## Volume Phase Transition Behavior of *N*-Isopropyl Acrylamide–*N*-Cyanomethyl Acrylamide Copolymer Gel Particles: The Effect of Crosslinking Density

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ABSTRACT: We prepared submicron-sized *N*-isopropyl acrylamide (NIPA)–*N*-cyanomethyl acrylamide (NCMA) copolymer gel particles by precipitation polymerization. Volume phase transition behaviors of gel particles with various compositions and crosslinking density were observed by using photon correlation spectroscopy (PCS). The experimental data showed that both the volume transition temperature and the swelling ratio of copolymer gel particles were varied with the mole ratio of NCMA and NIPA. We compared the swelling behaviors of given systems with the thermodynamic model based on the extended Flory–Huggins theory. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1091–1099, 1999

**Key words:** *N*-isopropyl acrylamide; *N*-cyanomethyl acrylamide; submicron-sized copolymer gel particle; swelling behavior

## INTRODUCTION

About 30 years ago, Dušek and Patterson<sup>1</sup> predicted theoretically that under suitable conditions, two polymeric phases might coexist in a network through an analysis of a classical Flory– Huggins equation for swelling equilibrium of polymer networks. Later, Tanaka et al.<sup>2,3</sup> observed a first-order transition in ionized gels and presented a theory of the phase transition with ions. Subsequently, Ilavsky performed a similar experiment.<sup>4</sup> Recently, extensive progress has been made since a hydrogel has widespread application, such as recyclable absorbents, sensors, and specialized separation systems.<sup>5–7</sup> Especially, temperature and/or pH-sensitive gels have been developed as drug delivery systems in the human body, where the gel releases a drug gradually or suddenly at a particular location in the body in response to the change of temperature and/or pH around the gel. For such technical applications of the phenomenon, it is naturally desirable that its response time be as short as possible.

Thermodynamically, both the free energy of mixing and the free energy of elasticity govern the swelling equilibrium of nonionic gel. In case of the ionic gel, the free energy of the osmotic pressure of counterions is added. Many research groups<sup>8-11</sup> studied a number of models for the swelling equilibria of gels.

It has been known that many gels undergo reversible and discontinuous volume changes in responsive to changes in temperature,<sup>2,12</sup> pH,<sup>3</sup> and ultraviolet  $(UV)^{13,14}$  and visible light.<sup>15</sup> A poly(*N*-isopropyl acrylamide) (NIPA) gel, which is approved by the Food and Drug Administration (FDA), USA, in water, undergoes a volume phase

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transition from swollen to shrunken state by elevating temperature. Its volume transition temperature  $(T_v)$  is around 34°C,<sup>16</sup> which is around the human body temperature. The volume transition of the gel is due to the dissociation of hydrophobic interaction between NIPA and water. The volume transition temperature of the NIPA copolymer gel is varied by the different hydrophobicity of comonomers.

In the past decade, the swelling characteristics of the N-alkylacrylamide gels have been observed by many groups through copolymerization with comonomers, which have different hydrophobicities with various conditions.<sup>17–22</sup> Ilmain et al.<sup>23</sup> reported that a phase transition is controlled by cooperative interactions between the molecules, which result from hydrogen bonding in an interpenetration polymer network. Baker et al.<sup>24</sup> reported the effect of initial total monomer concentration (T%) on the swelling behavior of hydrogels. Their experimental results indicated that the network chain interpenetration increased with rising T%. In our previous work,<sup>25</sup> we observed phase behaviors of NIPA-ethyl N-acryloylglycine (ENAG) copolymer gel particles with various compositions and compared the extended Flory-Huggins model with obtained data. The experimental data showed that the volume transition temperature of the NIPA-ENAG copolymer gels decreased with an increase in the mole ratio of the ENAG monomer in the copolymer gel particles.

Our purpose of the present study is to observe swelling equilibria for a series of NIPA–*N*-cyanomethyl acrylamide (NCMA) submicron-sized copolymer gel particles with various compositions. Another purpose of this study is to investigate the effect of crosslinking density on the swelling behavior of copolymer gel particles. All the copolymer particles prepared by the precipitation polymerization showed very narrow size distribution. We measured the hydrodynamic radius of the gel particles using a photon correlation spectroscopy (PCS) technique to determine the swelling ratio of the copolymer gel particles. Experimental results are also compared with the extended Flory–Huggins model.

