

Thermal Phase Transition of Poly(*N*-propionylethyleneimine) Hydrogel

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ABSTRACT: This article presents the preparation of the hydrogel of poly(*N*-propionylethyleneimine) and its interpenetrating polymer network (IPN) hydrogel containing polyacrylamide by means of γ -ray radiation and a study of the phase transition temperature of these hydrogels. As a result, the hydrogel of the crosslinked poly(*N*-propionylethyleneimine) exhibited swelling below and shrinking above the phase transition temperature (about 61°C), as well as the lower critical solution temperature (LCST) of the liner polymer–water system. The experiment also showed that the LCST of the IPN hydrogel could be adjusted by the incorporation of the second component polyacrylamide. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2457–2461, 1999

Key words: poly(*N*-propionylethyleneimine); lower critical solution temperature; hydrogels; interpenetrating polymer network polymer

INTRODUCTION

Thermally sensitive hydrogels consist of a 3-dimensional network of crosslinked polymers when immersed in water (or water–organic solvent mixture). It can swell or shrink below or above its thermal phase transition temperature suddenly. Since Tanaka's discovery in 1978 of the thermally sensitive hydrogel that has a lower critical solution temperature (LCST) in its phase graph,¹ there has been more and more interest in the field of controlled drug delivery,^{2,3} immobilization of enzymes⁴ and cells,⁵ dewatering of protein solutions,⁶ and even artificial muscle.⁷ The chemical structures needed for these hydrogels are still in dispute. As far as literature reports are concerned, a few kinds of polymeric hydrogels exhibit

an LCST. Most of these reports are related to *N*-substituted polyacrylamide in an acetone (42%)–water system,¹ poly(*N*-isopropylacrylamide) in a water system,^{2,3,8,9} poly(*N,N*-dimethylacrylamide),^{10–12} and so on. There are a few reports dealing with poly(acrylic acid) in the earlier literature, for example, a poly(acrylic acid)–poly(ethylene oxide)–water system exhibiting an LCST.¹³ Another example of the thermally sensitive hydrogels is a poly(vinyl methyl ether)–water system,⁷ which swells below and shrinks above 38°C (at LCST).

Recently, we found that the poly(*N*-propionylethyleneimine)–water system showed a homogeneous phase at a lower temperature and phase separation at a higher temperature, and the phase separation temperature had a inverse bell-shaped polymeric concentration profile and the lowest value (above 61°C, i.e., the LCST). We prepared a hydrogel by using γ -ray irradiation on an aqueous solution of poly(*N*-propionylethyleneimine). The hydrogel of the crosslinked poly(*N*-propionylethyleneimine) exhibited swelling below

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and shrinking above the phase separation transition temperature. We also prepared another hydrogel of a crosslinked interpenetrating polymer network (IPN) consisting of poly(*N*-propionylethyleneimine) and poly(acrylamide). We found that the IPN hydrogel still exhibited an LCST, and the LCST could be adjusted by the incorporation of the polyacrylamide in the IPN hydrogels. This article is concerned with the preparation of the thermally sensitive hydrogels and the temperature-dependent swelling behavior of the hydrogels.

EXPERIMENTAL

Measurement of LCST of Aqueous Solution of Poly(*N*-propionylethyleneimine)

The poly(*N*-propionylethyleneimine) (Dow Chemical Company, Ltd.) was dissolved quantitatively in distilled water to prepare a series of polymer solutions in different concentrations. The turbidity method was then explored to determine the phase separation temperature through both heating and cooling procedures.

Preparation of Crosslinked Poly(*N*-propionylethyleneimine) by Irradiation

The aqueous solutions of poly(*N*-propionylethyleneimine) with concentrations from 5 to 20 wt % were prepared in 5-mL tubes. Nitrogen gas was used to protect against oxygen retarding polymerization. These tubes were stuffed with rubber covers and were then radiated by a γ -ray (supported by Shanghai Hexin Radiation Factory) with a series of radiation dosages from 10 to 150 kGy. These samples were all crosslinked, forming transparent hydrogels (I) with different strengths.

Preparation of IPN of Poly(*N*-propionylethyleneimine)–Polyacrylamide

The acrylamide monomer was quantitatively added into the tubes containing aqueous solutions of poly(*N*-propionylethyleneimine) with different concentrations and a 1 : 2 ratio of acrylamide to poly(*N*-propionylethyleneimine). Nitrogen gas was also used as the protective atmosphere. These samples were then stuffed with rubber covers and initiated to polymerize by radiation with a γ -ray with various radiation dosages from 10 to

150 kGy to form muddy IPN hydrogels (II) in the water medium.

