Swelling–Shrinking Hysteresis of Poly(*N*-isopropylacrylamide) Gels in Sodium Dodecylbenzenesulfonate Solutions

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ABSTRACT: The swelling and shrinking behaviors of a series of poly(*N*-isopropylacrylamide) (PNIPA) hydrogels are studied in aqueous solutions of sodium dodecylbenzenesulfonate (SDBS). Between 0 and 3 mol % 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS) is used as an ionic comonomer in the hydrogel synthesis. It is shown that the collapsed PNIPA gels in water at 52°C start to swell above a critical SDBS concentration in the external solution. This critical concentration decreases as the ionic group content of PNIPA gel increases. A comparison of the swelling and shrinking experiments in SDBS solutions indicates strong hysteresis behavior of PNIPA gels. A more diluted solution is required to make a swollen gel start to reshrink than to cause gel swelling. The results show strong attractive forces between the isopropyl groups of the PNIPA network and the DB groups of SDBS molecules. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1228–1232, 2002

Key words: poly(*N*-isopropylacrylamide) gels; hydrogels; swelling; sodium dodecylbenzenesulfonate

INTRODUCTION

A poly(*N*-isopropylacrylamide) (PNIPA) hydrogel swollen in water is a typical temperature-sensitive gel that exhibits a volume-phase transition in response to temperature changes.[1] Several recent studies focused on the effects of various additives on the swelling behavior of PNIPA gels.[2–5] Kokufuta et al. showed that the addition of ionic surfactants significantly affects the temperature-induced volume-phase transition of nonionic PNIPA gels.[6,7] The transition temperature and the extent of volume change during the transition both increased with increasing concentration of ionic surfactants in the external solution. These results suggest that the PNIPA network absorbs ionic surfactants because of the attractive hydrophobic interactions between the surfactant tail and the hydrophobic (isopropyl) groups of the network. Indeed, it was found that the concentration of ionic surfactant inside the gel is much higher than that in the external solution.[7,8] Because the absorption of ionic surfactant by the nonionic gel converts the gel into an ionic gel, the nonionic PNIPA–ionic surfactant systems exhibit swelling properties that are typical for ionic PNIPA hydrogels.[6]

Although extensive works are reported in the literature on systems consisting of ionic surfactants and hydrogels,[8–13] none of these works have

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yet reported on the reversibility of the swelling behavior of hydrogels in surfactant solutions. To clarify whether the surfactant-induced swelling transition of PNIPA gels is reversible, we conducted swelling and shrinking experiments with PNIPA gels immersed in surfactant solutions. Sodium dodecylbenzenesulfonate (SDBS) was used as an anionic surfactant in the swelling experiments. A series of PNIPA hydrogels in the form of rods were prepared by free-radical crosslinking copolymerization of *N*-isopropylacrylamide (NIPA) and *N*,*N*′-methylenebisacrylamide (BAAm) monomers. 2-Acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS) was used as the ionic comonomer of NIPA in the gel synthesis. PNIPA hydrogels at 52°C in water were subjected to swelling and shrinking experiments in SDBS solutions of various concentrations.

EXPERIMENTAL

Materials

The monomer NIPA (Aldrich), the crosslinker BAAm (Fluka), the initiator ammonium persulfate (APS, Fluka), and the accelerator *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Aldrich) were used as received. The AMPS (AMPS-H^+, Merck) was crystallized from boiling methanol. AMPS stock solution was prepared by dissolving 20 g of AMPS-H^+ in about 40 mL of distilled water and 10 mL of a 30% NaOH solution was added to this solution under cooling. Then the solution was titrated with 1*M* NaOH to pH 7.00; finally, the volume of the solution was completed to 100 mL with distilled water. One milliliter of AMPS stock solution thus prepared contained 0.966 mmol AMPS. The SDBS was prepared by mixing equimolar amounts of dodecylbenzenesulfonic acid (Henkel) and NaOH (Merck) in aqueous solutions.

Gel Synthesis

PNIPA gels were prepared by free-radical crosslinking copolymerization of NIPA, AMPS, and BAAm in aqueous solutions. The initial monomer concentration and the crosslinker ratio (molar ratio of the crosslinker BAAm to the monomers NIPA and AMPS) were fixed at 8 g/100 mL and 1/85, respectively. The polymerization reactions were initiated using 3.5 m*M* APS and 0.24% (v/v) TEMED.

