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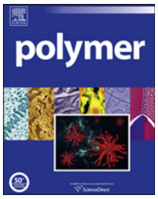

The effects of interaction energy on the volume phase transition of *N*-isopropylacrylamide-co-*N*-isopropylmethacrylamide nano-sized gel particles: Applicability of molecular simulation technique

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ABSTRACT

We investigated the volume phase transition temperatures of *N*-isopropylmethacrylamide (NIPMA)-co-*N*-isopropylacrylamide (NIPA) gels with various mole ratios. Nanometer-sized NIPA-co-NIPMA gel particles were prepared by precipitation polymerization and their swelling behaviors were measured using photon correlation spectroscopy (PCS). After applying the interaction energies found using the molecular simulation technique, we predicted the swelling equilibria for the hydrogels in a water system. For studying cross-linked hydrogel particles in water, we have combined the modified double-lattice theory with Flory and Erman's theory of elasticity. To correct for the deviation of the volume transition temperature, we considered the additional energy parameter (ε_h) between the cross-linker and solvent molecules. We used the corrected model to describe the swelling behavior of the hydrogel and the volume transition temperature. The corrected model was agreed well with their experimental data with no fitting parameters.

1. Introduction

Volume phase transition and phase behavior have a close relationship, due to the thermodynamic properties of mixtures containing polymers. Chemical process design for industrial applications is related to the separation and purification of fluid mixtures, which are based on thermodynamic equilibria. Therefore, the analysis of hydrogel volume phase transitions through understanding of fundamental properties of thermodynamics has received much attention.

Synthetic polymer hydrogels consisting of hydrophobic polymer chain networks have shown to represent a phase transition accompanying drastic discontinuous or continuous volume change with variation of surrounding conditions such as solvent composition or temperature [1–6]. These hydrogels are useful model systems to study the phase transition and free energy changes of rubber elasticity of the polymer chain networks.

Hydrogels consist of a hydrophilic group attached to a water molecule, and are induced by continuous change at various temperatures. Hirotsu theorized that the thermally induced volume phase transition of *N*-isopropylacrylamide gels explained thermoshrinking due to the destruction of hydrogen bonds between water molecules and hydrophilic groups, such as NH and C=O [7]. However, water molecules also interact strongly with non-polar hydrophobic solutes in the formation of a hydrophobic hydration structure [8]. Therefore, when hydrophobic solutes are introduced into water, two phenomena are simultaneously observed. One is hydrophobic hydration, in which the water molecules form cagelike structures around the hydrophobic solute. As a result of this hydration, non-polar molecules become soluble in water. The other is hydrophobic interaction, or the association of hydrophobic solutes. In general, increases in temperature result in reduction of the total number of water molecules structured around the hydrophobic solute, promoting the hydrophobic interaction. Consequently, a rise in temperature strengthens the hydrophobic interaction. Because of this phenomenon, thermally induced volume phase transitions are observed in thermoshrinking type hydrogels.

After performing molecular simulations, we obtained interaction energy parameters for the polymer and solvent and applied to the Oh and Bae's [9] modified double-lattice model (MDL), which is based on Hu et al.'s double-lattice model [10], to predict the swelling equilibrium for a hydrogel in water system. The effects of volume phase transition temperatures of the hydrogel can be attributed to the presence of the methyl group in the main chain unit structure. For cross-linked hydrogels in water the elastic free energy is formulated according to Flory and Erman's theory of elasticity [11], which takes into account the nonaffine displacements of the network junctions under strain or at a high degree of

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swelling. We combined MDL theory with Flory and Erman's rubber elasticity theory. Experimentally, nanometer-sized NIPA-co-NIPMA gel particles were prepared by precipitation polymerization and their swelling behaviors were examined using the photon correlation spectroscopy (PCS) technique. The proposed model was compared with actual swelling data, and the effect of the methyl group on the volume phase transition temperature of the gel particles was investigated.

2. Experimental section

N-Isopropylacrylamide (NIPA, MW = 113.16) and *N*-isopropylmethacrylamide (NIPMA, MW = 127.18) were obtained from Sigma–Aldrich Co. and recrystallized before use. *N*,*N*′-Methylenebisacrylamide and ammonium persulfate were used as a crosslinker and an initiator, respectively. NIPA and NIPMA have different hydrophobicities. Non-ionic surfactant TWEEN 20 was used to prevent aggregation among particles. We prepared the gel particles by precipitation polymerization at 70 °C for 4 h under nitrogen [12]. Distilled, deionized water was used as a solvent. The introduced comonomer was measured by weight. The proposed sample compositions are listed in Table 1.

