



Short communication

Ionic comonomer effect of poly(*N*-isopropylacrylamide) copolymer containing D- π -A type pyran-based fluorescent dye

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ABSTRACT

Temperature and pH responsive poly(*N*-isopropylacrylamide) (poly(NIPAM)) copolymer containing D- π -A type pyran-based fluorescent dye (fluorophore) and basic comonomer, *N*-[3-(dimethylamino)propyl]-methacrylamide (DMAPAM) was prepared by free radical polymerization. With increase of pH values, aqueous poly(NIPAM-co-DMAPAM-co-fluorophore) solution showed decrease of a lower critical solution temperature (LCST) and increase of fluorescence intensity, due to a change in the ionization state. And also hydrodynamic radius of poly(NIPAM-co-DMAPAM-co-fluorophore) changed correspondingly to changes of temperature and pH values.

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1. Introduction

Stimuli-responsive polymers can provide a variety of applications as super-smart polymer systems. Temperature is the most widely used physical stimuli in environmentally responsive polymer systems. Most popular temperature-responsive polymer has a LCST at which a polymer solution undergoes phase transition from a soluble to an insoluble state by above the critical temperature; since it exhibits a phase transition caused the coil-to-globule transition in solution [1–3]. Most applications of temperature-responsive polymers are related to LCST-based polymer systems [4–7]. For industrial applications, it is necessary to effective LCST control of polymer by using suitable synthesis parameters.

Poly(*N*-isopropylacrylamide) (poly(NIPAM)) is the most popular temperature-responsive polymer having a LCST which exhibits a sharp phase transition in water at 32 °C. The reason for this sharp phase transition is a good balance between hydrophilic and hydrophobic interactions in the polymer [3].

D- π -A type dyes owing instinct intramolecular charge transfer properties have gained much attention due to their applications suitable as probes for the determination of solvent polarity, potential applications for colorimetric chemosensors [8,9] and the

recognition and sensing toward harmful metal ions and so on [10–13]. In our previous papers, we have reported the acid/base-induced optical switching of the D- π -A type dyes [14–18]. Also reported has been thermo-responsive behavior and optical switching in poly(NIPAM) copolymers with D- π -A type dyes [19–23].

Some research groups have been reported the phase transition behavior of NIPAM copolymers having ionic group in their side group [24–27]. As an attempt to obtain more sensitive functional polymers with potential device application, we have designed and synthesized copolymer which responds to change in temperature and pH value. This paper concerns about effect of ionic comonomers on LCST and fluorescence intensity of poly(*N*-isopropylacrylamide) copolymer containing D- π -A type pyran-based fluorescent dye.

2. Experimental

The weight-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer was measured on an Alliance e2695 chromatograph at 25 °C using tetrahydrofuran (THF) as the eluent and standard polystyrene as the reference. Fluorescence spectra were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer. The UV–vis spectra and transmittance were obtained on an Agilent 8457 UV–vis spectrophotometer. The LCST values were also determined by spectrophotometric detection of the changes in transmittance of aqueous polymer solutions heated at a constant rate (0.2 °C min⁻¹) with a thermostatically controlled cuvette.

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2.1. Materials

N-Isopropylacrylamide (Aldrich) was purified by recrystallization from a mixture of toluene/hexane (1/4) and dried in vacuum. 2,2'-Azobis-(isobutyronitrile) (AIBN) was recrystallized from methanol. The other chemicals were of the highest grade available and were used without further purification. All employed solvents are analytically pure and were employed without any further drying or purification. The D- π -A type pyran-base fluorescent dye monomer (fluorophore) was prepared by previously described procedures [19].

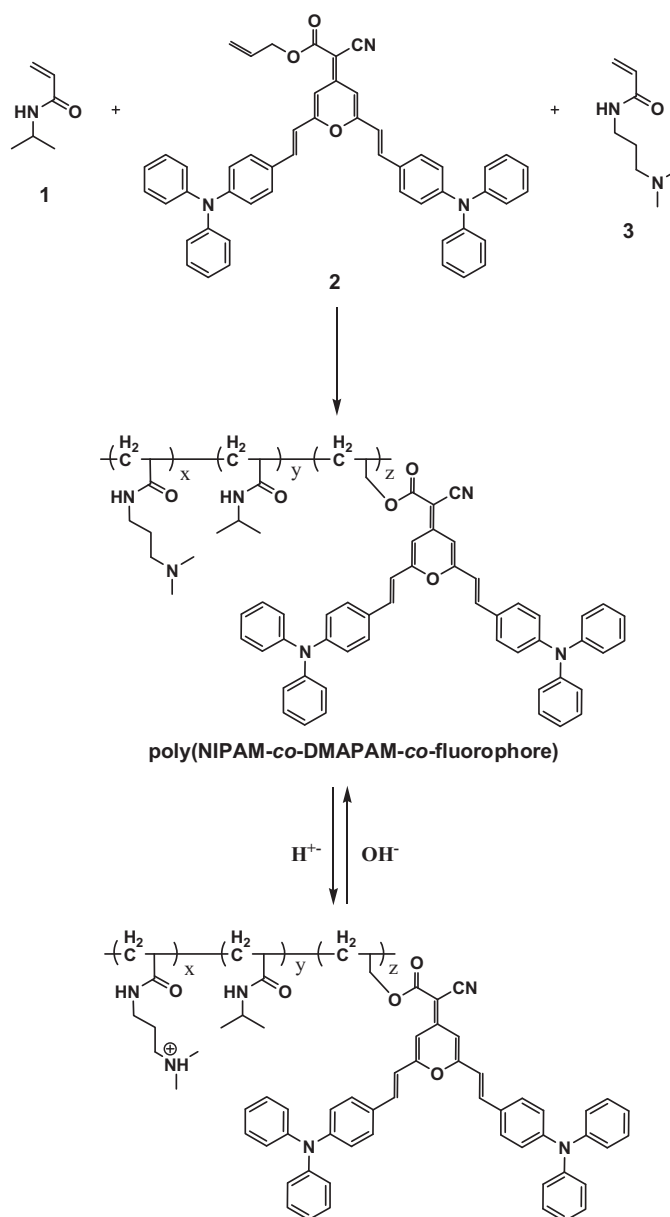
2.2. Synthesis of poly(*NIPAM-co-DMAPAM-co-fluorophore*)