#### **EXPERIMENTAL**

#### **Materials**

N-isopropyl acrylamide (NIPA) ( $M_W = 113.16$ ) was purchased from TCI (Tokyo). N-cyanomethyl acrylamide (NCMA) was synthesized, and the preparation methods are explained in detail in the later section. N,N'-methylenebisacrylamide (BIS) and ammoniumpersulfate (APS) were purchased from Aldrich Chemical Co. All reagents were used as received. Water was distilled and deionized (DDI water) with ultrapure water system (MILLI-Q<sub>plus</sub>, Millipore, USA).

## Preparation of N-Cyanomethyl Acrylamide

Acryloyl chloride and aminoacetonitrile, purchased from Aldrich Chemical Co. (Milwaukee, WI), were used without further purification.<sup>26</sup> Ethyl acetate and tetrahydrofuran were used after drying over calcium hydride. Silica gel (70– 230 mesh ASTM) was purchased from Merck (Germany).

To a cold solution of aminoacetonitrile hydrochloride (8.33 g, 90 mmol) and sodium hydroxide (7.56 g, 189 mmol) in 30 mL of ethyl acetate and 45 mL of water, acryloyl chloride (8.96 g, 99 mmol) in 90 mL of dry ethyl acetate was added dropwise. The solution temperature was raised to room temperature after 1 h, and the solution was stirred for 5 h. The ethyl acetate layer was separated and dried over anhydrous magnesium sulfate. Ethyl acetate was evaporated, and the product was purified by the chromatography on a silica gel column eluting with hexane–ethyl acetate (1 : 1) to give a pure *N*-(cyanomethyl) acrylamide as a white solid (7.12 g; 72% yield, 62–64°C mp).



## Synthesis of Submicron-Sized Copolymer Gel Particles

Submicron-sized copolymer gel particles were prepared by precipitation polymerization in DDI water. BIS was used as a crosslinking agent. APS was used as an initiator. Nonionic surfactant, Tween20, which does not affect the swelling behavior of nonionic gel,<sup>27</sup> was used to prevent aggregating of gel particles during polymerization. The nominal gel compositions are determined by the relative moles of monomers. The used  $\chi$  values, the mole fraction of NCMA to NIPA, were 0.25, 0.5, and 0.75. In addition, the amount of BIS was used differently in the preparation of gel particles. The following variables, C% and T%, are convenient for defining crosslinking density and initial monomer concentration, respectively.

Monomer		Crosslinker					
NIPA (g)	NCMA (g)	Mole Ratio	BIS (g)	<i>C%</i>	Initiator APS	Surfactant Tween 20	Solvent DDI Water
0.1567	0.0442	3:1	$0.0099 \\ 0.0057$	3.52			
0.1081	0.0918	1:1	$0.0103 \\ 0.0059$	3.5 $2$	200 μL of 1 wt % solution	100 μL of 1 wt % solution	20mL
0.0564	0.1436	1:3	$0.0107 \\ 0.0062$	3.5 2			

Table I Compositions of All Samples

$$C\% = \frac{\text{moles of crosslinker}}{\text{total moles of monomers}} \times 100 \quad (1)$$

$$T\% = \frac{\text{mass of monomers (g)}}{\text{volume of water (mL)}} \times 100$$
 (2)

The compositions of monomers and ิล crosslinker were listed in Table I. The initial monomer concentration of the prepared gels are fixed at 1 T%. To illustrate the synthetic procedure, we give details for the preparation of gel particles in the case of  $\chi = 0.25$  and C% = 3.5%. In the preparation of a monomer solution, 0.156 g of NIPA, 0.0443 g of NCMA, and 0.01 g of BIS were added to 20 mL of DDI water. The initiator solution was also prepared as follows: 0.2 g of APS was dissolved in 20 mL of DDI water. And 1 wt % solution of Tween20 was prepared. All solutions were stirred with magnetic spin bars for about 2 h. The prepared monomer solution was held in a thermostated water bath at 70°C and 200  $\mu$ L of APS were added to initiate the polymerization. Simultaneously, 100  $\mu$ L of Tween20 solution was introduced to a monomer solution. The polymerization was completed after 3 h under nitrogen condition.