The hydrodynamic diameters of gel particles were measured using PCS. To observe thermo-sensitive swelling behaviors, the scattering light intensities and autocorrelation functions at 90° angles were determined using PCS (PMT, Brookhaven Instrument Co., Model EMI9863). The incident light source used was an argon-ion laser (Lexel Laser Inc., Model 95-2) operated at a 514.5 nm wavelength and 100 mW intensity. The scattered light intensities and time autocorrelation functions were collected using the CONTIN method and were determined at various temperatures [13,14].

3. Theoretical consideration

3.1. Flory–Huggins theory

The simplest and best known theory of the thermodynamics of mixing and phase separation in the binary system is the Flory–Huggins model [15]. The general expression for the free energy of a mixture in a binary system is

$$\frac{\Delta G}{RT} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2 \qquad (1)$$

where ΔG is the free energy of mixing per mole of lattice site, and ϕ_i and r_i are the volume fraction and chain length of the component i, respectively. The χ parameter is defined as

$$\chi = \frac{z\Delta\varepsilon_{12}}{RT} \qquad (2)$$

where z is the coordination number of the model lattice and $\Delta\varepsilon_{12}$ is the energy of formation. $\Delta\varepsilon_{12}$ is calculated by

$$\Delta\varepsilon_{12} = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \qquad (3)$$

where ε_{ij} is the interaction energy of the i–j pair.

Table 1
Proposed hydrogel composition of a NIPA/NIPMA monomer.

Sample name	Composition (NIPA/NIPMA)	NIPA/g	NIPMA/g	BIS/g
HG1	1:0	0.2	0	0.011
HG2	3:1	0.15	0.05	0.011
HG3	1:1	0.1	0.1	0.011
HG4	1:3	0.05	0.15	0.011
HG5	0:1	0	0.2	0.011

3.2. Modified double-lattice model

Oh and Bae [9] defined the Helmholtz energy of mixing as a form of the Flory–Huggins theory. The expression is given by

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right)\ln\phi_1 + \left(\frac{\phi_2}{r_2}\right)\ln\phi_2 + \chi_{OB}\phi_1\phi_2 \qquad (4)$$

where N_r is the total number of lattice sites (coordination number $z = 6$), k is the Boltzmann constant, r_i is the number of segments, and ϕ_i is the volume fraction of component i. The subscripts 1 and 2 refer to the solvent and polymer, respectively. The new interaction parameter χ_{OB} is defined by

$$\chi_{OB} = C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_2 + C_\gamma\tilde{\varepsilon}^2\phi_2^2 \qquad (5)$$

where C_β and C_γ are universal constants. These constants are determined by comparison with Madden et al.'s Monte-Carlo simulation data [16]. The best-fit values of C_β and C_γ are 0.1415 and 1.7986, respectively. $\tilde{\varepsilon}$ is a reduced interaction energy parameter given by

$$\tilde{\varepsilon} = \frac{\varepsilon}{kT} = \frac{\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}}{kT} \qquad (6)$$

where ε_{11}, ε_{22} and ε_{12} are the corresponding nearest-neighbor segment–segment interactions.

To improve the mathematical approximation defect and to reduce the number of parameters, a new Helmholtz energy of mixing for the secondary lattice is defined by the fractional form. The expression is given by

$$\frac{\Delta A_{sec,ij}}{N_{ij,kT}} = \frac{2}{z}\left[\eta\ln\eta + (1-\eta)\ln(1-\eta) + \frac{zC_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}{1 + C_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}\right] \qquad (7)$$

where $\Delta A_{sec,ij}$ is the Helmholtz energy of mixing of the secondary lattice for i–j segment–segment pair, N_{ij} is the number of i–j pairs, $\delta\tilde{\varepsilon}(\delta\varepsilon/kT)$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions. For simplicity, we set η to 0.3, as suggested by Hu et al. [4]. C_α is a universal constant determined by comparison with Panagiotopolus et al.'s Gibbs-ensemble Monte-Carlo simulation [17] data of the Ising lattice. The best-fit value for C_α in this situation is 0.4881.

The secondary lattice contribution is a perturbation of the primary lattice. To incorporate a secondary lattice, we replace ε_{ij} with $\varepsilon_{ij} - \Delta A_{sec,ij}/N_{ij}$ in Eq. (6). If oriented interaction occurs in the i–j segment–segment pairs, we replace $\tilde{\varepsilon}$ with $(\varepsilon/kT) + 2(\Delta A_{sec,ij}/N_{ij}kT)$ in Eq. (6). If oriented interaction occurs in the i–j segment–segment pairs, we replace $\tilde{\varepsilon}$ by $(\varepsilon/kT) - (\Delta A_{sec,ij}/N_{ij}kT)$. In this study, we assume the oriented interactions occurs only in the i–j segment–segment pairs.

For calculating the phase equilibrium condition, we need a chemical potential for components 1 and 2. They are given by $(\Delta\mu_1/kT) = \partial(\Delta A/N_r kT)/\partial N_1$ and $(\Delta\mu_2/kT) = \partial(\Delta A/N_r kT)/\partial N_2$, respectively.