Determination of Swelling Ratio of Hydrogels (I) and IPN Hydrogels (II)

During the preparation of hydrogels (I) and (II), the produced linear polymer was not removed. The linear polymer left in the hydrogel affects the swelling ratio and the strength of the hydrogel, but it hardly affects the phase transition. The latter is the focus of this article.

A small piece of hydrogel (I) or IPN hydrogel (II) taken directly from each tube (experiments 2 and 3) was infused in water at various temperatures for a long time to reach the swelling equilibrium. Then the relative swelling ratio Q at a given temperature was defined as follows:

$$Q = W_w/W_d$$

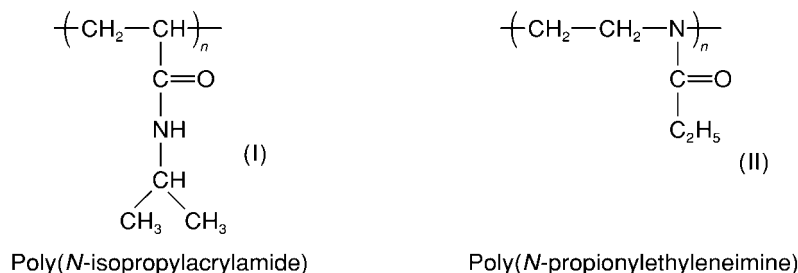
where W_w is the wet weight of the swollen sample and W_d is the dried weight of the same piece dried in a vacuum at 80°C for 24 h. The Q was then plotted as a function of temperature to show a phase graph. The critical phase separation temperature could be determined from this phase graph as the temperature at and from which the Q descends consumedly.

RESULTS AND DISCUSSION

Thermal Phase Transition of Poly(*N*-propionylethyleneimine)–Water System

The poly(*N*-isopropylacrylamide) hydrogel swells at a lower temperature and shrinks at a higher temperature and changes abruptly in volume at about 33°C (LCST).^{8–11} A hydrogen bond is responsible for the gel's absorption of water at a lower temperature, causing the volume of the gel expansion, rather than hydrophilic interaction. And dissociation of the hydrogen bond leads to exclusion of water; therefore, the gel shrinks as the temperature is raised.

The poly(*N*-propionylethyleneimine) [Scheme 1(II)] bears some common points to poly(*N*-isopropylacrylamide) [Scheme 1(I)] but differs in some others. The common point is that there is an amide group —CON— in structures I and II, which is able to form a hydrogen bond with water. So the linear poly(*N*-propionylethyleneimine) is soluble in water at a low temperature. As the



Scheme 1 The formulas for structures I and II.

temperature rises the hydrogen bond dissociates and the interaction of the polymeric molecules leads to phase separation of the polymer–water system. So the linear poly(*N*-propionylethyleneimine) exhibits an LCST as does the poly(*N*-isopropylacrylamide).

As for their differences there is a different charge density on the oxygen atom in structures I and II. In fact, the charge density on the oxygen atom in structure II is higher than in structure I. The reason is that the charge on the nitrogen atom attaching the two —CH₂— (excluding the stronger electron) in structure II is more than that on the nitrogen atom attaching one =CH— (excluding the weaker electron) in structure I, and it transfers to the oxygen in structure II more than in structure I through the configuration effect of the double bond in the carbonyl. Thereby, the ability of the corresponding oxygen in structure II to form a hydrogen bond with water is stronger than that in structure I. Thus, the LCST of the poly(*N*-propionylethyleneimine)–water system should be higher than that of the poly(*N*-isopropylacrylamide)–water system.

Figure 1 shows a curve of the phase separation temperature versus the concentration of the linear poly(*N*-propionylethyleneimine)–water system. Note that the phase separation temperature has a inverse bell-shaped polymeric concentration profile and an LCST at about 61°C. This is counter to the common polymer–solvent system that has a bell-shaped polymeric concentration temperature and a higher critical solution temperature (HCST).