#### **Swelling Equilibriation Time**

The motion of the polymer network of a gel during the time course of swelling and shrinking is described by a diffusion equation, called a collective diffusion equation, where the diffusion coefficient is defined as the ratio of the osmotic bulk modulus k of the polymer network and the frictional coefficient between the polymer network and liquid.<sup>28</sup> The frictional coefficient f is defined as the ratio of a force F exerted on the liquid while the network is held fixed and the relative velocity v of the liquid and the network for a unit volume of the network: f = F/v. The time needed for a gel to change its volume and shape is proportional to the square of a characteristic length of the gel.<sup>29</sup>

time = 
$$(\text{length})^2/(k/f) = (\text{length})^2/D_c$$
 (3)

For a spherical gel, the time is proportional to the square of its radius. The diffusion coefficient  $D_c$  of a gel is usually on the order of  $10^{-7}$  cm<sup>2</sup>/s. From eq. (3), the time needed for volume change is  $10^{-4}$  s for a spherical gel of 0.1  $\mu$ m radius. From this result, we expect that the equilibriation time for our submicron-sized copolymer particles ( $\approx 500-600$  nm) would be very short. In this study, however, our equilibriation time was about 2 h so that the gel particles surely reached to the equilibrium state.

#### Measurement of Swelling Behavior

The hydrodynamic radius of the submicron-sized gel particles was measured by means of PCS. The solution containing gel particles was diluted with pure DDI water to get an appropriate concentration for the light scattering experiment and then poured into the cylindrical sample cell. The sample cell was set inside a sample holder, and an incident beam was focused to the center of the cell. The source of light was used as an argon ion laser (Lexel Laser Inc. model 95-2) operated at 514.4 nm, and the intensity was 200 mW. The light scattered by gel particles was detected by a photomultiplier at scattering angle of 90°. The scattered light intensity, and the auto correlation function (collected from a Brookhaven BI-9000 AT Correlator with CONTIN method) were determined at various temperatures.

The average hydrodynamic radius  $R_h$  can be calculated by using the Stokes–Einstein relation, as follows:

$$R_h = k_B T / 6 \pi \eta D \tag{4}$$

where  $k_B$ , *T*, and  $\eta$  are the Boltzman constant, the temperature (K), and the solvent viscosity in poise, respectively. The volume swelling ratio is defined by

$$V/V_0 = (R_h/R_{h0})^3 \tag{5}$$

where  $V_0$  and V are equilibrium gel volumes at a reference and a given state, respectively.  $R_h$  and  $R_{h0}$  are the average hydrodynamic radius of the gel at a given temperature and the network formation, respectively.

## THEORETICAL BACKGROUND

#### Swelling Equilibria

Following Flory and Rehner, the change in Gibbs free energy consists of a mixing contribution,  $\Delta G_{\text{mix}}$ , and an elasticity contribution,  $\Delta G_{el}$ .

$$\Delta G_{\rm net} = \Delta G_{el} + \Delta G_{\rm mix} \tag{6}$$

The elastic contribution,  $\Delta G_{el}$ , is expressed as follows<sup>12</sup>:

$$\Delta G_{el} = \mathrm{R}T \left[ \left( \frac{3A \Phi_0^{2/3} v_e}{2} \right) (\phi^{-2/3} - 1) + B v_e \ln \phi \right] \quad (7)$$

where R is the gas constant, and  $\Phi_0$  is the polymer volume fraction at network formation. The number of elastically active chains is denoted by  $v_e$ , and  $\phi$  is the polymer volume fraction in the swollen network. The values of the factors *A* and *B* are suggested as a function of  $\phi$ , as follows:

$$A = \frac{f-2}{f} + \frac{2\phi}{f}$$
$$B = \frac{2\phi}{f}$$
(8)

where f is the functionality of the crosslinker. Equation (8) corresponds to Flory and Erman's junction fluctuation theory.<sup>30</sup> If the system contains N moles of lattice sites, we have  $v_c/N = \phi/m_c$ , where  $m_c$  is the number of lattice sites occupied by an average network chain. Then, eq. (7) can be written as

$$G_{AB} = \frac{\Delta G_{el}}{NRT}$$
$$= \left[ \left( \frac{3A\Phi_0^{2/3}}{2m_c} \right) (\phi^{1/3} - \phi) + \left( \frac{B}{m_c} \right) \phi \ln \phi \right] \quad (9)$$

