTA), were synthesized and characterized by FT-IR spectra and fluorescence spectroscopy. The PNIPAM had narrow polydispersity index (1.10–1.14). The results from experiments showed that the metal Eu(III) was not only bonded to oxygen and nitrogen atoms of polymer chain in PNIPAM, but also bonded to TTA. Different end groups of PNIPAM could affect the performance of complexes. The complexes had important temperature-responsive and fluorescence properties, which could be used for developing new applications in fluorescence and biomedical field.

Materials and instrument

N-isopropylacrylamide (Aldrich, 98%) was recrystallized twice from a hexane/benzene mixture (3/2, v/v). Eu_2O_3 (99%) was obtained from Changchun institute of applied chemistry. $EuCl_3$ was prepared according to the method described in the literature [22]. CuCl (Aldrich, 99%) was washed successively with acetic acid and ether, dried, and then stored under nitrogen. All of other chemicals were obtained commercially and were used as received unless otherwise stated.



Scheme 1 Synthesis of PNIPAM(1A–C)

Molecular weights (M_n) and polydispersity (M_w/M_n) were measured on a gel permeation chromatography (GPC) utilizing Waters 510 pump and Model 410 differential refractometer at 25 °C. Tetrahydrofuran (THF) was used as a mobile phase at a flow rate of 1.0 mL min^{-1}. Shimadzu RF-5301PC fluorescence spectrophotometer was used to measure fluorescence spectra. Infrared spectra were measured using a Shimadzu IR-8400S spectrometer by incorporating samples in KBr disks. The LCSTs of the polymer solutions were determined by turbidimetry, using Shimadzu-1240 UV–Vis spectrophotometer, the heating rate was 1 °C/5 min.

General procedure for ATRP of PNIPAM (1A–C)

Typically, a mixture of CuCl (17.5 mg, 0.176 mmol) and Me_6TREN (47.8 μL, 0.176 mmol) in isopropanol (1.0 mL) was placed on one side of an H-shaped glass ampoule and stirred at room temperature. NIPAM (1.0 g, 8.8 mmol), phenyl 2-chloropropionate (25.7 μL, 0.176 mmol), and isopropanol (2 mL) were added to the other side of the ampoule. Nitrogen was bubbled through both mixtures for 5 min to remove any oxygen, and then three freeze–pump–thaw cycles were performed to degas the solution. Both mixtures were mixed, and kept at 25 °C for 3 h. The polymerization was stopped by exposure to air. The reaction mixture was diluted with THF and passed through a neutral Al_2O_3 column, using THF as eluent, to remove the copper complex. After precipitation by adding the polymer solution of THF into hexane for three times, the white polymer 1A was collected by filtration, and then dried under vacuum overnight (325 mg, conv., 32.5%). $M_n = 3700$ g mol^{-1}, $M_w/M_n = 1.14$.

Table 1 The polymerization data of *N*-isopropylacrylamide (NIPAM)

Polymer	$[NIPAM]_0/[I]_0$	Time (h)	Conv.[a] (%)	$M^{b}_{n,th}$ (g mol^{-1})	$M^{c}_{n,GPC}$ (g mol^{-1})	M_w/M_n
1A	50:1	3	32.5	2040	3700	1.14
1B	50:1	3	41.3	2620	4400	1.10
1C	50:1	3	43.8	2830	4600	1.11

[a] Determined by gravimetric measurement

[b] $M_{n,th} = M_{NIPAM}[NIPAM]_0 conv/100[I]_0 + M_{Initiator}$

[c] Determined by GPC using polystyrene standards

Synthesis of Ar-PNIPAM/Eu(III)/TTA complexes (2A–C)

Typically, a certain volume of ethanol solution of $\mathrm{EuCl_3}$, PNIPAM (W_{Eu}^{3+}:$W_{\mathrm{PNIPAM}} = 0.08{:}1$), and TTA ($\mathrm{Mol_{TTA}}$:$\mathrm{Mol_{PNIPAM}} = 4$) were added to a flask. The mixture was stirred by a magnetic stirring bar for 48 h. The product was purified and then dried under vacuum at room temperature, and the Ar-PNIPAM/Eu(III)/TTA complexes were obtained.