The NIPA (4 g) and BAAm (0.064 g) were dissolved in 50 mL of distilled water and the solution was purged with nitrogen gas for 10 min. Then 5 mL of this solution was mixed with APS (4 mg) and various volumes (0–0.15 mL) of the AMPS stock solution. After the addition of TEMED (0.012 mL), the solution was transferred to small 5.5-mm diameter tubes. After 1 day of polymerization at 21°C, the gels were cut into specimens of approximately 10-mm length and immersed in a large excess of water to wash out any unreacted monomers and the initiator. A series of PNIPA gels were prepared in this way at AMPS contents between 0 and 3 mol %.

Swelling Measurements

For the swelling measurements the PNIPA gel samples were immersed in vials filled with water or aqueous SDBS solutions. Aqueous SDBS solutions were prepared by the dilution of a 61.35 m*M* SDBS stock solution with various volumes of water. The volume of the SDBS solutions in the vials was much larger than the gel volume so that the concentration of the solution was practically unchanged. The vials were set in a temperature-controlled bath with a variance of ±0.1°C. In order to reach the equilibrium degree of swelling, the gels were immersed in solutions at least for 1 week, during which the solutions were refreshed every other day. The diameter of the gel samples was measured by a calibrated digital compass. The measurements were also conducted using an image analyzing system consisting of a stereo microscope (Olympus Stereomicroscope SZ), a video camera (TK 1381 EG), and a Pentium II PC with data analyzing software (BS-200 BAB). The equilibrium volume of the gel normalized with respect to its volume in the collapsed state (V_r) was calculated as

$$V_r = (D/D_c)^3$$

where D is the diameter of the gel after equilibrium swelling and D_c is the diameter of the collapsed gel in water at 52°C.

RESULTS AND DISCUSSION

Figure 1 illustrates the dependence of the equilibrium degree of swelling of PNIPA gels with 0–3 mol % AMPS on the swelling temperature. The swelling degrees were expressed using the vol-

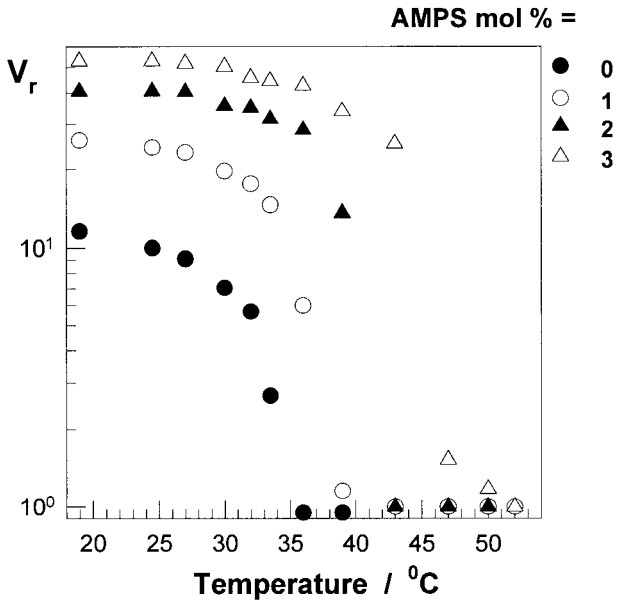

Figure 1 The equilibrium reduced volume (V_r) of PNIPA gels shown as a function of the swelling temperature.

ume of the gel samples normalized by the fully collapsed volume V_r. It is seen that all the gels undergo a volume-phase transition between the swollen and collapsed states at a definite swelling temperature. Increasing the AMPS content of the networks (i.e., increasing the degree of ionization) increases the volume of the gels in the swollen state and shifts the transition temperature toward higher values. This swelling behavior is expected and was also reported in many previous works for strong polyelectrolyte temperature-sensitive hydrogels.[14] At low temperatures the osmotic pressure due to the Na^+ ions of the AMPS units inside the gel dominates over the hydrophobic attractive interactions between the isopropyl groups of the PNIPA gel. As a result, the gels are in a highly swollen state at low temperatures. With rising temperature the extent of hydrophobic interactions increases and, above a critical temperature, these hydrophobic interactions dominate and lead to the collapse of the PNIPA gel. Accordingly, the higher the ionic group content of the PNIPA network, the higher the osmotic pressure of counterions inside the gel so that a higher temperature is required to balance this swelling pressure by hydrophobic interactions and to induce a volume-phase transition to the collapsed state.