The Flory's interaction parameter  $\chi$  was expressed as a function of both temperature and composition for an uncrosslinked homopolymer solution. We employed Bae et al.'s expression<sup>31</sup> of the interaction parameter  $\chi$  as follows:

$$\frac{\Delta G_{\text{mix}}}{NRT} = \phi_0 \ln \phi_0 + \phi \int_{\phi}^{1} \chi(T, \phi) \ d\phi \qquad (10)$$

$$\chi(T, \phi) = D(T)B(\phi) \tag{11a}$$

$$D(T) = d_0 + \frac{d_1}{T} \tag{11b}$$

$$B(\phi) = \frac{1}{1 - b\phi} \tag{11c}$$

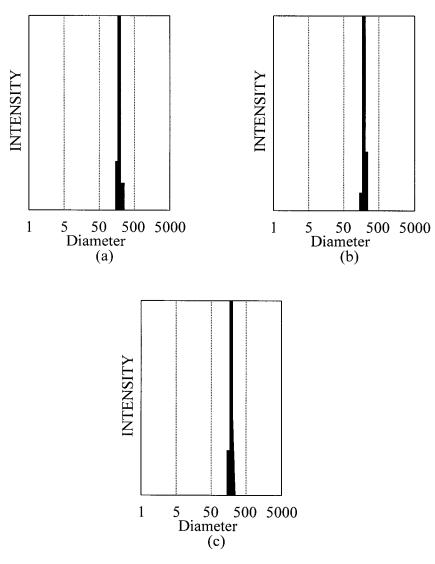
where  $\phi_0$  is the solvent volume fraction in the swollen gels, respectively, and  $d_0$ ,  $d_1$ , and b are adjustable model parameters. From eqs. (8) and (9), the chemical potential of a solvent in the gel coexisting with pure solvent is given by

$$\frac{\Delta\mu_0}{\mathbf{R}T} = G_{AB} - \phi C_{AB} + \left[\phi + \ln(1-\phi)\right] + D(T) \left(\frac{\phi^2}{1-b\phi}\right) \quad (12)$$

where

$$\begin{split} C_{AB} &= \Phi_0^{2/3} \bigg[ \bigg( \frac{A}{2m_c} \bigg) (\phi^{-2/3} - 3) + \bigg( \frac{3}{fm_c} \bigg) (\phi^{1/3} - \phi) \bigg] \\ &+ \bigg( \frac{B}{m_c} \bigg) (\ln \phi + 1) + \bigg( \frac{2\phi}{fm_c} \bigg) \ln \phi \quad (13) \end{split}$$

The equilibrium condition for the gel/solvent system is given by



**Figure 1** Particle size distribution of each sample at  $T = 70^{\circ}$ C and C% = 3.5: x equals (a) 0.25, (b) 0.5, and (c) 0.75.

$$\Delta \mu_0 = 0 \tag{14}$$

## Interaction Parameter for Copolymer Gel

Net interaction parameter between copolymer chain and solvent,  $\chi_{net}$ , is given by

$$\chi_{\rm net} = (1 - x)\chi_{AC} + x\chi_{BC} \tag{15}$$

The  $\chi_{\text{net}}$  is a function of mole fraction of comonomer in the polymer chain, x. In eq. (15),  $\chi_{ij}(i = A \text{ or } B, j = C)$  is the interaction parameter between i segment in copolymer chain and j solvent.

We assume that the existence of different types of A and B segments only affect their interaction

parameters with solvent. We also neglect the interaction parameter between A and B segments in the copolymer chain.

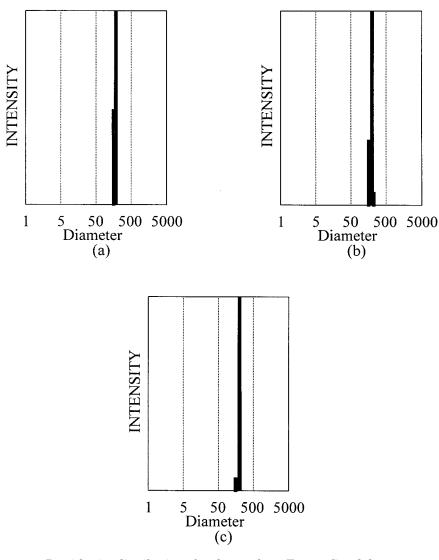
Therefore, from eq. (11),  $\chi_{ij}$  is given by

$$\chi_{ij}(T, \phi) = D_{ij}(T)B_{ij}(\phi)$$
(16a)

$$D_{ij}(T) = d_{0,ij} + \frac{d_{1,ij}}{T}$$
 (16b)

$$B_{ij}(\phi) = \frac{1}{1 - b_{ij}\phi}$$
(16c)

where  $d_{0,ij}$ ,  $d_{1,ij}$ ,  $b_{ij}$  are adjustable model parameters for each i-j pair.