3.3. Swelling behavior for cross-linked NIPA gel

According to Flory [15], the chemical potential of a solvent in a gel phase in the presence of pure solvent is given by

$$\mu_1 - \mu_1^0 = \Delta\mu_1 = \Delta\mu_{1,mix} + \Delta\mu_{1,ela} \qquad (8)$$

where $\Delta\mu_{1,mix}$ and $\Delta\mu_{1,ela}$ represent the mixing and elastic contributions, respectively.

The mixing contribution $\Delta\mu_{1,\mathrm{mix}}$ is similar to those described above for systems containing non-cross-linked polymer. In a system containing a cross-linked polymer network, the $1/r_2$ term is negligible because r_2, the segment number of polymer molecules, is considered to be infinite. Therefore, the chemical potential for the gel systems is simplified as follows:

$$\Delta\mu_{1,\mathrm{mix}}/kT = \ln\left(1-\phi_\mathrm{g}\right)+\phi_\mathrm{g}+r_1\left[\left(C_\beta+\tilde{\varepsilon}+C_\gamma\tilde{\varepsilon}^2\right)+2\left(1-2C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_\mathrm{g}+3C_\gamma\tilde{\varepsilon}^2\phi_\mathrm{g}^2\right]\phi_\mathrm{g}^2 \tag{9}$$

where ϕ_g is the volume fraction of the gel in the gel phase.

We used an expression given by Flory and Erman [11] to obtain the contribution of the elastic forces to the chemical potential. For a perfect tetrafunctional network, the chemical potential for an elastic contribution is given as

$$\frac{\Delta\mu_{1,\mathrm{ela}}}{kT} = \left(\frac{\phi_\mathrm{g}^0}{2x_\mathrm{c}}\right)\lambda^{-1}[1+K(\lambda)] \tag{10}$$

where

$$K(\lambda) = B\left[\dot{B}(1+B)^{-1}+\left(\frac{\lambda}{\kappa}\right)^2\left(B+\lambda^2\dot{B}\right)\left(1+\frac{\lambda^2B}{\kappa}\right)^{-1}\right] \tag{11}$$

with

$$\dot{B} = \frac{\partial B}{\partial\lambda^2} = B\left[\left(\lambda^2-1\right)^{-1}-2\left(\lambda^2+\kappa\right)^{-1}\right] \tag{12}$$

and λ is the linear swelling ratio, as determined by

$$\lambda = \left(\frac{V}{V^0}\right)^{\frac{1}{3}} = \left(\frac{\phi_g^0}{\phi_g}\right)^{\frac{1}{3}} \tag{13}$$

where V and V_0 are the volume of the gel network and the volume in the reference state, respectively, and ϕ_g and ϕ_g^0 are the corresponding volume fractions of the gel. The network parameter κ relates x_C and ϕ_g^0 as follows [11]:

$$\kappa = \frac{1}{4}P\phi_\mathrm{g}^0x_\mathrm{c}^{\frac{1}{2}} \tag{14}$$

where the parameter κ represents the constraints on fluctuations of the junctions due to the surrounding chains in which they are embedded. If these fluctuations could be suppressed, κ would equal 0 and the real network would approach a "phantom network," in the limit of high degree of swelling. If fluctuations can be fully suppressed, $\kappa \to \infty$, the network is called an "affine network". The dimensionless parameter P depends on the characteristics of the polymer and the molar volume of the solvent. We assume that for a phantom network model $P = 0.001$, an affine network model $P = \infty$, and x_C is the average chain length between cross-linking points. Substituting Eqs. (9) and (10) into Eq. (8), the reduced chemical potential of a solvent in gels is expressed by

$$\frac{\Delta\mu_1}{kT} = \left(\frac{\phi_\mathrm{g}^0}{2x_\mathrm{c}}\right)\lambda^{-1}[1+K(\lambda)]+\ln\left(1-\phi_\mathrm{g}\right)+\phi_\mathrm{g}+r_1\left[\left(C_\beta+\tilde{\varepsilon}+C_\gamma\tilde{\varepsilon}^2\right)+2\left(1-2C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_\mathrm{g}+3C_\gamma\tilde{\varepsilon}^2\phi_\mathrm{g}^2\right]\phi_\mathrm{g}^2 \tag{15}$$

The equilibrium condition for the gel in a solvent system is given by

$$\frac{\Delta\mu_1}{kT} = 0 \tag{16}$$

3.4. *Interaction energy for copolymer gel [19]*

We consider a solution of uncross-linked copolymer [A–B] in solvent C, where A and B refer to two different types of segments. We used three different hypotheses, expressed below, in order to calculate the interaction energy of copolymer blends, χ_blend.

