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Synthesis and Properties of Poly(N-isopropylacrylamide-co-acrylamide) Hydrogels

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Summary: Poly (N-isopropylacrylamide-co-acrylamide) [Poly(NIPAAm-co-AAm)] with different feed ratios were obtained by radiation polymerization using Co^{60} γ -rays. Swelling equilibrium data in various media: deionized water, aqueous NaCl solutions and different pH buffer solutions, were determined. It appeared that the lower critical transition temperature (LCST) of the hydrogels increased with an increasing acrylamide content and decreased with increasing ionic strength. Moreover, LCST was affected by pH.

Keywords: hydrogel; ionic strength; LCST; pH-sensitive; Poly(N-isopropylacrylamide-co-acrylamide)

Introduction

Recently, the reversible phase transition of Poly (N-isopropylacrylamide) (PNIPAAm) has attracted much attention. This phase transition has many potential applications in various fields because PNIPAAm is volume collapse at lower critical transition temperature (LCST). But, how to control the LCST to desired temperatures is still a problem and has been widely studied.

Theoretically, Tanaka [1-3] first indicated that the constituent polymer chains must have sufficient stiffness and/or sufficient ionized groups in order for a gel to undergo a discontinuous phase transition. With the advancement of the research, many people came to agree that the hydrogen bonding effect and hydrophobic force was the most important reason in the phase transition process [4, 5]. Therefore, some scientists tended to change the ratio of hydrophilic and hydrophobic groups in the polymer to adjust the LCST to match the desired "critical region"[6-8]. Furthermore, different media will affect the swelling behavior and the LCST of the hydrogel.

In our previous paper [9], the effect of pH on the LCST of Poly (N-isopropylacrylamide) and Poly (N-isopropylacrylamide-co-acrylic acid) was introduced. Therefore, in this paper,

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besides the effect of pH, the effects of ionic strength and the hydrophilic monomer (acrylamide) content are considered simultaneously.

Experimental

Materials

NIPAAm, Wako Pure Chemical Industries Ltd., was kindly supplied by Professor Kaetsu of Kink University. Prior to the reaction, NIPAAm was recrystallized from a mixture of n-hexane and benzene. Acrylamide (AAm), Shanghai Reagent Company, was used without any purification. All other chemicals were of analytical grade and used without any purification.

Synthesis of Hydrogels

Hydrogels of Poly (NIPAAm-co-AAm) were prepared by radiation polymerization, by Co^{60} γ-ray (300kCi, Shanghai Hexing Radiation Factory) with the dose of 25kGy. A total of 3 g of NIPAAm and AAm, in different molar percentages (see Table 1), were dissolved in 27 mL of deionized water. Radiation polymerization was carried out at room temperature in a moving state. The prepared hydrogels were cut into small pieces, approximately 10x5x2mm in size and soaked in deionized water for 24 h. The water was changed periodically to remove unreacted compounds. Then, the hydrogels were dried at 60°C in a vacuum oven.

Table 1. Codes and compositions of hydrogels studied.

Sample code	Molar percentage of comonomer (%)	
	NIPAAm	AAm
NA100	100	0
NA97	97	3
NA92.5	92.5	7.5
NA84	84	16
NA75	75	25
NA0	0	100

Determination of Swelling Ratio

The swelling experiments were performed in different media (deionized water, solution of different ionic strengths and various pH buffer solutions). The dried samples (30~40 mg) were immersed in the above solutions, respectively. After swelling equilibriums were researched, the gels were removed from the solutions and weighed, after excess surface water had been removed by blotting within two filter papers. The procedure was repeated at various temperatures. Each sample was measured three times and the final result was the average value. The swelling ratio was obtained from Eq. 1.

$$\text{Swelling ratio (times)} = \frac{W_s - W_d}{W_d} \qquad (1)$$

where W_s and W_d were the weights of the swelled and dried samples, respectively.

