

# Swelling Behavior of Thermosensitive *N*-Isopropylacrylamide–Ethyl *N*-Acryloylglycine Submicron-Sized Copolymer Gel Particles

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**ABSTRACT:** Submicron-sized *N*-isopropylacrylamide (NIPA)–ethyl *N*-acryloylglycine (ENAG) copolymer gel particles with various compositions were prepared by precipitation polymerization in water. Their swelling behaviors were determined by photon correlation spectroscopy (PCS). Our results showed that the volume transition temperature of copolymer gel particles decreased with increasing the mole ratio of ENAG. In model development, we modified the extended Flory–Huggins theory as a free energy of mixing term and employed the modified Flory–Rehner theory for the elastic contribution and compared the proposed model with our swelling data. The model predicted fairly well the swelling behaviors of copolymer gel particles. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 799–806, 1998

**Key words:** swelling behavior; *N*-isopropylacrylamide; ethyl *N*-acryloylglycine; copolymer gel particles

## INTRODUCTION

Gels are most generally understood to be polymeric networks that absorb enough solvent to cause macroscopic changes in the sample dimension. Many gels will undergo reversible and discontinuous volume changes in responsive to changes in solvent composition,<sup>1,2</sup> ionic composition,<sup>3</sup> pH,<sup>2</sup> ultraviolet (UV),<sup>4–6</sup> or visible light,<sup>7</sup> and temperature.<sup>1,2,8</sup> The most important property of the gel is its swelling degree due to its practical application, such as in switches, sensors, drug delivery devices, recyclable absorbents, and specialized separation systems.

Hydrophilic gels in aqueous solutions have been the most widely studied. The swelling and mechanical properties of hydrogels can be controlled by the modification of polymer backbone

structure and/or the crosslinking density. Most polymers are crosslinked to form a gel that swells in a sufficiently good quality solvent. Phase equilibria of gels have been extensively studied both theoretically and experimentally.

A poly(*N*-isopropylacrylamide) gel in water undergoes a volume phase transition from a swollen to shrunken state by elevating temperature. Its transition temperature ( $T_v$ ) is around 34°C.<sup>9</sup> It is due to the dissociation of the hydrophobic interaction between *N*-isopropylacrylamide (NIPA) and water. Therefore, it is very desirable to control the hydrophobic interaction for varying volume transition temperature of the gel. By copolymerizing NIPA with comonomers that have various hydrophobicity groups,  $T_v$  can be controlled.

In the past decade, there have been many attempts to control thermally induced volume phase transition of *N*-alkylacrylamide gels through copolymerization with comonomers that have different hydrophobicity. Many research groups<sup>10–16</sup> have observed *N*-alkylacrylamide copolymer gels such as *N*-acryloxysuccinimide–acrylamide,

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poly(*N-n*-propylacrylamide)–NIPA, *N,N*-diethylacrylamide–NIPA, *N,N*-dimethylacrylamide–acrylate, NIPA/*N-tert*-butylacrylamide, NIPA–*N*-cyclopropylacrylamide, and so on. Their results showed that the polymer composition determined the swelling characteristics of the gels due to pH or temperature.

Thermodynamically, the swelling equilibrium of nonionic gel is governed by both the free energy of elasticity and the free energy of mixing. In a NIPA gel–water system, water diffuses into the network by forces given by the difference of the chemical potential of water between the network inside and outside. Finally, the swelling gels reach the equilibrium state at a higher concentration of water in the gel phase. This stability is caused by contributions of elastic forces to the chemical potential of the solvent (water), which prevent the polymer from becoming completely dissolved.

Prange et al.<sup>17</sup> applied an oriented quasi-chemical model to the swelling equilibria of gels that take into account the strong specific interaction between CONH group in the network and water. Marchetti et al.<sup>18,19</sup> also introduced lattice–fluid model, which considered holes in the lattice as a component for the free energy of mixing and compared the model with their swelling data. Moerkerke et al.<sup>20</sup> suggested a simple model in which the polymer–solvent interaction parameter depends not only on the temperature but also on the concentration of polymer and fitted it to Inomata's swelling data.