1. The chains are random copolymers, and the A and B segments are distributed in random sequences.
2. The existence of different types of A and B segments affects their solvent interaction parameters.
3. The interaction parameter between the A and B segments in a copolymer chain is negligible.

Based on these hypotheses, the general equation for the free energy, was adopted from Eq. (4), is as follows:

$$\frac{\Delta A}{N_\mathrm{r}kT} = \left(\frac{\phi_1}{r_1}\right)\ln\phi_1+\left(\frac{\phi_2}{r_2}\right)\ln\phi_2+\phi_1\phi_2\sum_{i,j}m_{i,j}\chi_{i,j} \tag{17}$$

where the coefficient $m_{i,j}$ is the function of the copolymer compositions, with $0 \le m_{i,j} \le 1$. The copolymer [A–B] in solvent C interaction parameter is given by

$$\chi_\mathrm{blend} = x\chi_\mathrm{AC}+(1-x)\chi_\mathrm{BC} \tag{18}$$

where x represents the mole fraction of co-monomer in the polymer chain.

3.5. *Simulation technique*

Blends, a component of the commercial software MATERIALS STUDIO (ver. 4.4) from Accelrys, was used for the simulation. The segmental units of the polymer molecules, poly (*N*-isopropylacrylamide) and poly (*N*-isopropylmethacrylamide), and the solvent molecules were investigated.

For each polymer, the repeating unit was first built and its geometry optimized by energy minimization using the COMPASS Force Field (CFF) [20]. The structures of water molecules were modeled and minimized energetically on the basis of the CFF. The application of CFF to the treatment of organic molecules is useful for predicting the organic structures and conformational energy differences in simple organic molecules. The nonbond interactions include the van der Waals terms, and the electrostatic interactions between pairs of atoms, those that are separated by two or more intervening atoms, or those that belong to different molecules. From this method, three Boltzmann-averaged pairwise interaction energy values were obtained for each model (ε_{11}, ε_{22}, and ε_{12} are for the corresponding nearest-neighbor segment–segment interaction).

The energy of mixing can be determined from atomistic modeling. Using molecular dynamics simulations with the CFF, it is possible to estimate energy parameters. First, using the sketching tools in the Materials Visualizer, we constructed the monomer repeating unit and the solvent molecule. We next optimized the geometry of the structures using the appropriate force field. After the translation, we calculated the pair interaction energy. Finally, we repeated these steps and calculated ε_{12} by averaging all of the accepted configurations.

The chemical structures of the polymer and polymer repeat unit are given in Fig. 1. Since the polymer segment is connected to the repeating molecules, we considered the effects of chain connectivity by introducing dummy atoms at the connecting positions of the