Results and discussion

NIPAM was polymerized using phenyl 2-chloropropionate, (4′-phenyl) phenyl 2-chloropropionate, and (2′,6′-diphenyl) phenyl 2-chloropropionate as initiators and CuCl/$\mathrm{Me_6TREN}$ as catalytic system in the solvent of isopropanol (Scheme 1). The NIPAM conversion was determined by gravimetric measurement. The M_n and M_w/M_n were determined by GPC. Table 1 lists the results of the polymerization of NIPAM. We can see that when the feed ratio of NIPAM, initiator, CuCl, and $\mathrm{Me_6TREN}$ was 50/1/1/1, the NIPAM conversion reached 32.5, 41.3, and 43.8% for the polymerization time of 3 h, respectively. The number-average molecular weights ($M_{n,\mathrm{GPC}}$) ranged from 3700 to 4600 g $\mathrm{mol^{-1}}$, the polydispersity indices (M_w/M_n) were low values between 1.10 and 1.14. These results indicate that the reactive activity of the three initiators was different and the products were assigned to the end-functionalized poly(*N*-isopropylacrylamide) with aromatic groups.

IR spectra of TTA, Ar-PNIPAM, and Ar-PNIPAM/Eu(III)/TTA are shown in Fig. 1. From Fig. 1a(i), the band at 3300 $\mathrm{cm^{-1}}$ is assigned to the stretching vibration ($\nu_{\mathrm{N-H}}$) of acylamino group. Since the amide chains are included in the PNIPAM structure, the band at 1647 $\mathrm{cm^{-1}}$ is ascribed to amide I [mainly the carbonyl stretching vibration ($\nu_{\mathrm{C=O}}$)] and the band at 1551 $\mathrm{cm^{-1}}$ is ascribed to amide II [mainly the N–H bending vibration ($\delta_{\mathrm{N-H}}$)]. Upon the formation of Ar-PNIPAM/Eu(III)/TTA, the stretching vibration ($\nu_{\mathrm{N-H}}$) of acylamino group is shifted to 3284 $\mathrm{cm^{-1}}$, the bands of amide I and amide II are shifted to 1645 and 1543 $\mathrm{cm^{-1}}$, respectively. The redshift of the characteristic bands mentioned above can be explained that when Eu(III) is bonded to O and N atoms of acylamino group, the electron density and vibration frequency of N–H and C=O decrease [23]. On the other hand, it is seen that the characteristic absorption of hydroxy at 3111 $\mathrm{cm^{-1}}$ of TTA is absent for complex. The result indicates that the enol of TTA which lost proton is bonded to $\mathrm{Eu^{3+}}$. The IR spectra of complexes 2B (Fig. 1b) and 2C (Fig. 1c) are similar to that of 2A.