Real copolymer gels consist of three different segments, as follows: two types of monomers and a crosslinker. Although we generally neglect effects of crosslinker on the mixing contribution, it is impossible to ignore the effects of comonomer on the interaction parameter in the enthalpy of mixing. Therefore, the swelling behavior of such copolymer gels is governed by the interaction between solvent molecule and two types of polymer segments.

In this study, we investigated the effect of hydrophobicity for the submicron-sized gel particles by copolymerizing NIPA with ethyl *N*-acryloylglycine (ENAG). Copolymer gels with various compositions were prepared and their swelling behaviors in water were examined using the photon correlation spectroscopy (PCS) technique. We modified an extended Flory–Huggins model as a free energy of mixing term and employed the modified Flory–Rehner theory for the elastic contribution. In our proposed model, net interaction pa-

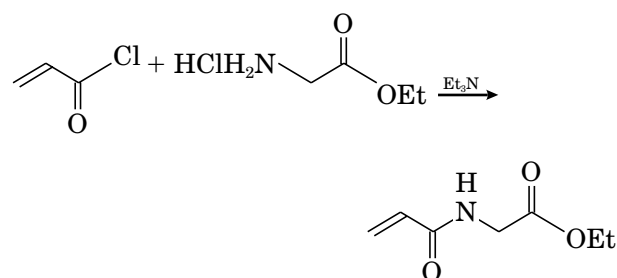
rameter ( $\chi$ ) was separated into  $\chi_{AC}$  (interaction parameter between the *A*-type segment and solvent *C*) and  $\chi_{BC}$  (interaction parameter between the *B*-type segment and solvent *C*), each of which has three adjustable parameters related to the extended Flory–Huggins theory. Finally, we compared the proposed model with experimental results.

## EXPERIMENTAL

### Preparation of Ethyl *N*-Acryloylglycine

Synthesis method of ENAG was reported elsewhere.<sup>21</sup> In this study, we prepared ENAG as follows. Acryloyl chloride and glycine ethyl ester hydrochloride, purchased from Aldrich Chemical Company, were used without further purification. Ethyl acetate, tetrahydrofuran, and triethylamine (Aldrich Chemical Co.) were used after drying over calcium hydride. Hexane (Aldrich Chemical Co.) was used as received. Silica gel (70-230 mesh ASTM) was purchased from Merck.

To an ice-cold solution of glycine ethyl ester, hydrochloride (8.58 g, 61.5 mmol) and triethylamine (15.56 g, 153.8 mmol) in 100 mL of tetrahydrofuran was added acryloyl chloride (5.57 g, 61.5 mmol) in 50 mL of ethyl acetate in a dropwise manner. The mixture was stirred at room temperature for 5 h. The precipitated solid (Et<sub>3</sub>NHCl), which was gradually separated during the reaction, was filtered off, and the filtrate was evaporated under reduced pressure to give a crude solid. This product was purified by chromatography on a silica gel column eluting with hexane–ethyl acetate (1 : 1) to give a pure ethyl *N*-acryloylglycine as a white solid (7.14 g; yield 73%; *mp* = 39–40°C).



### Copolymerization

Precipitation polymerization was used to prepare submicron-sized copolymer gel particles. In addi-

**Table I The Compositions of Samples**

Monomers			Crosslinker	
NIPA (g)	ENAG (g)	Mole Ratio	Bis (G)	C%
0.1367	0.0633	3 : 1	0.009	4%
0.0838	0.1162	1 : 1	0.009	4%
0.0387	0.1613	1 : 3	0.0085	4%

tion, *N,N'*-methylenebisacrylamide (BIS) (purchased from Aldrich Chemical Co.) was used as a crosslinking agent. A series of hydrogels was prepared such that *C*% was fixed at 4%, where *C*% is defined as follows:

