Journal of Luminescence 136 (2013) 437–443

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Study on the novel rare-earth nanocrystals/PNIPAM complex hydrogels prepared by surface-initiated living radical polymerization

Qiusheng Song *, Yang Yang, Kang Gao, Haihong Ma

School of Chemical Engineering, Hefei University of Technology, Hefei 230009, China

ARTICLE INFO

Article history:
Received 6 July 2012
Received in revised form
7 August 2012
Accepted 4 December 2012
Available online 14 December 2012

Keywords:
Nanocrystal
Complex hydrogel
Surface-initiated living radical polymerization
Thermosensitive
Fluorescence

ABSTRACT

A series of novel rare-earth nanocrystals/PNIPAM complex hydrogels were prepared by surface-initiated living radical polymerization with different contents of $NaYF_4$:Eu^{3+} nanocrystals. The microstructure and performance of the $NaYF_4$:Eu^{3+} nanocrystals and the complex hydrogels were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), differential scanning calorimetry (DSC) and photoluminescence (PL). The thermosensitive fluorescence behaviors of the complex hydrogels and the mechanisms were investigated. The results suggested that the nanocrystals were incorporated into PNIPAM gels with covalent bonding and the fluorescence performance of complex hydrogels was influenced greatly by either the ambient temperature or the content of nanocrystals. The PL intensity of the complex hydrogels increased with increasing temperature. The higher content of nanocrystals in the complex hydrogels, the sharper the transitions of volume phase variation around low critical solution temperature (LCST).

1. Introduction

Thermosensitive hydrogels can swell or shrink in response to external stimuli, which is derived from the thermally induced volume transitions. Due to their low critical solution temperature (LCST) and abrupt change of their volume around LCST, thermosensitive hydrogels are drawing more and more attention for their potential applications in genes, drug delivery systems, sensors, actuators, and shape memories [1,2].Till now, many thermosensitive hydrogels, such as poly(N-isopropylacrylamide) (PNIPAM), poly(N-vinylcaprolactam-co-glycidyl-methacrylate), or poly(ethylene glycol methyl methacrylates), have been reported [3,4]. Among them, PNIPAM represents the most extensively studied thermosensitive material [5,6].

On the other hand, inorganic nanocrystals are another family of important materials due to their unique optical and electronic properties [7]. Compared with organic fluorophores, inorganic nanocrystals, especially semiconductor quantum dots (QDs), are paid more attention for their applications in the areas of solar energy system, molecular imaging, optoelectronics and catalysis fields [8–12].

Currently, incorporation of QDs with PNIPAM hydrogels has attracted great interest [13–16]. For example, Wang et al. [17] reported a highly photoluminescent (PL) gel by immobilizing CdTe QDs onto PNIPAM thermosensitive gel physically. Shen et al. [18] described a new method for the preparation of fluorescent composite microgels by loading QDs into PNIPAM microgels via reversible transfer from organic solvents to water. Agrawal et al. [19] developed a method for preparing fluorescent thermosensitive hybrid PNIPAM microgels by covering covalently immobilized CdTe QDs on their surface. When the temperature was under the LCST of the polymer, the PL intensity of the QDs was strongly quenched, whereas with the temperature above the LCST, the PL intensity was restored.

Although nanocrystals based fluorescent stimuli-responsive gels are very promising, it is difficult to prepare these complex gels. Polymerization of monomers in the presence of nanocrystals has been proved to be a simple strategy, but there are many difficulties to overcome, such as phase separation between the polymer and the nanocrystals, and aggregation of the nanocrystals during polymerization [20]. In another aspect, the type of the bond, which affects the variation of PL intensity according to the temperature change, is one of the most important factors. [21]. If nanocrystals diffuse or entrapped within gels without covalent bonds, such as with hydrophobic forces, hydrogen bonding or electrostatic interactions, the PL intensity would decrease with

Abbreviations: PNIPAM, poly(N-isopropylacrylamide); LCST, lower critical solution temperature; FRP, free-radical polymerization; ATRP, atom transfer radical polymerization; LSS, liquid–solid–solution synthesis; PMDETA, pentamethyldiethylenetriamine; BIS, *N,N'*-methylenebisacrylamide; NIPAM, N-isopropylacrylamide; BPO, Benzoyl peroxide; THF, tetrahydrofuran; TEM, transmission electron microscopy; XRD, X-ray diffraction; FTIR, Fourier transform infrared; DSC, differential scanning calorimetry; PL, photoluminescence.

* Corresponding author. Tel./fax: +86 551 2901450.
E-mail address: sqshfut@126.com (Q. Song).

0022-2313/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2012.12.005

increasing temperature. Conversely, if nanocrystals were incorporated into PNIPAM gels with covalent bonds, the PL intensity would increase with increasing temperature.

Till now, many nanocrystals based PNIPAM gels with covalent bonding have been fabricated by free radical polymerization in the presence of the nanocrystals. But there is no direct evidence about the bond type between nanocrystals and PNIPAM networks. In order to further demonstrate the relation between PL performance and bond type of the nanocrystals based complex hydrogels, the surface-initiated nanocrystals based complex hydrogel is a good candidate to prove the facts.