The collapsed PNIPA gels at 52°C ($V_r = 1$) were immersed in aqueous SDBS solutions of various concentrations. Two sets of experiments were carried out: swelling experiments and shrinking experiments. In the swelling experiments the collapsed gels in water were transferred in aqueous SDBS solutions at 52°C, which contained increasing amounts of SDBS. In the shrinking experiments the collapsed gels in water were immersed into a 10 m*M* SDBS solution at 52°C. After attaining the equilibrium state, the SDBS concentration in the solution was gradually decreased and finally the gels were transferred to pure water. The results are collected in Figure 2, which shows the reduced volume of the gel V_r plotted as a function of the SDBS concentration in the external solution. The experimental data obtained by swelling and shrinking experiments are shown by filled and open symbols, respectively.

It is seen that the PNIPA gels in the collapsed state at 52°C start to swell above a critical SDBS concentration (Fig. 2). This critical concentration is about 1.5 m*M* for the nonionic PNIPA gel, which is close to the critical micelle concentration of SDBS (1.2 m*M* at room temperature). The critical SDBS concentration decreases as the ionic

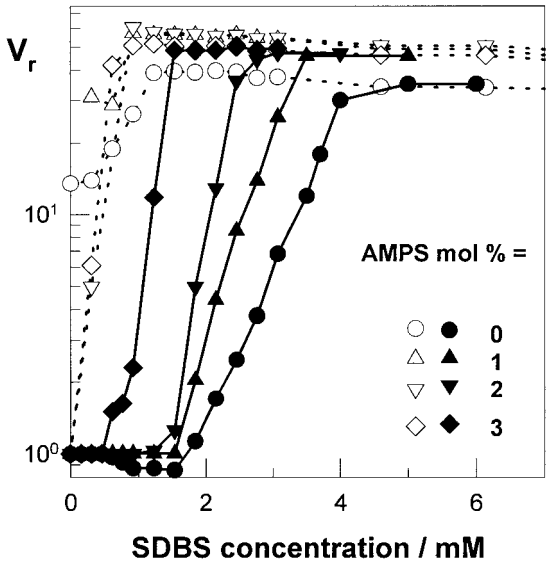

Figure 2 The equilibrium reduced volume (V_r) of PNIPA gels at 52°C shown as a function of the SDBS concentration of the external solution. In the shrinking experiments the volume of PNIPA gel with 1% AMPS in water is not given in the figure because of the large nonhomogeneity of the collapse in water (see Fig. 3). The volume of the nonionic PNIPA in water is calculated from the averages of the measurements made at both ends and in the middle of each gel sample. The experimental data obtained by (●, ▲) swelling and (○, △) shrinking experiments are shown.

group content of the PNIPA network increases and becomes 0.5 m*M* for the PNIPA network with 3 mol % AMPS. Furthermore, increasing the SDBS concentration beyond its critical value leads to an increase in the gel volume until a limiting value is reached.

Somewhat different behavior was observed in the shrinking experiments (i.e., by decreasing the SDBS concentration in the outer solution starting from 10 m*M*, Fig. 2). In this case the gels that are swollen in 10 m*M* surfactant solution remain in the swollen state up to about 1 m*M* SDBS. Thereafter they start to deswell with a further decrease in the SDBS concentration. A comparison of the swelling and shrinking curves in Figure 2 indicates strong hysteresis behavior of the PNIPA gels. A more diluted solution was required to make a swollen gel start to reshrink than to cause the gel to swell. Figure 2 also shows that the extent of hysteresis increases with decreasing ionic group content of the PNIPA network. We observed in the shrinking experiments that the nonionic PNIPA gel or the PNIPA gel with 1 mol % AMPS does not shrink homogeneously even after 2 weeks of equilibration time in pure water. For example, Figure 3(A) shows a micrograph taken from the gel sample with 1 mol % AMPS in water at 52°C. Both ends of the gel sample underwent volume collapse in pure water whereas the central portion of the gel remained in the swollen state. However, the gels with higher ionic group contents (2 or 3 mol % AMPS) fully collapsed in water [Fig. 3(B)].