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

Distilled–deionized (DDI) water was used as a solvent during polymerization. Ammonium persulfate (APS) (from Aldrich Chemical Co.) was used to initiate the polymerization in this study. Dried nitrogen gas was bubbled through the monomers–solvent mixture during polymerization to remove oxygen dissolved in the reaction mixture. As a surfactant, Tween20 was used. Tween20 is a nonionic surfactant that does not affect the swelling behavior of nonionic gel.<sup>22</sup> The compositions of sample used in this study are listed in Table I. We explain how to prepare the gel particles in case that *x*, which is mole fraction of ENAG in polymer chain, is 0.25. In order to prepare monomer solution, 0.1367 g of NIPA, 0.633 g of ENAG, and 0.009 g of BIS were added to 20 mL of DDI water. The monomer solution was stirred with magnetic spin bar at ambient temperature for several hours. The completely dissolved solution was held in a thermostated water bath at 70°C. The reaction was initiated by adding 200  $\mu$ L of 1 wt % solution of APS. Simultaneously, 100  $\mu$ L of 1 wt % solution of Tween20 to prevent aggregation during polymerization. The reaction condition was continued under nitrogen with gentle stirring (60/min) at 70°C for 3 h.

### Photon Correlation Spectroscopy

In order to characterize the swelling behavior of the submicron-sized copolymer gel particles, we used the PCS technique. An incident beam (514 nm) from an Ar-ion laser (Lexel Laser Inc., Model 95-2) was focused to the center of the cylindrical

sample cell. The scattered light intensity and the time autocorrelation function (collected from a Bookhaven BI-9000 AT Correlator with CONTIN method) were determined at various temperatures.

We used the CONTIN method to analyze and calculate the average size of copolymer gel particles. The volume swelling ratio is defined by

$$V/V_0 = (R_h/R_{h0})^3 \quad (2)$$

where  $V_0$  and  $V$  are the equilibrium gel volume at a reference and interesting state obtained from PCS measurement, respectively.  $R_h$  and  $R_{h0}$  are the average hydrodynamic radius of the gel at a given temperature and the network formation, respectively. The average hydrodynamic radius  $R_h$  can be calculated by using the Stokes–Einstein relation, as follows:

$$R_h = k_B T / 6\pi\eta D, \quad (3)$$

where  $k_B$ ,  $T$ , and  $\eta$  are the Boltzmann constant, the temperature in Kelvin, and the solvent viscosity in poise, respectively.

## THEORETICAL CONSIDERATION

### Swelling Equilibria of Homopolymer Gel in Solvent

The change in Gibbs free energy of the gel network,  $\Delta G_{\text{net}}$ , due to isotropic deformation by swelling of nonionic gel is given by

$$\Delta G_{\text{net}} = \Delta G_{\text{el}} + \Delta G_{\text{mix}} \quad (4)$$

where  $\Delta G_{\text{el}}$  is the Gibbs free energy of elasticity and  $\Delta G_{\text{mix}}$  is the Gibbs free energy of mixing.

The elastic contribution,  $\Delta G_{\text{el}}$ , is expressed as follows<sup>20,23</sup>:

$$\begin{aligned} \Delta G_{\text{el}} &= RT \left[ \left( \frac{3A\Phi_0^{2/3}\nu_e}{2} \right) (\phi^{-2/3} - 1) + B\nu_e \ln \phi \right] \quad (5) \end{aligned}$$

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  $\nu_e$ , 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:

$$A = \frac{f-2}{f} + \frac{2\phi}{f}$$

$$B = \frac{2\phi}{f} \quad (6)$$

where  $f$  is the functionality of the crosslinker. Equation (6) corresponds to Flory and Erman's junction fluctuation theory.<sup>24</sup> If the system contains  $N$  moles of lattice sites, we have  $\nu_e/N = \phi/m_c$ , where  $m_c$  is the number of lattice sites occupied by an average network chain. Then, eq. (5) can be written as

$$G_{AB} = \frac{\Delta G_{el}}{NRT}$$

$$= \left[ \left( \frac{3A\Phi_0^{2/3}}{2m_c} \right) (\phi^{1/3} - \phi) + \left( \frac{B}{m_c} \right) \phi \ln \phi \right] \quad (7)$$

Qian et al.,<sup>25,26</sup> Petrovic et al.,<sup>23</sup> and Bae et al.<sup>27</sup> suggested the Flory's interaction parameter  $\chi$  as a function of both temperature and composition for an uncrosslinked homopolymer solution. In this study, we employed Bae et al.'s expression<sup>27</sup> of the interaction parameter,  $\chi$ , as follows:

$$\frac{\Delta G_{mix}}{NRT} = \phi_0 \ln \phi_0 + \phi \int_{\phi}^1 \chi(T, \phi) d\phi \quad (8)$$

$$\chi(T, \phi) = D(T)B(\phi) \quad (9a)$$

$$D(T) = d_0 + \frac{d_1}{T} \quad (9b)$$

$$B(\phi) = \frac{1}{1 - b\phi} \quad (9c)$$

where  $\phi_0$  is the solvent volume fraction in the swollen gels, and  $d_0$ ,  $d_1$ , and  $b$  are adjustable model parameters.

