

Phase Behavior of *N*-Isopropylacrylamide/Acrylic Acid Copolymer Hydrogels Prepared with Ultrasound

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ABSTRACT: *N*-Isopropylacrylamide/acrylic acid copolymer hydrogels were synthesized with ultrasound. The thermoresponsive phase behaviors of gels synthesized with ultrasound (US gels) were investigated and compared with those of gels synthesized in the absence of ultrasound (FR gels). The US gels showed thermoresponsive swelling behavior with a large hysteresis over a wide range of temperatures around its phase-transition temperature. The hysteresis became larger with an increasing copolymerized acrylic

acid content. The US gels were also characterized from the viewpoint of chemical, hydration, and macroscopic physical structures. Little difference was observed in the chemical and hydration structures of the FR gels and US gels. The macroscopic physical structure of the US gels was, however, distinct from that of the FR gels. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2449–2452, 2003

Key words: hydrogels; phase behavior; ultrasound

INTRODUCTION

Stimuli-sensitive polymer hydrogels have been attracting much attention because of their scientific and engineering importance. Many researchers have reported the phase behaviors of gels in various environments in the past 2 decades. *N*-Isopropylacrylamide (NIPPAm) gel is a stimuli-sensitive hydrogel that undergoes a volume-phase transition at a lower critical solution temperature through a hydrophobic interaction.^{1–4} The thermoresponsive swelling behaviors of NIPPAm and its copolymer gels have been studied as functions of the comonomer,^{5–9} preparation temperature^{10–12} additives,^{13–16} and network structure.^{17–20} The effect of a synthetic method of the NIPPAm gel on its thermoresponsive swelling behavior has also been studied for synthesis by γ -rays,²¹ plasma,²² and freezing followed by hydration.²³

Recently, ultrasound has attracted much attention in the fields of inorganic and organic material synthesis because of its specific effects on material processing.^{24–26} It is widely recognized that the effects caused by ultrasound can be mainly attributed to (1) the rapid movement of fluids due to the variation of sonic pressure, which accelerates mass transfer; (2) the formation and collapse of microbubbles (cavitation), creating localized high-temperature and high-pressure

conditions; and (3) microstreaming, in which a large amount of vibrational energy is applied to small volumes.²⁷ However, the effects of ultrasound on the synthesis and phase behavior of hydrogels have not been studied well.

In this study, the synthesis of *N*-isopropylacrylamide/acrylic acid (NIPPAm-AA) copolymer hydrogels with ultrasound was performed. The thermoresponsive phase behavior of the ultrasonically synthesized hydrogels (US gels) was studied and compared with the phase behavior of NIPPAm-AA hydrogels synthesized by a conventional method in the absence of ultrasound (FR gels). The phase behaviors of the gels were examined from the viewpoint of the chemical and hydration structures of the gels. The macroscopic physical structures of the gels in their dry state were also observed.

EXPERIMENTAL

A mixture (400 mmol) of NIPPAm (Kojin Co., Ltd., Tokyo, Japan) and acrylic acid (AA) was dissolved in 50 mL of dimethylformamide (DMF) for the preparation of an 8000 mM solution of NIPPAm-AA (solution A). Solutions (800 mM) of the *N,N'*-methylenebisacrylamide (BIS) crosslinker (solution B) and azobisisobuthronitryl (solution C) were prepared with DMF. Solutions A, B, and C were then mixed for the preparation of the reaction mixture with a volume ratio of A/B/C = 10:1:2.5. The preparation conditions are summarized in Table I. One set of the reaction mixtures was polymerized at 333 K for 6 h in a temperature-controlled water bath in the absence of ultra-

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TABLE I
Preparation Conditions of the Gels