N-Isopropylacrylamide (5.3 g, 0.047 mol), fluorophore (0.05 g, 0.06 mmol), DMAPAM (3.44 g, 0.02 mmol), and AIBN (0.0196 g, 0.1 mmol) were dissolved in anhydrous THF (40 ml) under dry nitrogen. After heating for 3 days at 65 °C, the resultant mixture was precipitated from ether. The resulting polymer was dried in vacuum to give satisfactory yield. Yield: 51%, gel permeation chromatography (GPC): M_n : 9300, M_w : 11,500, M_w/M_n : 1.23.

3. Results and discussion

To study polymer which responds to change in temperature and pH value, poly(*N*-isopropylacrylamide) copolymer based on NIPAM, fluorophore, and a third compound having basic group was prepared by traditional free radical copolymerization. First of all, one of comonomers used as fluorophore, the D- π -A type pyran-base fluorescent dye monomer was prepared by previously described procedures [19]. The synthetic route of the poly(*NIPAM-co-DMAPAM-co-fluorophore*) is depicted in Scheme 1. We considered following points for the synthetic strategy; at first, poly(*NIPAM*) is thermosensitive polymer hydrogel and shows a LCST as it has both hydrophilic amino groups and hydrophobic isopropyl groups in its side chains. Second, incorporation of the ionic comonomer could lead to change the hydrophilicity of the polymer by altering the pH value, resulting in a change in the LCST. As shown in Scheme 1, reaction of NIPAM **1** and fluorophore **2** with basic DMAPAM **3** in anhydrous THF affords orange-colored powder of poly(*NIPAM-co-DMAPAM-co-fluorophore*), and the synthetic route was very simple. The basic comonomers in the synthesized poly(*NIPAM-co-DMAPAM-co-fluorophore*) exist charged state in acidic or neutral aqueous solution, however the basic comonomers change from charged state to noncharged state by increasing of pH value.

The phase transition temperature can be measured by a few methods, e.g. light scattering [28], turbidimetric measurements [29] or differential scanning calorimetry (DSC) [30], but UV-vis spectrometry is an easy and widely used method for the determination of the phase transition temperature. The absorption spectra of aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*) solutions having various pH values at different temperature is shown in Fig. 1(a)–(c). Although aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*) solutions having different pH values from pH 9 to pH 11 showed different absorbance graphs, they all became turbid as solutions are heated and formed complete gels above much higher temperature of LCST, which shows same behaviors as aqueous pure poly(*NIPAM*) polymer does. It is well-known that LCST behavior in neutral pure poly(*NIPAM*) is caused by a critical hydrophobic/hydrophilic balance of the polymer side groups [3] and the LCST of poly(*NIPAM*) copolymers is strongly influenced by the nature of the comonomer [25]. Fig. 1(d) shows pH value effect on transmittance of aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*) solution at different temperatures. With increase



Scheme 1. Synthesis and pH response of poly (*NIPAM-co-DMAPAM-co-fluorophore*).

of pH value, obvious transmittance of aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*) solutions started to decrease at the lower temperature. These LCST shifts are caused by a change in the ionization state in response to changes in pH value. DMAPAM has an amino group in its structure, and therefore it becomes more hydrophilic in acidic medium [28]. By increasing of pH value, basic monomer in poly(*NIPAM-co-DMAPAM-co-fluorophore*) becomes more hydrophobic as it changes from charged state to non-charged state, therefore the LCST shift to the lower temperature of poly(*NIPAM-co-DMAPAM-co-fluorophore*) could be explained.

Fig. 2 shows pH value effect on fluorescence intensity of aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*) solution at different temperatures. The fluorescence intensity of aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*) solutions were increased with increase of pH value. These phenomena could be explained by increasing of hydrophobic units, resulting in decreasing of ionization by increasing of pH value. The fluorescence intensity of aqueous poly(*NIPAM-co-DMAPAM-co-fluorophore*)

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