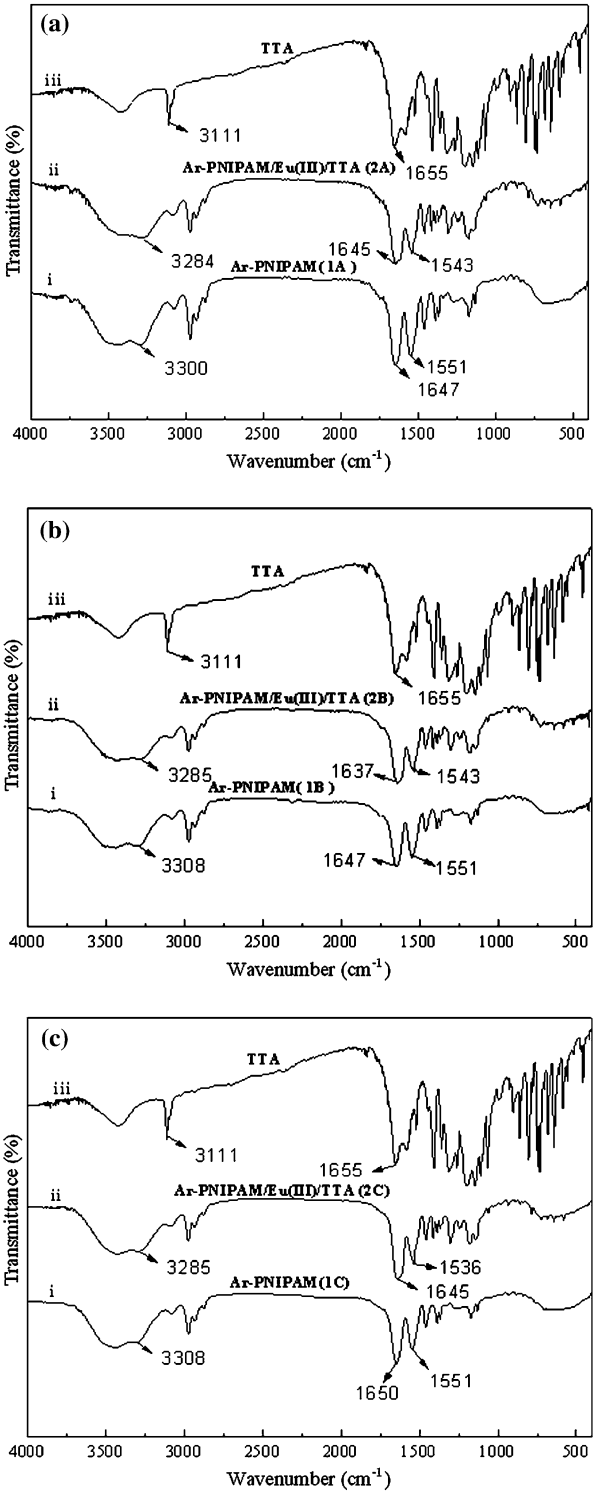


Fig. 1 FT-IR spectra of Ar-PNIPAM(1A–C), Ar-PNIPAM/Eu(III)/TTA (2A–C), and TTA

The excitation and emission spectra of $\mathrm{EuCl_3}$ and Ar-PNIPAM/Eu(III)/TTA complexes are shown in Fig. 2. The excitation and emission spectra were obtained under excitation at 613 nm. In Fig. 2a, $\mathrm{EuCl_3}$ shows negligible absorption at the ultraviolet area. Ar-PNIPAM/Eu(III)/TTA complexes show a different spectral shape, and the absorption peak intensity gradually increases in the range of 275–375 nm. This phenomena attributes to the π–π* transition by exciting the carbonyl and phenyl group of Ar-PNIPAM/Eu(III)/TTA. As shown in Fig. 2b, $EuCl_3$ exhibits very weak characteristic emission peaks of Eu(III); 2A, 2B, and 2C display three narrow and strong characteristic emission peaks at 579, 591, and 613 nm, corresponding to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ electronic transition which occur from the excited state *D* to the multiplet *F*, and the most pronounced peak is situated at 613 nm ($^5D_0 \rightarrow {}^7F_2$). Owing to the shielding of 4*f* orbital from the environment by an outer shell of 5*s* and 5*p* orbital, the *f*–*f* absorption bands are very narrow [24]. The maximum emission intensity of Ar-PNIPAM/Eu(III)/TTA (2A–C) complexes at 613 nm is enhanced about 22, 27, 33 times compared with that of the corresponding Eu(III) (Table 2).

The order of the fluorescence intensity is 2C > 2B > 2A, this phenomena can be explained that the ligands structure and conjugation of substituents affect luminescence efficiency of rare earth ions. End groups of the PNIPAM have conjugated π bonds. The larger conjugated π bond system is, the more likely delocalized π electronic excitated, and fluorescence is more likely to occur. Meanwhile, Eu(III) coordination number has been met because of the introduction of PNIPAM and TTA, the phenomenon of fluorescence decay has not been found for 6 months.

LCST is one of the basic physical properties of thermoresponsive water-soluble polymers. For linear PNIPAM homopolymers, Stover and co-workers [13] recently elucidated the effects of end group hydrophobicity and molecular weight on their LCST values. In the current case, Ar-PNIPAM and Ar-PNIPAM/Eu(III)/TTA possess the same sequences of NIPAM, but the latter possesses Eu^{3+} and TTA which coordinate with PNIPAM. Thus, they prove to be a suitable system for the investigation of end group, Eu^{3+}, and TTA effects on the thermal phase transition behavior of PNIPAM. To determine LCST for the liquid–solid phase transition, the transmittance (%) of an aqueous solution (2 mg mL^{-1}) was measured using UV–Vis spectroscopy upon raising the temperature at the heating rate of 1 °C/5 min. We used 90% transmittance points (90% *T*) as the LCST.