Sample	AA/(NIPPAm-AA) (mol/mol)	BIS/(NIPPAm-AA) (mol/mol)	Synthesis	Swelling volume (V/V_{278K} of FR2-gel)	T_p (K)
FR2	0.02	0.01	333K (6 h)	1.00	301.5
FR10	0.10	0.01	333K (6 h)	1.17	299.6
FR20	0.20	0.01	333K (6 h)	1.33	297.8
US2	0.02	0.01	Ultrasound (10 min) + 333 K (6 h)	1.53	302.2
US10	0.10	0.01	Ultrasound (10 min) + 333 K (6 h)	2.00	300.7
US20	0.20	0.01	Ultrasound (10 min) + 333 K (6 h)	2.90	296.8

sound (FR gels). Another set of the reaction mixtures was polymerized with ultrasound (US gels). Sonic energy was provided by an ultrasonicator (Sonifier 450D, Branson Sonic Power Co., Tokyo, Japan), which generated 20-kHz ultrasound waves. A sonic probe made of Ti (10 mm in diameter and 100 mm long) was dipped into the reaction mixtures. The reaction mixtures were exposed to ultrasound for 10 min at room temperature under ambient condition without any other experimental control. A vigorous mixing of the reaction mixtures was induced by the application of ultrasound. The temperature of the reaction mixtures increased up to 333 K within 6 min by sonication. The gelation of the reaction mixtures occurred quickly after about 6 min of sonication. The gelation samples were kept at 333 K for 6 h after 10 min of sonication. All the synthesized gels were crushed into pieces and washed with a large amount of distilled water to wash away residual chemicals. The gels were sieved to determine the particle sizes of the gels (between 250 and 425 μm) after drying at 363 K for 24 h. Fourier transform infrared spectra of the dried gels were obtained with an FT/IR-610 (Jasco, Hashioji, Japan) with a KBr pellet technique at a resolution of 2 cm^{-1} . Scanning electron microscopy (SEM) images of the gels freeze-dried *in vacuo* in liquid nitrogen were obtained.

The amount of copolymerized AA in the gels was estimated with an adsorption test of iron ions.²⁸ Na-exchanged synthesized gels were used to confirm the amount of copolymerized AA in each gel. The synthesized gels were swelled in a large amount of a 1M NaCl aqueous solution for 24 h, and this was followed by washing with a large amount of distilled water and drying at room temperature. The dried gels (0.5 g) were put into a 20-mL aqueous solution of FeCl_3 containing an equivalent amount of Fe ions 1.2 times greater than the introduced amount of AA in the gels at the preparation stage. The initial molar concentration (C_{ini}) of Fe^{3+} ions in the solution was determined in advance to attain the maximum adsorption of the gels. The slurries were kept at room temperature for 24 h with shaking to complete the ion exchange between the Na^+ ions in the gels and the Fe^{3+} ions. The molar concentration of Fe^{3+} ions in the solution after equilibrium adsorption (C_{eq}) was measured by induc-

tively coupled plasma emission spectrophotometry. The amounts of AA (q_{AA} ; mol/g of dry gel) in the gels were calculated by a mass balance based on the following equation:

$$q_{\text{AA}} = 3(C_{\text{ini}} - C_{\text{eq}})V/w_{\text{gel}}$$

where V and w_{gel} are the solution volume (L) and weight (g) of the dried gel, respectively.

The thermoresponsive swelling behavior of the synthesized gels was observed with a packing column method.²⁹ The dried gels (0.1 g) were placed in flat-bottom glass tubes filled with 10 mL of distilled water. The glass tubes with the gels were kept in a temperature-controlled water bath for 24 h. The swelling volume of the gels after 24 h at each temperature was measured from the packing height of the gels. The swelling ratios were calculated from the packing height between the swelling gel (V) and the gel at 278 K (V_{278K}). Differential scanning calorimetry (DSC) heating charts of the synthesized swelling gels were obtained with a DSC2000 (Seiko Instruments, Chiba, Japan) to evaluate the dehydration behavior of the synthesized gels. The scanning temperature range and scanning rate were 278–353 K and 3 K/min, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of gels synthesized with and without ultrasound (FR20 and US20). Little difference can be observed in the IR spectra between the FR gels and US gels. This indicates that the sonication did not induce a significant chemical modification of the constituents of the gels. The results of the adsorption tests showed that AA was copolymerized to the extent to which it was introduced during the preparation stage in both FR and US gels. Figure 2 shows SEM photographs of gels freeze-dried *in vacuo* with liquid nitrogen. The gel synthesized with ultrasound showed a network with small branches on the surface; this was not observed in the gel synthesized without ultrasound. This feature of US gels may be induced by sonication during the synthesis. It is thought that the