Determination of FTIR

The dried samples were cut into small pieces, approximately 5x5x1 mm in size. FTIR spectra were recorded with a Fourier transform infrared (FTIR) spectrometer (Avatar 370, Nicolet, USA) in the attenuated total reflectance (ATR) mode.

Determination of Tg

Differential scanning calorimetry was used to determine the Tg directly. A DSC 200PC, Phox, German instrument was used. The dried samples (about 10 mg) were heated from 20°C to 500 °C at the rate of 20 k°C/min in N_2 atmosphere.

Results and Discussion

Characterization of Copolymers

FT-IR spectra of the copolymers PNIPAAm (NA10) and PAAm (NA0) are shown in Fig.1. They were which are similar to standard spectra of Form the Gibbs-Dimarzio theory, the Tg of a copolymer can be predicted as follows:

$$Tg = \chi_A Tg_A + \chi_B Tg_B \ (2)$$

where χ_A, *and* χ_B are the molar fractions of components A and B; and Tg_A, *and* Tg_B are the Tg values of the homopolymers A and B.

According to Nielsen the Tg will increase if a polymer is crosslinked, and he proposed the following formula:

$$T_{gx} - T_{g0} \approx \frac{3.9\times10^4}{\overline{Mc}} \quad (3)$$

where T_{gx}, *and* T_{g0} are the Tg values of crosslinked and uncrosslinked polymers; and $\overline{Mc}$ is the number average molecular weight of the active chain between two crosslink points. It was found that the Tgs of the homopolymers PNIPAAm and AAm were about 135 °C and 150 °C. Form the data in Fig. 2 and Eq. 2, the calculated Tg of crosslinked PAAm was 242 °C. The following table was obtained based on Eq. 3.

Table 2. Tgs and $\overline{Mc}$s of the copolymers.

Sample Code	Tg (crosslinked, measured)	Tg (uncrosslinked, calculated)	$\overline{Mc}$
NA97	214.7	135.5	492
NA92.5	215.6	136.1	491
NA84	218.1	137.4	483

Due to the smaller size of the AAm group, compared to that of NIPAAm's, the interaction of AAm within the polymer network may be more evident. It is predicted that the interactions within the polymer network will increase with AAm's content. It is the chemical structure of the functional group that mainly determines the Tg.

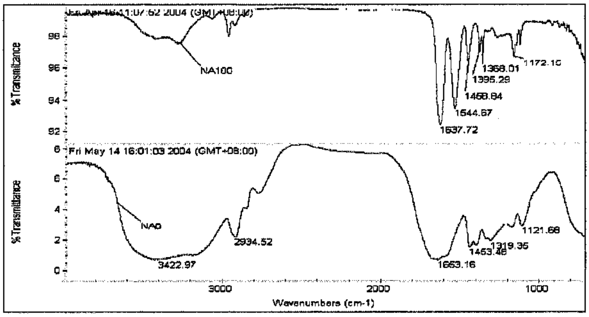

Fig. 1. FT-IR spectra of PNIPAAm and PAAm.

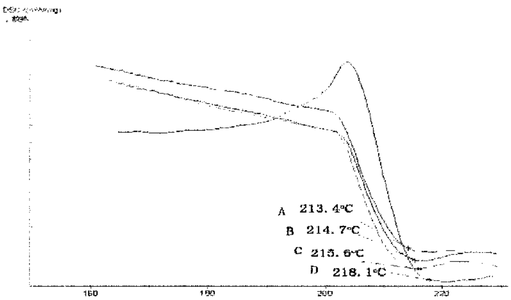

Fig.2. DSC curves of the copolymers (A: NA100; B: NA97; C: NA92.5; D: NA84.