From eqs. (7) and (8), the chemical potential of a solvent in the gel coexisting with pure solvent is given by

$$\frac{\mu\mu_0}{RT} = G_{AB} - \phi C_{AB} + [\phi + \ln(1 - \phi)]$$

$$+ D(T) \left( \frac{\phi^2}{1 - b\phi} \right) \quad (10)$$

where

$$C_{AB} = \Phi_0^{2/3} \left[ \left( \frac{A}{2m_c} \right) (\phi^{-2/3} - 3) \right.$$

$$\left. + \left( \frac{3}{fm_c} \right) (\phi^{1/3} - \phi) \right] + \left( \frac{B}{m_c} \right) (\ln \phi + 1)$$

$$+ \left( \frac{2\phi}{fm_c} \right) \ln \phi \quad (11)$$

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

$$\Delta\mu_0 = 0 \quad (12)$$

### Interaction Parameter for Copolymer Gel

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

$$\chi_{net} = (1 - x)\chi_{AC} + x\chi_{BC} \quad (13)$$

The  $\chi_{net}$  is a function of mole fraction of comonomer in the polymer chain,  $x$ . In eq. (13),  $\chi_{ij}$  ( $i = A$  or  $B$  and  $j = C$ ) 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 affects their interaction parameters with solvent. We also neglect the interaction parameter between A and B segments in the copolymer chain.

Therefore, from eq. (9),  $\chi_{ij}$  is given by

$$\chi_{ij}(T, \phi) = D_{ij}(T)B_{ij}(\phi) \quad (14a)$$

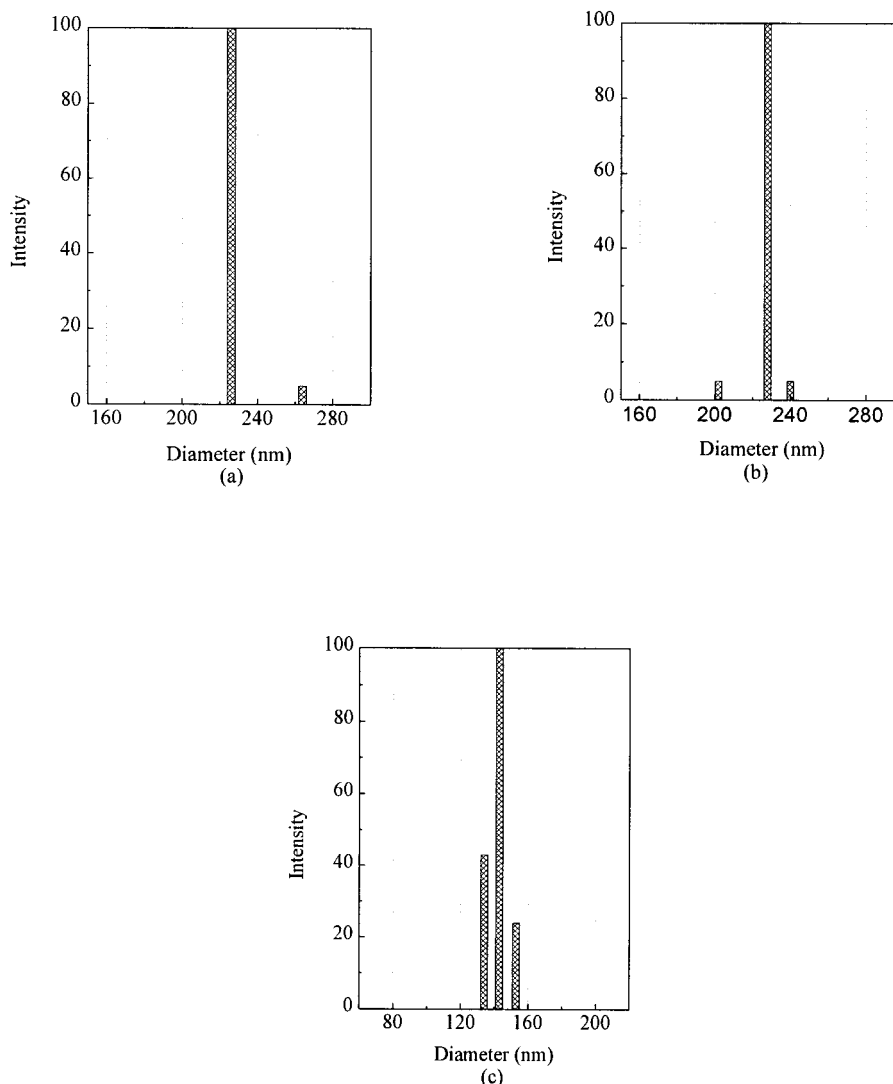
$$D_{ij}(T) = d_{0,ij} + \frac{d_{1,ij}}{T} \quad (14b)$$