**Figure 2** Particle size distribution of each sample at  $T = 70^{\circ}$ C and C% = 2: *x* equals (a) 0.25, (b) 0.5, and (c) 0.75.

## **RESULTS AND DISCUSSION**

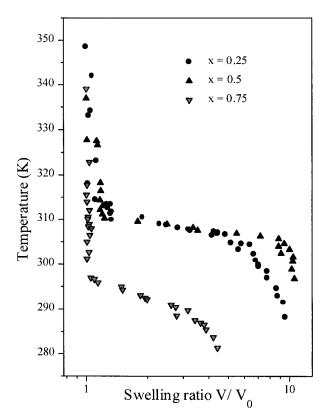
## The Hydrodynamic Radius of Gel Particles

We observed the hydrodynamic radius of gel particles with various compositions and temperatures. Figure 1(a-c) shows particle sizes and distributions of gel particles at  $T = 70^{\circ}$ C and C% = 3.5 with various x (0.25, 0.5, and 0.75). Figure 2(a-c) shows particle sizes and distributions of gel particles at  $T = 70^{\circ}$ C and C% = 2 with various x (0.25, 0.5, and 0.75). As shown in Figures 1 and 2, our prepared gel particles are monodisperse.

#### The Effect of N-Cyanomethyl Acrylamide (NCMA)

Figure 3 shows the swelling behavior of the prepared gel particles with C% = 3.5. Our submicron-sized copolymer gel particles showed a continuous volume transition, while bulk gels show a discontinuous volume transition.<sup>32</sup> Tanaka et al.<sup>29,32</sup> explained that it resulted from the structural inhomogeneties of particle gels. Wu and Zhou<sup>33</sup> reported that the stress inside gel would gradually increase until the shear modulus could not maintain the macroscopic shape of the gel, and the overall dimension of the bulk gel would change abruptly.

As shown in Figure 3,  $T_v$  decreases with increasing the mole ratio of NCMA in copolymer gel particles, which is due to the hydrophobicity of NCMA monomer. Generally, the swelling ratio of the hydrogel is affected by the crosslinking density. However, our results show that the swelling ratio decreases with increasing of the mole ratio



**Figure 3** Swelling behaviors with various mole fractions of NCMA in copolymer gel particles. Dark circles, dark triangles, and dark upside-down triangles are the swelling data of gel particles for x = 0.25, 0.5, and 0.75, respectively.

of NCMA. This may be driven by the hydrogen bonding among the network polymer chains. This cannot be interpreted as the entanglement because T% is fixed. Therefore, the observed result must be a considerable property in the future work.

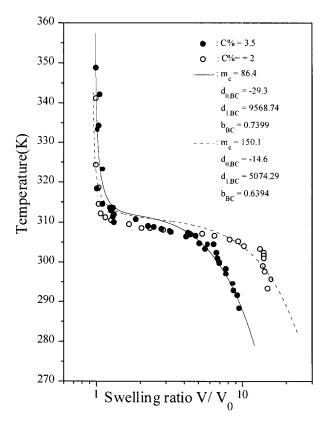
#### The Effect of the Crosslinking Density

Figures 4–6 represent the effect of crosslinking density on the swelling behavior of gel particles. Figure 4 shows that the mole fraction of NCMA in copolymer gel, x, is 0.25 with various crosslinking densities. In this figure, dark circles and open circles are C% = 3.5 and 2, respectively. Volume transition temperature  $T_v$  is observed at 306.6 K. The swelling ratios are 10.6 at C% = 3.5 and 15.8 at C% = 2. As observed in experimental data, the volume transition temperature is consistent with various crosslinking density, but the swelling ratio is not. With increasing crosslinking density,

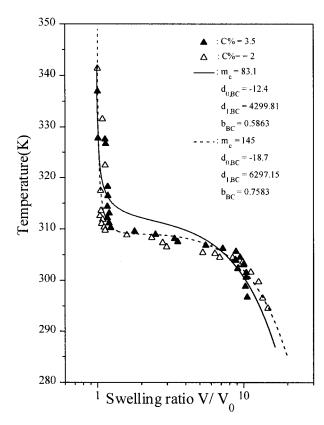
the swelling ratio decreases. As shown in Figure 5 (x = 0.25), the swelling ratio increases with decreasing C%. However,  $T_v (\approx 305.2 \text{ K})$  dose not change with various C%. Figure 6 (x = 0.75,  $T_v = 297.6 \text{ K}$ ) shows the same trend as well.