The addition of SDBS in the external solution of the collapsed PNIPA gel leads to the preferential absorption of SDBS molecules onto the polymer network.[8] Simultaneously, the counterions (Na^+) of SDBS penetrate into the gel phase because of the condition of electroneutrality. As a result, increasing the SDBS concentration also increases the counterion concentration inside the gel and, above a critical SDBS concentration, the swelling pressure of the counterions overbalances the hydrophobic attractive interactions in the collapsed gel and leads to gel swelling. Thus, the critical SDBS concentration for the onset of gel swelling shown in Figure 2 corresponds to a critical point at which the attractive forces between the isopropyl groups are balanced by the osmotic pressure of mobile ions (Na^+) of both the AMPS units and the SDBS molecules. Accordingly, the total counterion concentration inside the gel is equal to the sum of the AMPS and SDBS concentrations in the gel phase. Increasing the AMPS content also increases the total counterion concentration so that the gel starts to swell at a lower SDBS concentration (i.e., the critical SDBS concentration shifts to smaller values). The strong hysteresis behavior of the PNIPA gels shown in Figure 2 indicates strong attractive forces between the isopropyl groups of the PNIPA network and the dodecylbenzene groups of the SDBS molecules. The results show that a nonionic matrix together with a high temperature enhance SDBS–PNIPA interactions and the SDBS-bound PNIPA gel remains stable even in pure water.

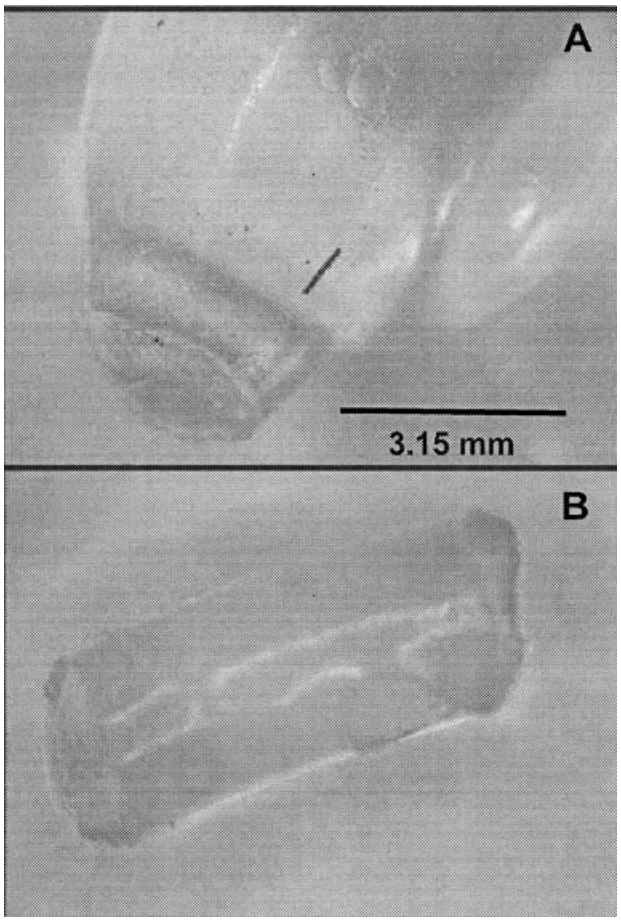

Figure 3 Micrographs of PNIPA gels with (A) 1 and (B) 2 mol % AMPS at 52°C in water. The gel samples are from the shrinking experiments.

CONCLUSION

We observed hysteresis behavior of PNIPA gels in SDBS solutions above the lower critical solution temperature of PNIPA. The decrease of the ionic group content of PNIPA gels increases the extent

of hysteresis. The results also show that the two opposite effects in PNIPA gel swelling, namely, the hydrophobic attractive interactions and the osmotic pressure of counterions, can be regulated by changing the swelling temperature and SDBS concentration, respectively, as external independent variables. The attractive interactions between PNIPA and SDBS at high temperature were found to be strong enough to keep SDBS-bound PNIPA gels stable even in water. The determination of the amount of SDBS in SDBS-bound PNIPA gels is in progress.

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