$$B_{ij}(\phi) = \frac{1}{1 - b_{ij}\phi} \quad (14c)$$

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

## RESULTS AND DISCUSSION

We prepared NIPA-ENAG submicron-sized copolymer gels with various compositions. The particle size and the distribution of prepared copolymer gel particles were measured by the PCS technique. Figure 1 shows that our prepared gel



**Figure 1** (a–c) Particle size distribution of each sample for  $x = 0.25, 0.5,$  and  $0.75,$  respectively.

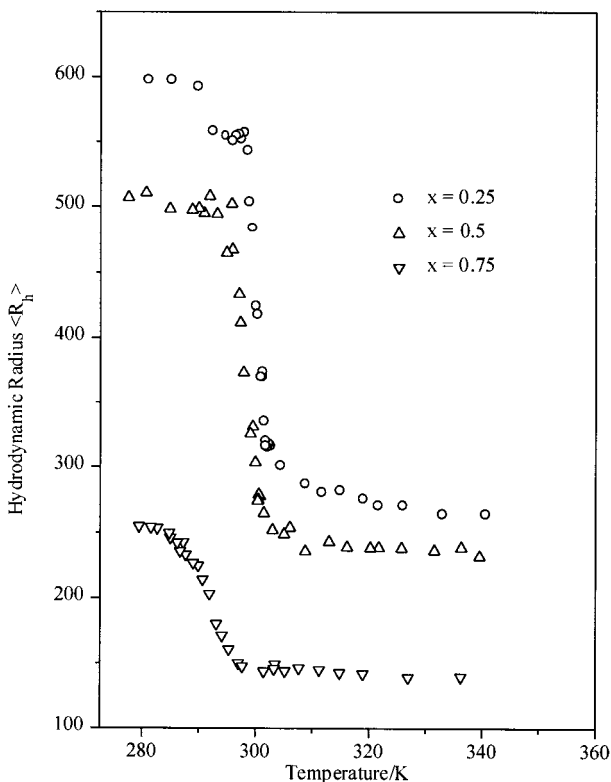
particles are monodisperse. Their variances are below 0.01. Figure 1(a–c) shows particle size distributions of each sample for  $x = 0.25, 0.5,$  and  $0.75,$  respectively. The particle size and the variance of each component at the preparation temperature ( $70^{\circ}\text{C}$ ) are 262 nm (variance = 0.001), 228 nm (variance = 0.001), and 142 nm (variance = 0.002), respectively. Figure 2 represents that the average hydrodynamic radius,  $\langle R_h \rangle,$  decreases with increasing temperature. Furthermore,  $\langle R_h \rangle$  of each composition at the same temperature decreases as the mole ratio of the comonomer ENAG in copolymer gels increases.