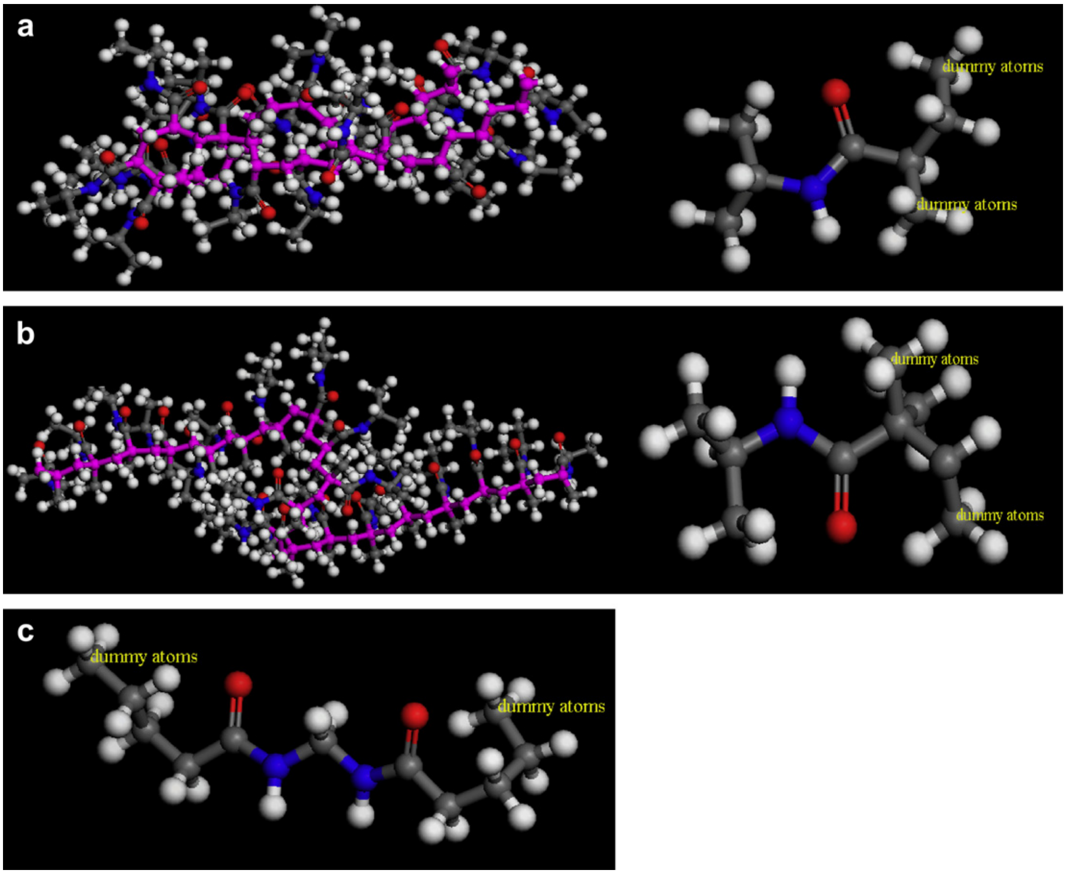

Fig. 1. The model structure of a polymer and its repeating units are (a) and (b), and the model structure of a cross-linker is (c).

polymer segments, rendering these positions of the polymer segments inaccessible to the other segments. In this figure, the methyl group represents the dummy atoms. The dummy atoms are considered as methyl group in the united atom approximation. In calculation of the number of configurations, any configurations containing contacts with dummy atoms were rejected and interaction energies associated with the dummy atoms were generated for each calculation.

Next, we considered specific interactions, such as hydrogen-bonding or dipole–dipole interactions, between *i* and *j* segment pairs. If strong or oriented interactions from hydrogen bonding or other specific forces exist in the system, they can greatly affect the shape and form of the phase diagrams [21]. Because specific interactions between the water and CONH within NIPA and NIPMA exist, illustrated by lower critical solution temperature (LCST) due to the hydrogen bond between the CONH group in the poly (NIPA) and poly (NIPMA) and water, the specific interaction energy was calculated. It was assumed that only in systems with both an electron acceptor, such as an –OH group, and an electron donor, such as an –O or –N group, can there be specific interactions of hydrogen bonding. It was we also assumed that water has both electron donor and acceptor groups. We used this method described by Yang and Bae [22].

In order to calculate the specific interaction, it was assumed that the interaction occurs only between a solvent molecule and a specific group in the polymer repeat unit. In the structure of PNIPA and PNIPMA, ═O and –N– are calculated independently after separation, as shown in Fig. 2.

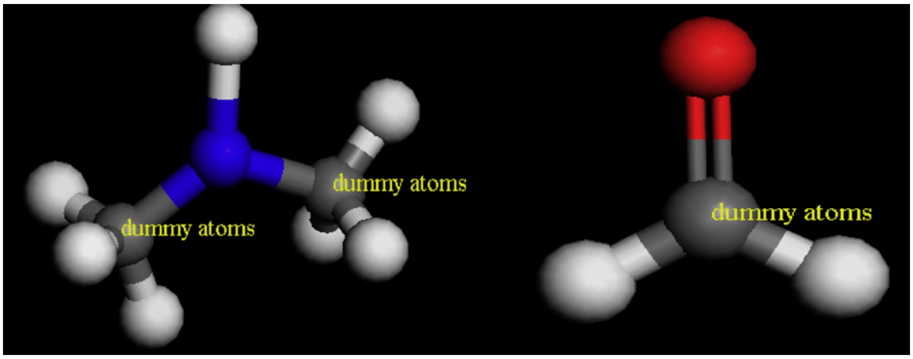

Fig. 2. –N– and ═O represent a simplified specific polymer group.

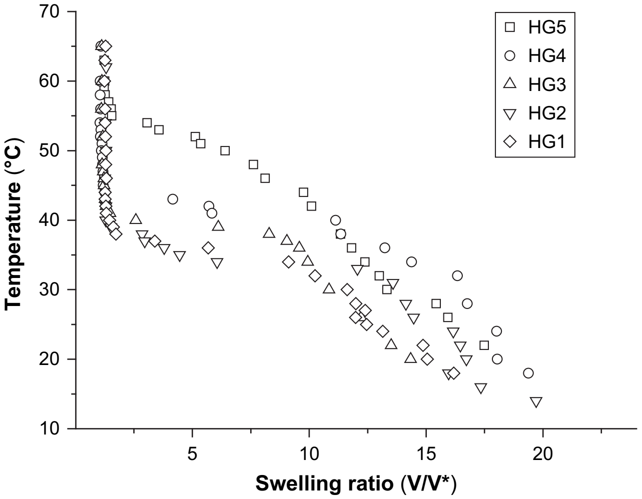

Fig. 3. Swelling behaviors of nanometer-sized hydrogel particles. The volume is calculated from the hydrodynamic diameter, measured using PCS (with CONTIN method). V^* is the volume at the synthesis condition (at 70 °C).