Temperature Sensitivity

It was mentioned that the polymer chain of PNIPAAm began to shrink at 25 °C [10]. Moreover, it shrank apparently when the temperature was raised to above 30 °C, which was lower than the well-known LCST, 32 °C. Therefore, in Zhang and Zhuo's paper [5], LCST was defined as the temperature at which that the swelling ratio decreased fast with an increase in temperature. Fig.3 illustrates the effect of AAm molar percentage of copolymer on the swelling ratio as a function of temperature. As the AAm content increases, the gradients of the curves become flatter at higher temperature. The LCST shifting to higher temperature is attributed to the increasing hydrophilicity.

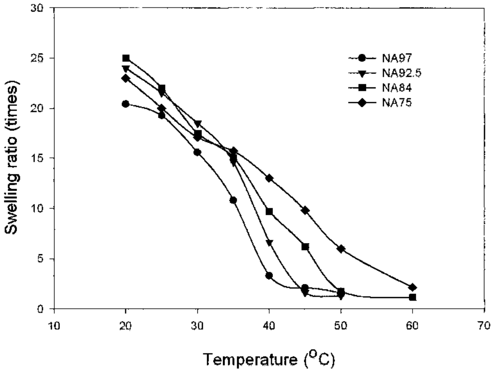

Fig.3. Effect of temperature on the swelling ratio of Poly (NIPAAm-co-AAm) as a function of AAm molar percentage.

Response to Ionic Strength

According to Tanaka's assumption [1, 2], hydrogels will appear sensitivity when the polymer chains can fit certain stiffness. With an increase in the NaCl content, the polymer chains will process a coil-globule transition gradually. Due to the decrease of the degree of polymer chain stiffness, the phase transition temperature declines [11-13]. Considering the effects of ionic strength of solution and AAm content simultaneously, as shown in Fig.4, the LCSTs rise as the AAm content increases. This is consistent with the results shown in Fig. 3. Parks and Hoffman [12] presumed that "chloride ions might bind specifically to certain portions (perhaps polar amide groups) of the polymer segment and/or might interact with hydrated water molecules which are associated with polar or hydrophobic polymer segments", which might lower the LCST of PNIPAAm. It could be assumed that the effect of ionic strength on the LCST might be related to the "stiffness" of the polymer chains, which had been suggested as one of the requirements for exhibiting the phase transition behavior. "The structure and extent of hydration sheath around the polymer chain may be adequately matched up with the chloride ion concentration and the temperature, so that the chain stiffness satisfies that requirement for an abrupt phase transition elicited by the small change in chloride ion concentration."

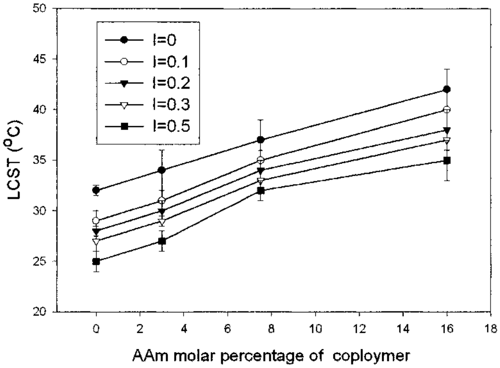

Fig.4. Effect of AAm molar percentage of copolymer on LCST as the function of ionic strength.

pH Sensitivity

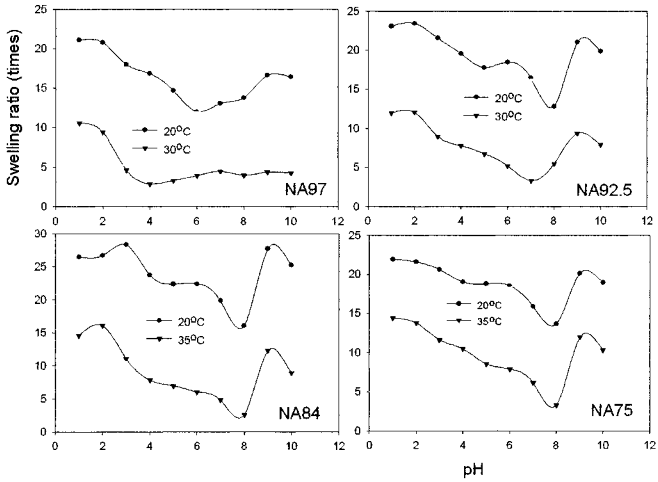

Fig. 5. Effect of pH on swelling ratio of Poly (NIPAAm-co-AAm) as a function of temperature.