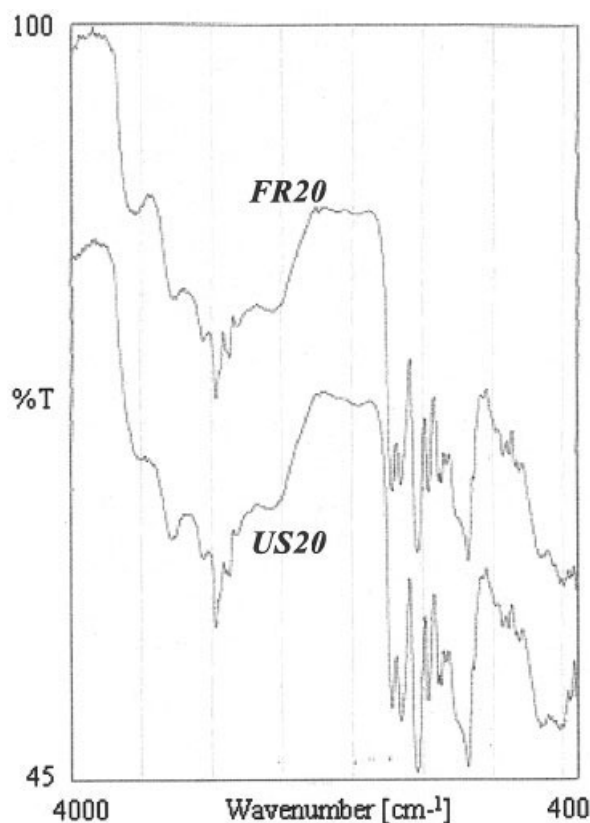


Figure 1 IR spectra of US and FR gels.

structures of gels in the dry state reflect the network structures in the swelling state containing water.

Figure 3(a,b) shows the thermoresponsive swelling behaviors of the gels as a function of the solution temperature. The swelling behavior of FR gels is well known. Contrary to the swelling behavior of the FR gels shown in Figure 3(a), the US gels showed a specific swelling behavior with a larger hysteresis, as shown in Figure 3(b). The US gels showed larger swelling volumes than the FR gels for equivalent common temperatures and AA contents, as shown by the swelling volume ratios at 278 K (V/V_{278K} for the FR2 gel) in Table I. These results should be due to a lower degree of crosslinking in the US gels than expected from the introduced amount of the crosslinker during

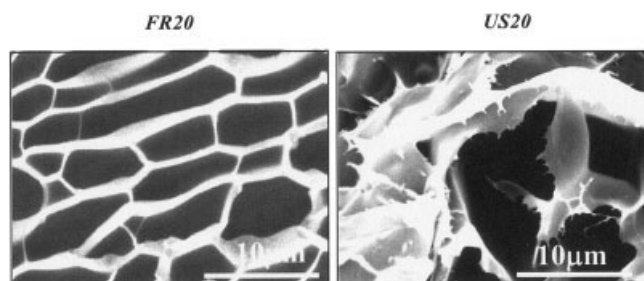


Figure 2 SEM images of synthesized gels freeze-dried *in vacuo* in liquid nitrogen.