4. Results and discussion

We prepared nanometer-sized gel particles, with hydrodynamic radii smaller than 200 nm. Fig. 3 shows volume phase transitions of nanometer-sized NIPA, NIPA-co-NIPMA and NIPMA gel particles at various temperatures. The average hydrodynamic diameter, D_h, of equilibrium gels at each temperature was measured using PCS with the CONTIN method. The volume ratios of gel particles at a given temperature under the synthesis condition were calculated from the hydrodynamic diameters using a simple relationship: $V/V^* = (D_h/D_h^*)^3$ where the asterisk represents the synthesis condition.

For results obtained from the molecular dynamics simulations, pair attractions are given a negative pair potential. As interaction energy is defined as the energy required to distance two bodies to an infinite intermolecular separation, we used the absolute value of the potential as the interaction energy. Pair interaction energies are listed in Table 2. Ordinary polymer solutions need only the pair interaction energies, while associated polymer solutions employ a perturbation to account for oriented interactions. Because specific interactions exist between the polymer segment and the water molecule, we considered $\delta\varepsilon_{12}$ as an additional energy parameter in calculation; $\delta\varepsilon_{11}$ and $\delta\varepsilon_{22}$ are neglected. The specific interaction energies are listed in Table 3. Two interaction energy parameters obtained from the molecular dynamics simulation are used for the prediction of the swelling equilibrium for the hydrogels in the water system.

If the gel network is formed in the absence of solvent and if change of volume of gel at reference state, V_0, may be ignored, the ideal reference state is very close to that at preparation condition of the gel and then $\phi_g^0 = 1$. The nanometer-sized gel particles in this work, however, were prepared in the presence of water, and the polymer–solvent interaction was inherently present in the formation of the gel, resulting in a nonrandom and perturbed state. Furthermore, since NIPA-co-NIPMA gels are representative thermosensitive hydrogels, V_0 depends on temperature; this leads to difficulties in determining the reference state. Khokhlov [23] reported that V_0 in the presence of solvent is close to that of the so-called Θ temperature [18]. When a solution of non-cross-linked, high molar mass systems shows partial miscibility, the liquid–liquid critical state usually occurs at a very small polymer concentration, known as the Θ state. In this work, the Θ temperature was set at the volume transition temperature since the volume phase transition of hydrogel occurs at its critical temperature. In this limitation of determination of the reference state, ϕ_g^0 can be estimated from the experimental asymptotic value of the swelling ratio [24], $\phi_g^0 = 0.89$ for the gel particles with a cross-linker mole fraction of 0.0123. x_c is approximately estimated from the cross-linker mole fraction as follows [25]:

Table 2
Interaction energy parameters between polymer and solvent and also between cross-linker and solvent.

	ε_{11}/K	ε_{22}/K	ε_{12}/K	Unit
PNIPA/water (298.15 K)	835.334	993.244	1274.34	K
PNIPMA/water (298.15 K)	835.375	1011.02	1235.04	K
Cross-linker/water (298.15 K)	3942.94	1381.61	951.538	K

Table 3
Specific interaction energy parameters between specific groups and water.

	$\delta\varepsilon_{12}$/K	Unit
=O/water (298.15 K)	716.21	K
–N–/water (298.15 K)	598.57	K

$$x_c \approx \left(\frac{1}{2\phi_j}\right)\left(\frac{V_m}{V_l}\right) \tag{19}$$

where is ϕ_j is the mole fraction of cross-linker, and V_m and V_l are the molar volumes of monomer and solvent, respectively.

In our model, as a result of considering only a single type of interaction polymer segment, there were many deviations while predicting the experimental data. In order to diminish these derivations, we introduced a new interaction energy into the reduced interaction energy, $\tilde{\varepsilon}$, in Eq. (6). The corrected energy parameter, $\tilde{\varepsilon}_c$, is expressed as

$$\tilde{\varepsilon}_c = \frac{\varepsilon}{kT}+\frac{\varepsilon_h}{kT} = \frac{\left(\varepsilon+\frac{z\Delta A_{\mathrm{sec},12}}{N_{12}}\right)}{kT}+\frac{\left(\varepsilon_h+\frac{z\Delta A_{\mathrm{sec},12}}{N_{12}}\right)}{kT} \tag{20}$$

where ε_h is an interaction energy between a cross-linker segment and a solvent molecule.