The effect of pH on several swelling ratio curves (NA97, NA92.5, NA84 and NA75) of Poly (NIPAAm-co-AAm), as a function of temperature, is shown in Fig. 5. The swelling ratios are smaller in range of pH 6-8 and are larger at the lower and higher pH values. This may due to the ease of hydrolysis of AAm in strong acid/base [1], which will lead to electrostatic repulsion making the network extend. Comparing the swelling ratio curves at higher temperatures, 30 °C has arrived or exceeded the LCST of the copolymer in the pH 4-10 range (swelling ratios < 5), in the case of NA97. But in the case of NA92.5, only shrunk quickly at pH 6-8. With the AAm component increasing, in NA84 and NA75, the LCST within that range had increased to about 35 °C. This indicates the pH-sensitivity of the copolymer and the effect of the AAm content on the swelling ratio.

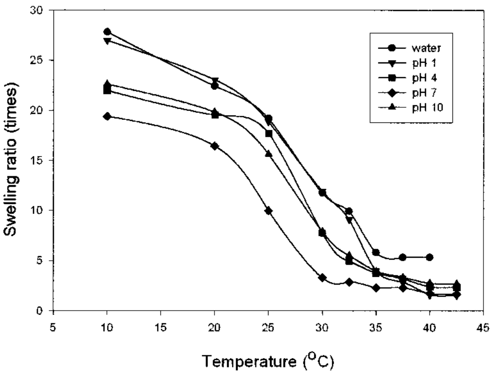

Fig.6. Effect of temperature on swelling ratio of NA92.5 as the function of pH (I=0.4).

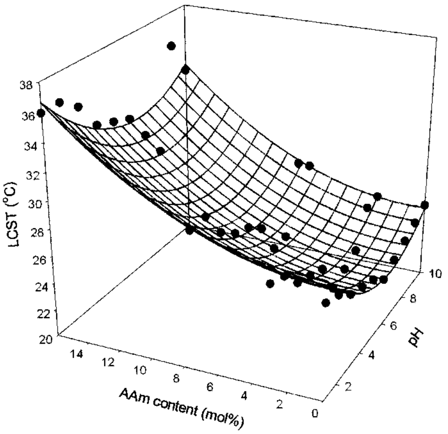

Fig. 7. Effect of pH and AAm content on LCST of the copolymers.

The effect of temperature on the swelling ratio of NA92.5 as the function of pH is shown in Fig.6. Results are similar to what was reported in our previous paper [9]. The swelling ratio of poly (NIPAAm-co-AAm) hydrogel in all pH buffer solutions appears to decrease with an increase in temperature, such as in the case of the swelling behavior in deionized water. The decrease is differed in various pH buffer solutions, which indicates that the LCST is affected by pH. Generally, the LCST decreased with an increase in pH within the range of pH 1-7; however, it increased when the pH exceeded that range. Considering the effects of pH and AAm content on the LCST of the copolymers simultaneously, we obtained Fig. 7. The desired LCST may be obtained in a certain range, by adjusting the pH and/or AAm content, while the ionic strength of the solution is 0.4M. Therefore, the application of this kind of thermosensitive hydrogels can be extended.

Conclusion

The thermosensitive Poly(NIPAAm-co-AAm) hydrogels were obtained by radiation polymerization using Co^{60} γ -ray.

The swelling ratio and the LCST of copolymers were affected by ionic strength, AAm content and pH value of the solution.

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