Phase Transition Temperature of Poly(*N*-propionylethyleneimine) Hydrogel

It is well known that the phase transition temperature of a polymeric hydrogel should be the same as that of the aqueous solution of the uncrosslinked original polymer, which is concerned

with the concentration of the polymer and has a critical value (here the LCST not HCST). The question is what temperature (either the phase separation temperature or the LCST correlated to the concentration of the polymer) should the phase transition temperature of the hydrogel under discussion here correspond to. The experiments (Fig. 2) showed that the three hydrogels in the same swelling ratio *Q* (about 7%) obtained from the different aqueous concentrations of the original uncrosslinked poly(propionylethyleneimine) that had the same irradiation dosage had the same phase transition temperature (about 61°C), as did the linear polymer–water system and were independent of the original concentration of the polymer. The experiments (see Fig. 3) also showed that the three phase transition temperatures of the three hydrogels with different degrees of crosslinking (using different irradiation dosage and therefore different swelling ratios *Q*) had the same values (about 61°C) and were independent of the original concentration of the polymer and irradiation dosage for the aqueous solution of the polymer. So why is the phase tran-

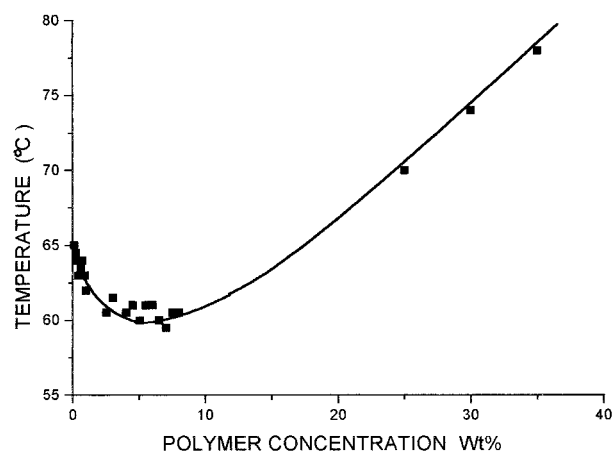


Figure 1 The phase graph of the aqueous solution of poly(*N*-propionylethyleneimine).

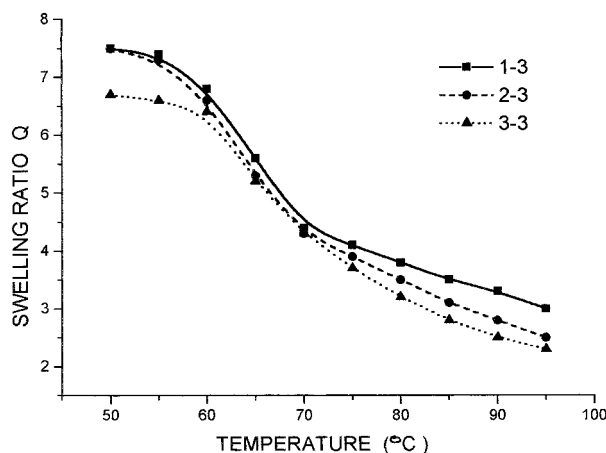


Figure 2 The dependence of the swelling ratio of the hydrogels on temperature. The radiation dosage is 150 kGy. The concentrations (wt %) of the aqueous solution of the polymer for irradiation are 5, 10, and 20 for samples 1-3, 2-3, and 3-3, respectively.

sition temperature of the hydrogel always the same as the LCST of the aqueous solution of the uncrosslinked polymer and independent of the swelling degree (depending on the crosslinking degree determined by the radiation dosage)? This is a subject worthy of further theoretical research.

Component-Dependent Phase Transition Temperature of IPN Hydrogel

It can be conjectured that a mixture of the aqueous solution of the poly(*N*-propionylethylene-

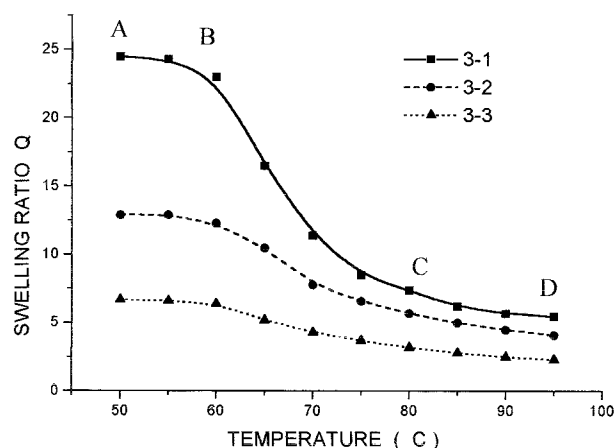


Figure 3 The dependence of the swelling ratio of the hydrogels on temperature. All the concentrations of the aqueous solutions of the polymer for irradiation are the same (20 wt %) and the radiation dosages (kGy) are 50, 100, and 150 for samples 3-1, 3-2, and 3-3, respectively.