Swelling behaviors of NIPA–ENAG copolymer gels with various compositions are shown in Figures 4 and 6. As shown here, gels are in the

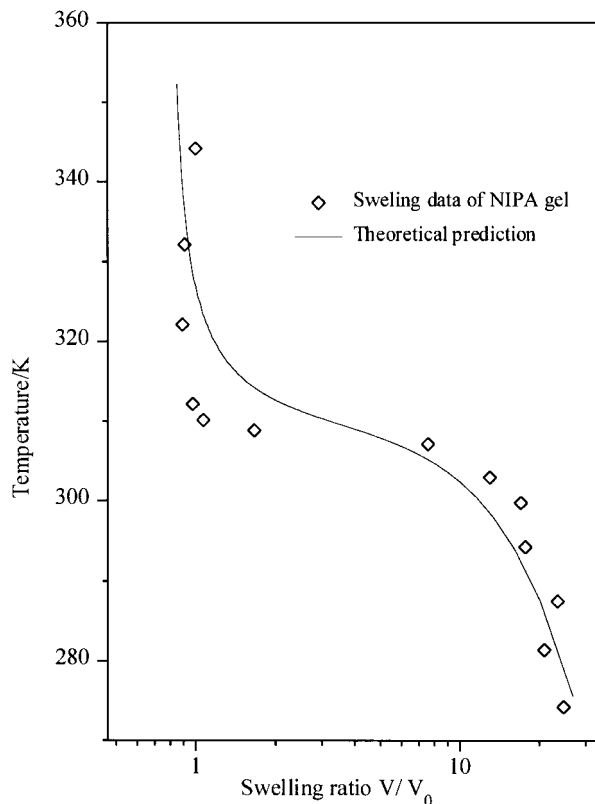
shrunk state above the transition temperature and undergo swelling below  $T_v.$  Experimental results show that our prepared submicron-sized copolymer gel particles undergo continuous volume transition compared to that of the conventional bulk gel. Hirose et al.<sup>28,29</sup> reported that it results from the structural inhomogeneities of the submicron gel particles. Wu and Zhou<sup>30</sup> explained that the stress inside the gel will gradually increase until the shear modulus cannot maintain the macroscopic shape of the gel and the overall dimension of the bulk gel will change abruptly. Generally, the swelling ratio of the gel is affected by the crosslinking density. In this study, we fixed  $C\%$  at 4% to avoid the effect of the crosslinker on each composition of NIPA–ENAG copolymer gel particles.

As shown in Figures 4 and 6,  $T_v$  decreases with increasing the mole ratio of ENAG in copolymer gel particles. Furthermore, the swelling ratio decreases with increasing the mole ratio of ENAG in copolymer gel particularly. A strong hydrogen bonding related to ENAG among the network polymer chains plays a significant role as a physical crosslinker.

Our proposed model for copolymer gel has basically 9 parameters ( $m_c$ ,  $\Phi_0$ ,  $x$ ,  $d_{0,AC}$ ,  $d_{1,AC}$ ,  $b_{AC}$ ,  $d_{0,BC}$ ,  $d_{1,BC}$ , and  $b_{BC}$ ). Some of those parameters can be obtained from experimental condition and swelling data for NIPA homopolymer gel–water system.  $x$  can be estimated from the mole fraction of comonomer (ENAG) at the reaction condition. Since we use the water molecule as the lattice site (on a weight basis), the average molar mass of the network chain is  $18 m_c$ . The doubly unsaturated crosslinker has a molar mass of 154, and with  $f = 4$ , half of this weight ratio of monomer to crosslinker in the network is  $(18 m_c)/(154/2) = 20$ .<sup>20</sup> From this calculation, we obtained  $m_c = 85.56$ .  $d_{0,AC}$ ,  $d_{1,AC}$ , and  $b_{AC}$ , which are related