Figure 3a shows temperature-dependent transmittance at a wavelength of 500 nm obtained for aqueous solutions of Ar-PNIPAM (1A) and Ar-PNIPAM/Eu(III)/TTA (2A) at

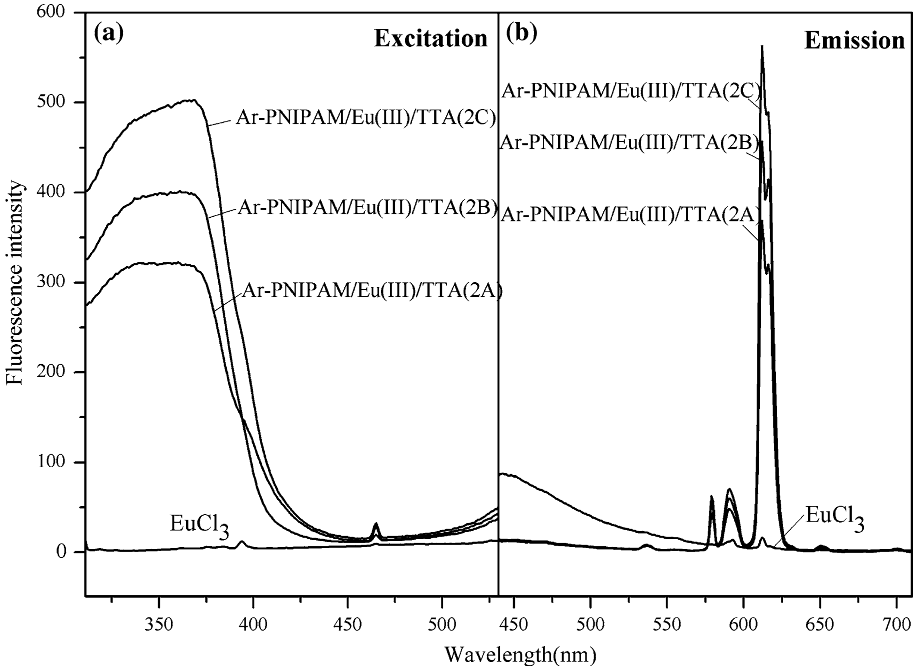


Fig. 2 Excitation and emission spectra of $EuCl_3$ and Ar-PNIPAM/Eu(III)/TTA (2A–C) (Ex/Em slit: 3/3 nm)

Table 2 The fluorescence intensity of $EuCl_3$ and Ar-PNIPAM/Eu(III)/TTA (2A–C)

Compound	$^5D_0 \rightarrow {}^7F_0$	$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$	$^5D_0 \rightarrow {}^7F_3$
$EuCl_3$		591(14)	613(17)	
Ar-PNIPAM/Eu(III)/TTA(2A)	579(44)	591(48)	613(368)	650(5)
Ar-PNIPAM/Eu(III)/TTA(2B)	579(57)	591(60)	613(456)	650(6)
Ar-PNIPAM/Eu(III)/TTA(2C)	579(63)	591(71)	613(562)	650(8)