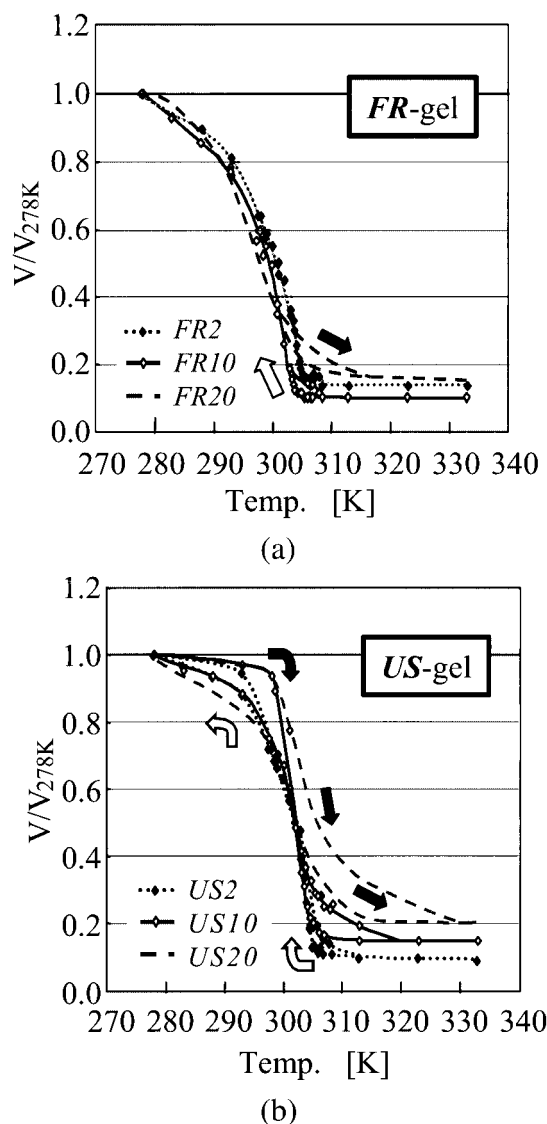


Figure 3 Thermoresponsive swelling behavior of the synthesized gels: (a) FR gels and (b) US gels.

the preparation stage. The degrees of crosslinking of the gels calculated with the Flory–Rehner equation³⁰ were 0.024 mol/dm^3 for FR20 and 0.0034 mol/dm^3 for US20. The hysteresis in the US gel became larger with an increasing AA content.

Figure 4 shows DSC heating charts of the synthesized gels. The phase-transition (dehydration) temperatures (T_p 's) of the gels were determined from the endothermic dehydration main peaks of the gels and are summarized in Table I (T_p is defined as the cross-point between the baseline and slope of the peak and is shown as dots in the figure). The decrease of T_p with the AA content was observed in both gels. The decrease of T_p was due to interpolymer and/or intrapolymer hydrogen bonding between carboxyl groups of AA and amide groups of NIPPAM in the gel.²⁹ The US gels showed sharp dehydration endothermic peaks contrary to the broad endothermic peaks with

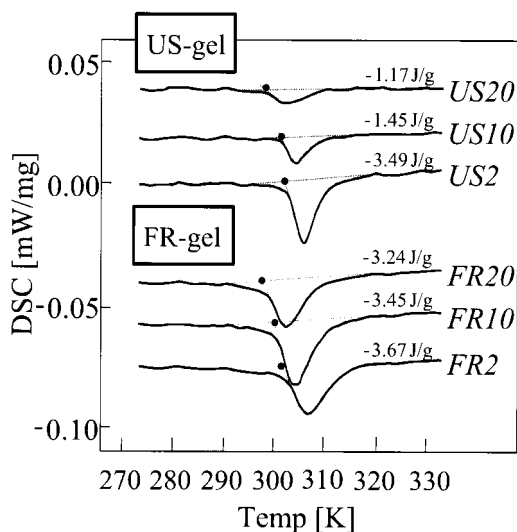


Figure 4 DSC heating charts of synthesized gels.

shoulders at the postedge of the peaks in the FR gels. The US gels showed a moderate collapse depending on the content of AA in a higher temperature region (303–325 K) above the temperature with their steepest collapse [Fig. 3(b)]. An endothermic peak accompanied by a moderate collapse in the higher temperature region was not observed in the DSC charts of the US gels shown in Figure 2. If water molecules existing in a US gel in the higher temperature region hydrate to the network of the gel, an additional endothermic peak or tailing of the main endothermic peak corresponding to dehydration of the water molecules may appear in the higher temperature region (>305 K) in the DSC chart because of the stronger interaction of hydration. The water molecules still existing inside the gel in the higher temperature region may be free water. The US gels may form a network structure with a large interpolymer distance with a low elasticity in the swelling state because of the low crosslink density, and this results in a moderately collapsing phase behavior with no endothermic peak of dehydration in the DSC heating chart in the higher temperature region. The swelling in the cooling process, lower than that in the heating process, at a low temperature below the T_p may also be the result of the network nature of the US gels. The heterogeneity of the network is another possible reason for the specific phase behavior of the US gels. Further research into the effects of ultrasound synthesis on the phase behaviors of gels is now in progress.

CONCLUSIONS

NIPPAm-AA copolymer gels can be synthesized with ultrasound. The thermoresponsive phase behaviors of gels synthesized with ultrasound show a large temperature-dependent hysteresis of their swelling with an increase in the AA content that can be observed over a wide range of temperatures around their T_p . Ultrasound can be used to create specific phase behaviors of gels.

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