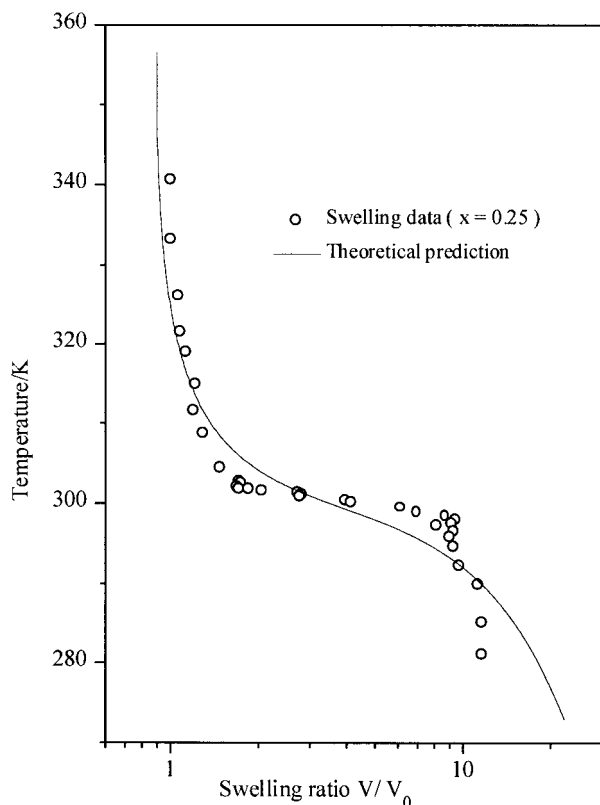
**Figure 2** Hydrodynamic radius,  $\langle R_h \rangle$ , with various compositions of NIPA/ENAG copolymer gel particles. Open circles are  $\langle R_h \rangle$  when  $x$  is 0.25. Open uptriangles and downtriangles are  $\langle R_h \rangle$  when  $x$  are 0.5, 0.75, respectively.



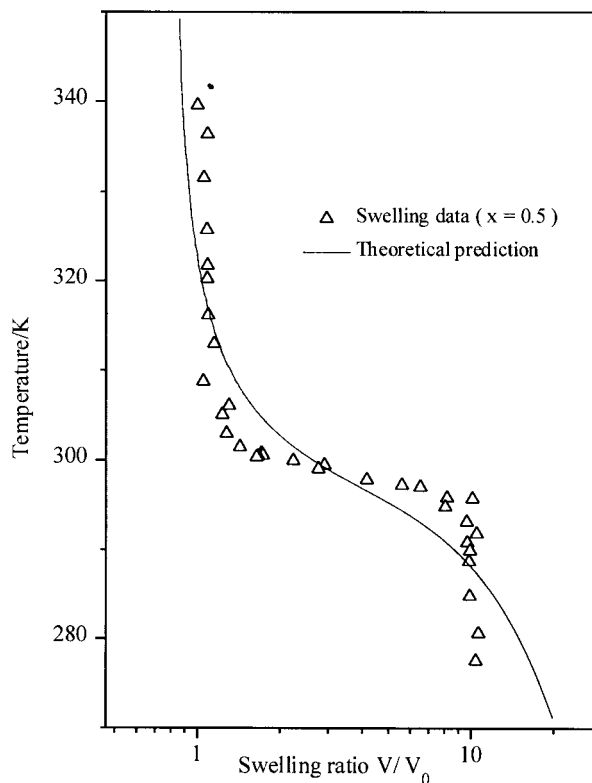
**Figure 3** Swelling equilibria of NIPA homopolymer gel particles in water. Solid line demonstrates theoretical prediction from our proposed model. Open diamonds are experimental results.

to the interaction parameter ( $\chi_{AC}$ ) between the NIPA segment (denoted by  $A$ ) and water (denoted by  $C$ ) and  $\Phi_0$ , can be obtained from the NIPA homopolymer gel–water system. Figure 3 shows the comparison of swelling data for NIPA homopolymer gel particles in water with calculated curve from eqs. (10–12). Obtained adjustable model parameters for NIPA homopolymer gel particles in water are  $d_{0,AC} = 14.228$ ,  $d_{1,AC} = -4377.9$  (K),  $b_{AC} = 0.7502$ , and  $\Phi_0 = 0.7961$ . In the prediction of swelling behavior for copolymer gel particles in water, we use parameters obtained from correlating swelling behaviors for the NIPA homopolymer gels particles–water system. Thus, the calculated curve shown in Figure 4 (swelling data of NIPA/ENAG,  $x = 0.25$ ) has been fitted to the experimental swelling data with three adjustable model parameters ( $d_{0,BC}$ ,  $d_{1,BC}$ , and  $b_{BC}$ ). This curve is a prediction based on the known gel particle composition at preparation and on independently obtained parameters. As shown in this figure,  $T_v$  is 301 K, which is lower than that of NIPA homopolymer gel (308 K). The values of