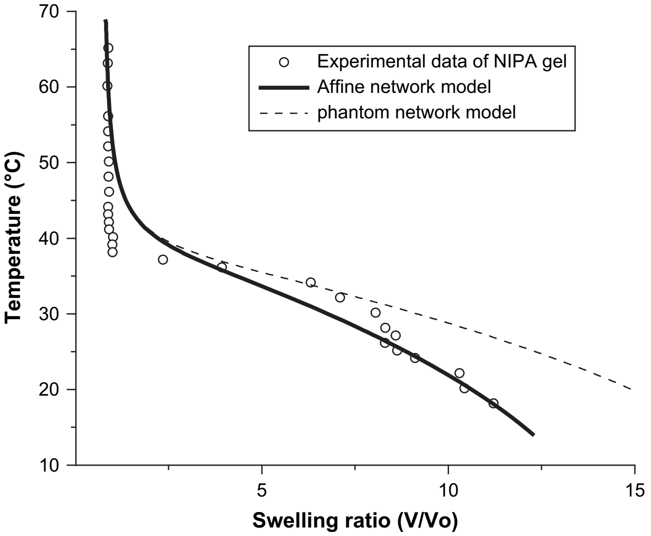

Fig. 4. Swelling behavior of NIPA gel particles and their theoretical prediction from the corrected MDL model, comparison of the affine network with a phantom network. The energy parameters are calculated from MD simulation for PNIPA/water and cross-linker/water system: $\varepsilon/k = 123.459$ K; $\delta\varepsilon_{12}/k = -1314.78$ K; $\varepsilon_h/k = 2131.26$ K; $\delta\varepsilon_{h,12}/k = -1314.78$ K (particle size 70 nm at Θ temperature 34 °C). ϕ_g^0 and x_c are estimated from experimental condition: 0.72 and 179.13, respectively.

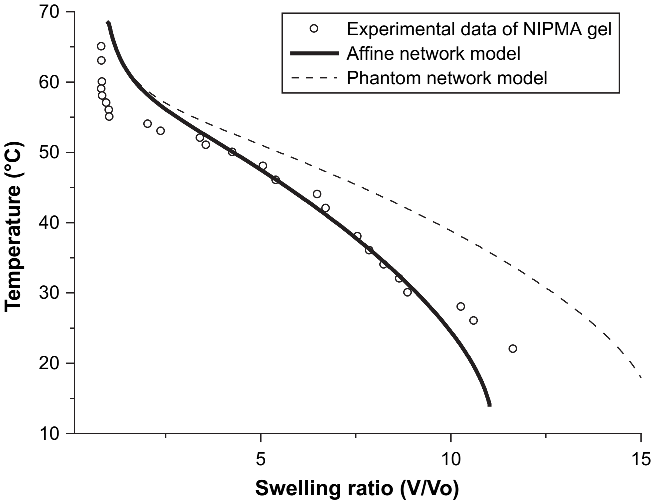

Fig. 5. Swelling curves calculated from the corrected MDL model, affine network and phantom network. The energy parameters are calculated from MD simulation for PNIPMA/water system: $\varepsilon/k = 48.3813$ K; $\delta\varepsilon_{12}/k = -1314.78$ K ($\phi_g^0 = 0.68$, $x_c = 155.08$ and particle size 71 nm at Θ temperature 55 °C).

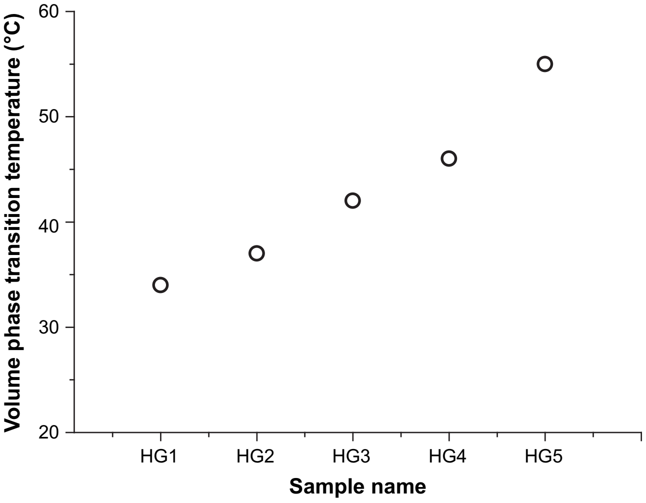

Fig. 7. The composition dependence of volume phase transition temperature for various NIPA/NIPMA hydrogel particles.

Fig. 4 shows a swelling curve calculated from the corrected MDL model; it also illustrates the comparison of a phantom network model and an affine network model with the swelling data of NIPA gel particles. It shows that an affine network model is more appropriate than a phantom network model for explaining the swelling behavior at a high swollen state. These results may be obtained in a network in which the junctions are assumed to be firmly embedded in the medium.