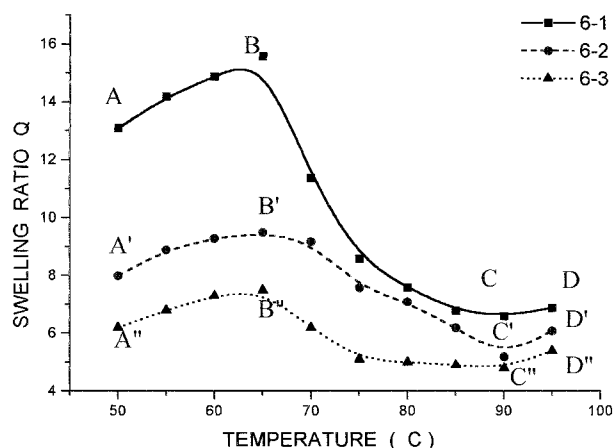


Figure 4 The dependence of the swelling ratio of the IPN hydrogels on temperature. The concentrations of the aqueous solutions of the monomer-polymer complex for irradiation are all 20 wt % and the radiation dosages (kGy) are 50, 100, and 150 for samples 6-1, 6-2, and 6-3, respectively.

imine) and acrylamide monomer can form a crosslinked IPN hydrogel under γ -ray irradiation. The IPN hydrogel should be in the homogeneous phase in the macrocosm and heterogeneous in the microcosm. Thus, the macrocosmic properties, for example, the swelling degree, of the IPN hydrogel should be a linear addend of the microcosmic properties of the separated components contained in the hydrogel. Based on this, let us try to make a conservation of the experimental results in Figures 3 and 4.

The polyacrylamide contained in the IPN hydrogel will cause the curve of the swelling ratio against the temperature to have two changes. One is curve shaped compared with no polyacrylamide in the hydrogel. Another is a shift of the phase transition temperature from lower to higher. It can be seen from Figure 3 that the middle part of the curve (any one of the three curves) is a sloped line and the two sides of it are approximately level lines. The abrupt turn point, B, of the swelling ratio of the poly(*N*-propionylethyleneimine) hydrogel versus temperature lies at about 61°C, which is the same as the LCST of the poly(*N*-propionylethyleneimine)-water system. In Figure 4 there is a peak (point B) on the left side and a valley (point C) on the right of the three curves. The abrupt turn point B of the swelling ratio of the IPN hydrogel against temperature is at about 65°C; the phase transition temperature of the IPN hydrogel shifts to 65°C from the 61°C of the poly(*N*-propionylethylene-

imine) hydrogel because of the incorporation of polyacrylamide in the IPN hydrogel. So for the existing peak (point B) and valley (point C) of the curve in Figure 4, this can be explained by the linear addend method mentioned above. It is well known that the swelling degree of the polyacrylamide hydrogel increases while the poly(*N*-propionylethyleneimine) hydrogel decreases (see Fig. 3) with rising temperature.

At the AB segment of the curve in Figure 4 the swelling ratio (Q_1) of the component poly(*N*-propionylethyleneimine) decreases slightly (refer Fig. 3) while the ratio (Q_2) of the component polyacrylamide increases more with the temperature. So the total swelling ratio Q offsets the Q_1 but still increases; namely, the AB segment goes up. As the temperature reaches 65°C, the increment (positive) of the Q_2 equals that (negative) of the Q_1 ; namely, the total increment of the Q equals zero and the Q reaches the peak value at 65°C. When the temperature exceeds 65°C, the shrinking rate of the component poly(*N*-propionylethyleneimine) increases suddenly but the swelling rate of the component polyacrylamide remains the same as before; the large shrinking amplitude of poly(*N*-propionylethyleneimine) as the temperature rises is offset slightly by the small swelling amplitude of the polyacrylamide. Thus, the curve of the total swelling ratio versus temperature still goes down quickly until reaching the valley (point C). After the point C the swelling ratio Q_2 of the polyacrylamide increases continuously while the swelling ratio Q_1 of the poly(*N*-propionylethyleneimine) is almost un-

changed (refer to Fig. 3). So the curve of the total swelling ratio Q of the IPN hydrogel against temperature therefore goes up again at the CD segment. Based upon the facts mentioned above, we could make a conclusion that by using the incorporation of a second component to form an IPN, the LCST of a crosslinked IPN hydrogel can be adjusted. This can be put to some particular uses.

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