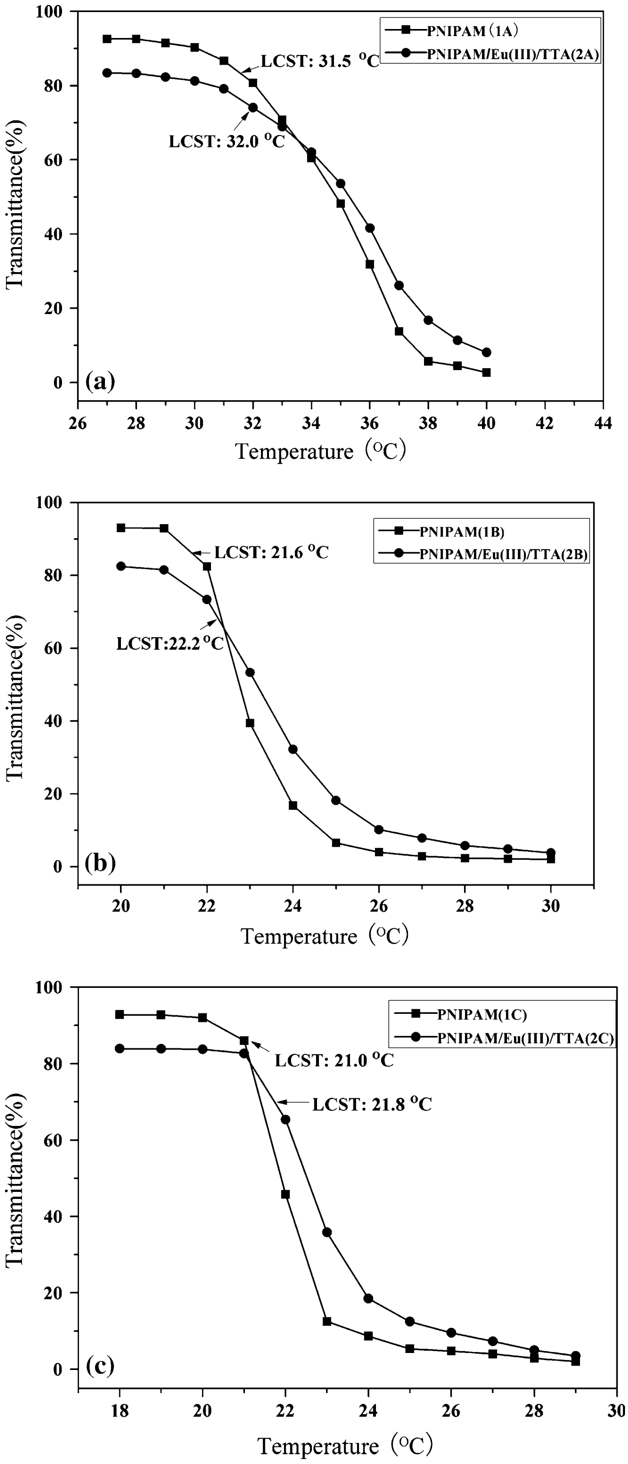


Fig. 3 Temperature dependences of optical transmittance at 500 nm obtained for aqueous solutions of Ar-PNIPAM(1A–C) and Ar-PNIPAM/Eu(III)/TTA (2A–C). The LCST was defined as the temperatures corresponding to 10% decrease of transmittance

a polymer concentration of 2 mg mL^{-1}. We can clearly see that, above 31.5 and 32 °C, transmittance starts to decrease for PNIPAM and Ar-PNIPAM/Eu(III)/TTA, respectively. This indicates that, above these two critical temperatures, interchain aggregation starts to occur, and scattering of the incident light due to the presence of aggregates will tend to decrease optical transmittance. Thus, LCST values of PNIPAM(1A) and Ar-PNIPAM/Eu(III)/TTA(2A) have been determined to be 31.5 and 32 °C, respectively (Fig. 3a). The drop of the LCST is observed more obviously for 1B (21.6 °C) and 1C (21.0 °C). This indicates that hydrophobic end groups decrease the LCST. We can also observe from Fig. 3 that PNIPAM exhibits a relatively sharp decrease of transmittance, whereas Ar-PNIPAM/Eu(III)/TTA shows a more gradual decrease of transmittance.

From Fig. 3, we can tell that the LCSTs of Ar-PNIPAM/Eu(III)/TTA are slightly greater compared with that of PNIPAM. Eu^{3+} of the complexes in solution can also be coordinated with water molecules, and the coordination bond energy is higher than that of water molecular's hydrogen bond. When the temperature of the solution is near to the LCST, more energy is consumed to destruct the coordination bonds of Eu^{3+} and water molecules, so that a higher temperature is required for the phase transition to occur. This also proves the formation of complexes between Eu^{3+} and PNIPAM.

Conclusion

We have successfully prepared three narrow-disperse PNIPAM with end-functional groups by ATRP. Then, Ar-PNIPAM/Eu(III)/TTA complexes formed by the interaction among Ar-PNIPAM, TTA, and Eu(III). The complexes exhibit intensive characteristic fluorescence of Eu(III), and the maximum emission intensity of Ar-PNIPAM/Eu(III)/TTA at 613 nm is enhanced compared to that of the corresponding Eu(III). The LCSTs of complexes are greater than that of corresponding PNIPAM. The complex may be a promising materials of functional polymer, and broaden the application of temperature-sensitive PNIPAM.

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