Fig. 5 illustrates swelling of the NIPMA gel particles. In comparison with the NIPA gel from Fig. 4, the results presented in Fig. 5 show a 18 °C increase in volume phase transition temperature and an approximate 75 K decrease in the polymer–solvent interaction energy, ε/k. In other words, a methyl group in the main

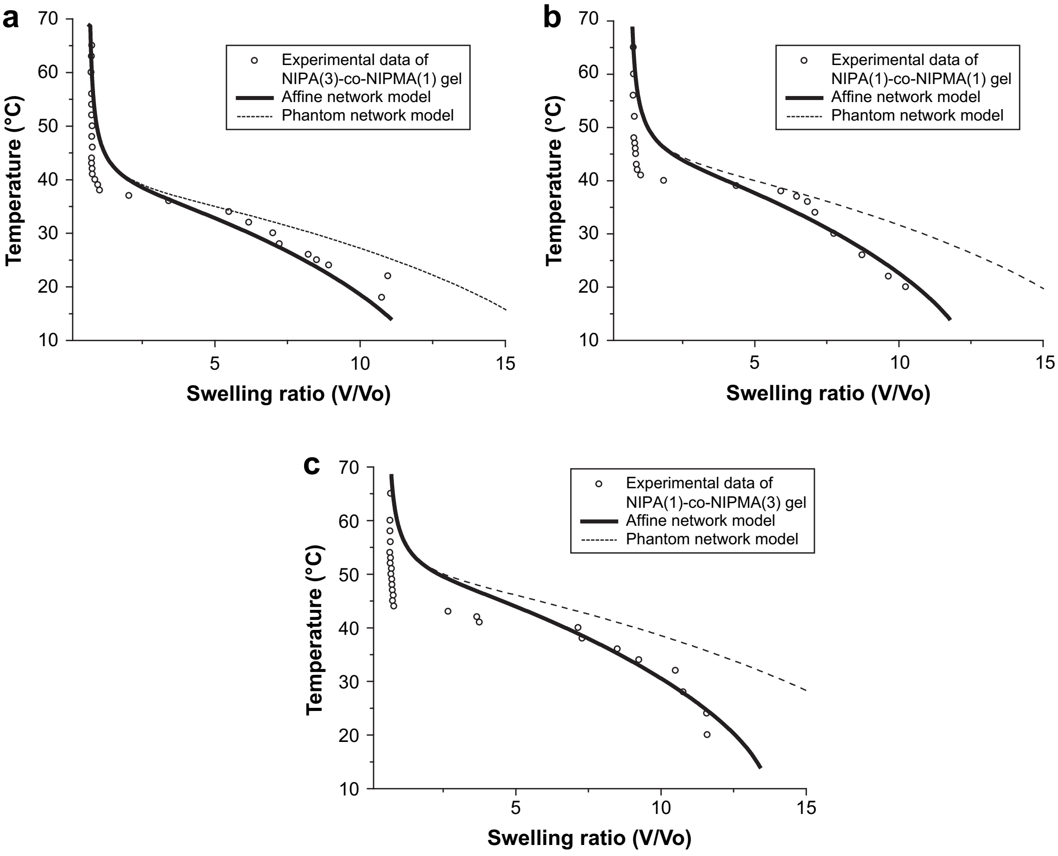

Fig. 6. Swelling curves calculated from the corrected MDL model, affine network and phantom network. Diagram a: NIPA mole fraction $x = 0.77$, $\phi_g^0 = 0.88$, $x_c = 173.60$ and particle size 58 nm at Θ temperature 37 °C. Diagram b: NIPA mole fraction $x = 0.529$, $\phi_g^0 = 0.89$, $x_c = 167.80$ and particle size 66 nm at Θ temperature 42 °C. Diagram c: NIPA mole fraction $x = 0.2725$, $\phi_g^0 = 0.91$, $x_c = 161.63$ and particle size 73 nm at Θ temperature 46 °C.

chain unit structure decreases the interaction energy, and in result, the hydrophobicity decreases while the volume phase transition temperature increases. Fig. 6 shows the copolymer swelling curve of NIPA and NIPMA with various compositions. In the case of NIPA-co-NIPMA gel, the incrementing of the volume phase transition temperature can be measured when the ratio of the methyl group increases. Fig. 7 shows that volume phase transition temperature increases with increasing mole ratio of NIPMA in copolymer gel.

Comparing NIPA, NIPMA and NIPA-co-NIPMA gel, it is shown that when the interaction energy parameter, ε/k, decreased, the volume phase transition temperature increased. Based on this result, it was concluded that the methyl group in the main chain unit structure increases the phase transition temperature.

5. Conclusions

In order to predict the swelling behavior of hydrogel, we combined the modified double-lattice theory and Flory–Erman's theory of elasticity. We used the interaction energy parameter, obtained from molecular dynamics simulations, to predict the swelling equilibrium for hydrogel in a water system, and considering the additional energy parameter in the MDL model, we were able to predict the volume phase transition temperature. In addition, comparison of a phantom network model and an affine network model with the swelling data shows that an affine network model is more appropriate for explaining the swelling data.

The volume phase transition temperature alternates due to the differences in interaction energies within the corrected model. A small error rate was calculated after comparison with experimental data.

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