## Comparison of Experimental Data With the Extended Flory-Huggins Model

The adopted model has basically nine model parameters  $(x, m_c, \Phi_0, d_{0,AC}, d_{1,AC}, b_{AC}, d_{0,BC}, d_{1,BC}, and b_{BC})$ . x can be estimated from the mole fraction of NCMA at the reaction condition.  $m_c$  can be calculated from the way presented by Moerkerke et al.<sup>11</sup>  $\Phi_0$ ,  $d_{0,AC}$ ,  $d_{1,AC}$ , and  $b_{AC}$  (A and C denote NIPA segment and water, respectively) are obtained from liquid–liquid equilibria data of the NIPA homopolymer–water system.<sup>25</sup> Therefore, there are three adjustable model parameters ( $d_{0,BC}$ ,  $d_{1,BC}$ , and  $b_{BC}$ , where B de-

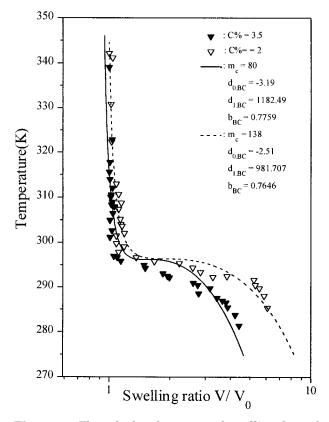


**Figure 4** The calculated curves and swelling data of gel particles at x = 0.25. Dark circles and the solid line (C% = 3.5) are experimental data and a calculated curve, respectively. Open circles and the broken line (C% = 2) are experimental data and a calculated curve, respectively.



**Figure 5** The calculated curves and swelling data of gel particles at x = 0.5. Dark triangles and the solid line (C% = 3.5) are experimental data and a calculated curve, respectively. Open triangles and the broken line (C% = 2) are experimental data and a calculated curve, respectively.

notes the NCMA segment) in the extended Flory-Huggins model. The values of model parameters are listed in Table II. In Figures 4-6, solid lines and broken lines, which are C% = 3.5 and 2, respectively, were calculated from eqs. (12)-(14). As shown in Figure 4, the swelling behaviors of gel particles are predicted well by our model. Both calculated curves give almost the same transition temperature and slightly overestimate  $T_{\nu}$ . In the swollen region, they also show a discrete discrepancy of the swelling ratio. In Figure 5 (x = 0.25), the calculated curve predicts very well the swelling behavior of gel particles for C% = 2. However, for the higher C% (=3.5), the model gives a poor agreement with experimental data. It might be that there is a discrepancy between the real  $m_c$ value and the calculated  $m_c$  values at experimental condition for higher C%. In Figure 6, for higher  $x \ (=0.75)$ , the same results are shown as that of Figure 5.



**Figure 6** The calculated curves and swelling data of gel particles at x = 0.75. Dark upside-down triangles and the solid line (C% = 3.5) are experimental data and a calculated curve, respectively. Open upside-down triangles and the broken line (C% = 2) are experimental data and a calculated curve, respectively.

## CONCLUSION

Copolymer gel particles prepared in this study were shown to display continuous volume transi-

# Table IIThe Values of Adjustable ModelParameters

$\chi^{\rm a}$	$m_c^{a}$	$d_{0,BC}$	$d_{1,BC} \atop (\mathrm{K})$	$b_{BC}$
0.25	86.4	-29.3	9568.74	0.7399
	150.1	-14.6	5074.29	0.6394
0.5	83.1	-12.4	4299.81	0.5863
	145	-18.7	6297.15	0.7583
0.75	80	-3.19	1182.49	0.7759
	138	-2.51	981.707	0.7646

 $\Phi_0 = 0.7961, d_{0,AC} = 14.28, d_{1,AC} = -4377.9, b_{AC} = 0.7502.$ 

<sup>a</sup> Calculated from the experimental conditions.

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tion regions. Our experimental results represented that the addition of comonomer with different hydrophobicity to a NIPA gel was affected dramatically by the volume transition temperature  $(T_v)$  and the swelling ratio.  $T_v$  decreased with an increase in the mole ratio of NCMA in copolymer gel particles. The higher the mole ratio of NCMA, the less gel particles swelled. Predicted swelling equilibria agreed reasonably well with experimental data over the investigated range of the temperature and degree of swelling.

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