$d_{0,BC}$ ,  $d_{1,BC}$ , and  $b_{BC}$  are 11.44–2838.994 (K) and  $-0.21398$ , respectively. The semiquantitative agreement of the predicted swelling equilibrium with experimental data is very encouraging. However, there is slight deviation between theoretical prediction and experimental data. Figure 5 shows NIPA–ENAG (1 : 1) copolymer gel particles in water. Solid line is obtained from the proposed model. Both  $T_v$  (298 K) and the degree of swelling ratio are smaller than those of NIPA–ENAG (3 : 1) copolymer gel particles. A slight deviation is also found in swollen state between calculated values and experimental results. In this system, the values of adjustable model parameters ( $d_{0,BC}$ ,  $d_{1,BC}$ , and  $b_{BC}$ ) are 12.966–3479.712 (K), and  $-0.52301$ , respectively. Figure 6 represents the swelling data of NIPA–ENAG (1 : 3) copolymer gel particles in water. In this system,  $T_v$  is 292 K, and the degree of swelling ratio is the smallest among presented systems. A slight deviation in presented systems might be due to the structural inhomogeneities of gel particles. The values of



**Figure 4** Comparison of swelling data with the proposed model. Open circles are swelling data of copolymer gel particles ( $x = 0.25$ ) in water. Solid line is calculated from the proposed model.

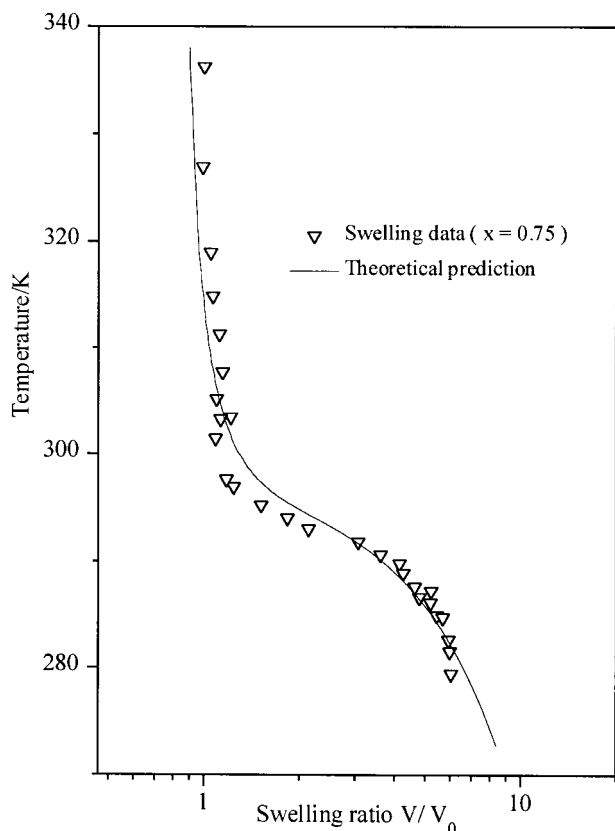


**Figure 5** Comparison of swelling data with the proposed model. Open uptriangles are swelling data of copolymer gel particles ( $x = 0.5$ ) in water. Solid line is calculated from the proposed model.

$d_{0,BC}$ ,  $d_{1,BC}$ , and  $b_{BC}$  are 0.6879, 7.932 (K), and 0.624, respectively.

## CONCLUSION

The prepared hydrogels in this study were shown to display sharp volume transition regions. The transition temperature ( $T_v$ ) and the swelling ratio of NIPA–ENAG copolymer gel particles decreased with increasing the mole ratio ENAG in copolymer gel particles. We explained that the strong hydrogen bonding among the network polymer chains plays a significant role as a physical crosslinker. In the proposed model, the interaction parameter was separated into  $\chi_{AC}$  and  $\chi_{BC}$  according to different hydrophobicities of monomer units.  $\Phi_0$  and  $\chi_{AC}$  were calculated from swelling data of the NIPA homopolymer gel–water system, and their adjustable model parameters were directly used in the NIPA–ENAG copolymer gel particle–water systems. A good agreement be-



**Figure 6** Comparison of swelling data with the proposed model. Open downtriangles are swelling data of copolymer gel particles ( $x = 0.75$ ) in water. Solid line is calculated from the proposed model.

tween experimental data and our proposed model was obtained.

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