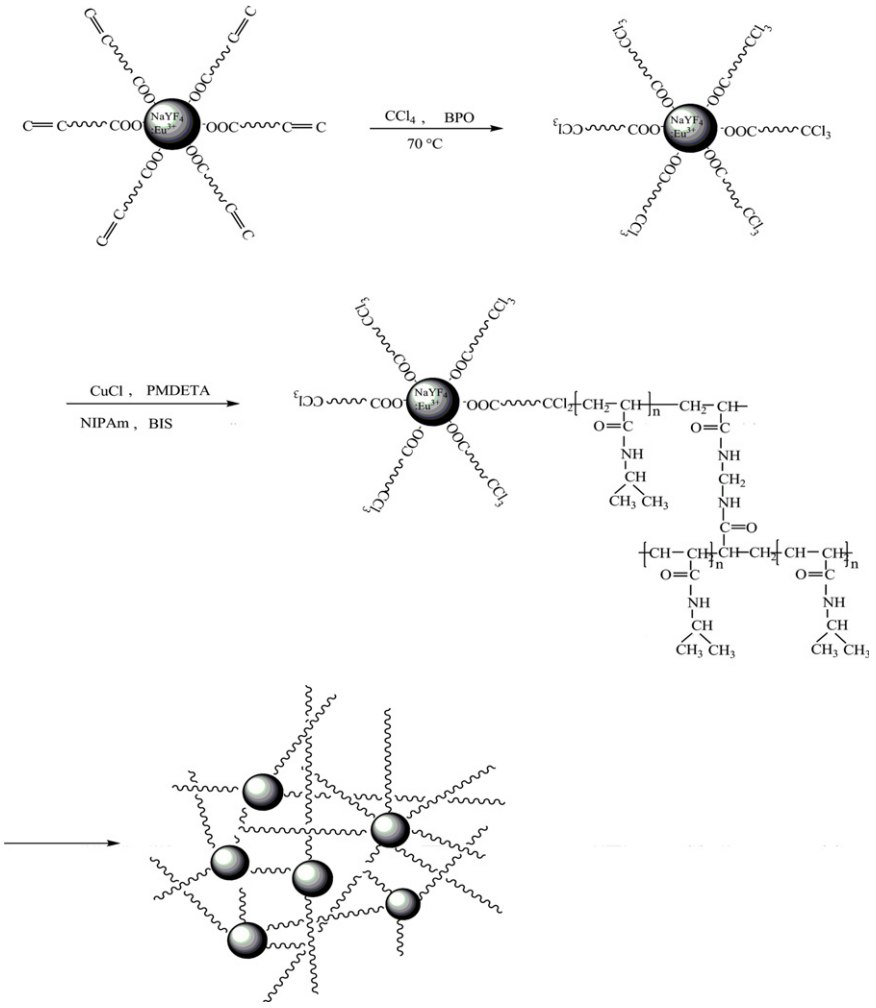
Rare-earth nanocrystals have different chemical structures from those of semiconductor QDs. They possess different luminescence performances and show different energy transferring mechanisms from those of the latter [22,23]. Size- and even shape-controlled rare-earth nanocrystals show potential applications in optics, optoelectronics, biological labeling, catalysis fields, and so on [24–26]. Chemical stability is the most important characteristic of rare-earth nanocrystals, so the surface of the nanocrystals can be decorated easily. Moreover, incorporating rare-earth nanocrystals into PNIPAM hydrogels implies a new type of nanocrystals based thermosensitive complex hydrogels.

Hence, we design a novel route to synthesize the nanocrystals based PNIPAM thermosensitive complex hydrogels. $NaYF_4$:Eu^{3+} nanocrystals are firstly synthesized by the liquid–solid–solution (LSS) strategy [27]. Then $NaYF_4$:Eu^{3+} nanocrystals/PNIPAM complex hydrogels are prepared by surface-initiated living radical polymerization, as presented in Scheme 1. It is found that the LCST of the complex hydrogels decreases gradually with the increase of the content of nanocrystals. The fluorescence performance of complex hydrogels is influenced greatly by either the ambient temperature or the content of nanocrystals. To the best of our knowledge, there are no similar researches available on the synthesis of rare-earth nanocrystals based complex hydrogels by atom transfer radical polymerization (ATRP) and investigation of their fluorescence stimuli–response behavior.

2. Experimental section

2.1. Materials

Europium nitrate hexahydrate ($Eu(NO_3)_3 \cdot 6H_2O$) and yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$, purity $>99.9\%$) were purchased from the Shanghai Chemical Reagent Company Co., Ltd., China, and used as received without further purification. Pentamethyldiethylenetriamine (PMDETA), carbon tetrachloride (CCl_4), sodium fluoride, undecylenic acid, sodium hydroxide, ethanol, chloroform, tetrahydrofuran(THF) and *N*,*N*′-methylenebisacrylamide (BIS) were of reagent grade quality and purchased from Beijing Chemical Reagent Company Co., Ltd., China, and used as received without further purification. N-isopropylacrylamide (NIPAM) was recrystallized in hexane. Benzoyl peroxide (BPO) was recrystallized in methanol. Cuprous chloride (CuCl) was



Scheme 1. Schematic illustration of synthesis of $NaYF_4$:Eu^{3+}/PNIPAM complex hydrogels.