Macromolecules **1998,** *31,* 7328−7335

Effect of Cross-Linking Density on Swelling Behavior of NIPA Gel Particles

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Received October 22, 1997; Revised Manuscript Received July 1, 1998

ABSTRACT: Submicrometer-sized *N*-isopropylacrylamide(NIPA) gel particles with various composition of cross-linker are prepared by precipitation polymerization and their swelling behaviors are examined by using photon correlation spectroscopy(PCS) technique. Theoretically, Hu et al.'s double-lattice model has been modified by introducing a new universal constant and simplifying the expression of the Helmholtz energy of mixing. The modified double-lattice model(MDL) describes very well the lower critical solution temperature (LCST) behavior of linear PNIPA/water system. For cross-linked NIPA gel particles in water, we have combined MDL theory with Flory and Erman's theory of elasticity, which takes into account the nonaffine displacements of network junctions under high degree of swelling. Energy parameters obtained from the linear PNIPA/water system were directly used to predict swelling equilibria for the NIPA gel/water system. Our results represented that an affine network model explained the swelling behavior at high swelling ratio more accurately than that of the phantom network model. To correct the deviation of the continuous volume transition temperature, we have considered the interaction energy parameter between cross-linker segment and solvent molecule. The corrected model was applied to the swelling equilibria of gel particles with various cross-linking density and agreed well with their experimental data with no adjustable model parameters.

Introduction

It is well-known that the volume phase transition of hydrogels are induced by a continuous change in various conditions of the network such as temperature,[1,2] pH,[3] electric field,[4] radiation of UV or visible light,[5,6] solvent composition,[2,7] salt concentration,[8,9] and type of surfactant.[10,11] In practical applications, these gels are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators. In many cases, quick and uniform responses are necessary for successful applications. The rate of response is inversely proportional to the square of the size of the gel.[12] Therefore, submicrometer-sized gel particles respond to the external stimuli more quickly than bulk gels and are more useful for experiment and practical application.

The swelling behavior of submicrometer-sized gel particles can be successfully characterized by PCS technique. Tanaka *et al.*[13] reported that submicrometer gel particles show a continuous volume phase transition, while bulk gels show a discontinuous volume phase transition. Recently, Wu *et al.*[14] compared the results of the linear poly(*N*-isopropylacrylamide) (PNIPA) and submicrometer *N*-isopropylacrylamide (NIPA) gel particles (spherical microgels) and showed that the volume change of a polymer gel is practically continuous because the inhomogeneity of the subchain between two neighboring cross-linking points in the gel makes the volume change more continuous.

Thermodynamically, gels are cross-linked-polymer networks that can absorb solvent but are insoluble in the solvent. The equilibrium solvent content of the gel depends on temperature, polymer−solvent interaction, and the elastic forces in the network that counteract swelling. Gels of polymers that exhibit an UCST are collapsed at low temperatures and swollen as the temperature rises. Gels of polymer that exhibit a LCST show inverted behavior; they are swollen at low temperatures and collapse as the temperature rises. It is well-known that the linear PNIPA/water system exhibits an lower critical solution temperature (LCST) because of the specific interaction (e.g. hydrogen bond between the CONH group in the polymer chain and water). Therefore, the cross-linked NIPA gel/water system shows the swelling behavior of a type of LCST.

The swelling of a cross-linked polymer by solvent is often used to assess either cross-linking density or the polymer solvent interaction parameter provided one of these two parameters is known from independent measurements. Prausnitz *et al.*[15] obtained the interaction energy parameters from liquid−liquid equilibria (LLE) for a linear PNIPA/water system by using an oriented quasi-chemical model that takes into account the strong specific or oriented interaction and applied these parameters to swelling equilibria of gels. Their theoretical prediction shows some deviation from experimental swelling data at the volume phase transition temperature and high degrees of swelling. However, it is worth noting that the model actually has no adjustable parameters in predicting the swelling behaviors of NIPA gels. Cussler *et al.*[16,17] also introduced Sanchez and Lacombe's lattice-fluid model, which considered holes in lattice as a component for the free energy of mixing and compared the model with their swelling data. They compared the predicted energy parameters for gels including an adjustable parameter with experimental data by differential scanning calorimetry and compared the fitted cross-linking density with experimental results.

To successfully predict LCST-type swelling equilibria for NIPA gel/water system, it is important to obtain the correct parameters related to the specific interaction

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10.1021/ma971554y CCC: $15.00

energy as well as the ordinary interaction energy between polymer segment and solvent from LLE for a linear PNIPA/water system. Recently, Hu *et al.*[18,19] reported a double lattice model to predict LCST and a closed loop behavior for polymer solution system. In their model, ordinary polymer solutions are described by the primary lattice, while a secondary lattice is introduced as a perturbation to account for the specific interaction.

In this study, we modified Hu *et al.*'s[19] double-lattice model by introducing a new universal constant and simplifying the expression of the Helmholtz energy of mixing. Using our proposed model, we investigated phase behaviors of linear PNIPA/water system, and the interaction energy parameters are directly used to predict the swelling equilibria for the NIPA gel/water system. For cross-linked NIPA gel in water, the elastic free energy is formulated according to Flory and Erman's theory of elasticity,[20] which takes into account the nonaffine displacements of network junctions under strain or at a high degree of swelling. We combined the MDL theory with the rubber elasticity theory. Experimentally, submicrometer-sized NIPA gel particles with various composition of cross-linker are prepared by precipitation polymerization, and their swelling behaviors are examined by using the PCS technique. The proposed model is compared with the swelling data, and the effect of cross-linking density on swelling behavior of the gel particles is investigated.

Experimental Section

N-Isopropylacrylamide (NIPA) provided by TCI Co. was used after recrystallization. *N*,*N*′-Methylenebis(acrylamide) (BIS) and ammonium persulfate (APS) were used as a cross-linker and an initiator, respectively. Tween-20 was selected as a nonionic surfactant to stabilize the submicrometer gel particles without affecting the swelling behavior. We prepared three NIPA gel particles with various C% (=moles of cross-linker in feed/total moles of monomer (monomer + cross-linker) in feed × 100); C% values were 1.23, 2.50, and 3.88, respectively. Then 0.2 g of NIPA and the corresponding amount of BIS were dissolved in the excess amount of distilled deionized (DDI) water filtered through 0.45 μm pore size Millipore filter. After the monomer solution was poured into a batch reactor, 100 μL of 1% APS solution and 500 μL of 1% Tween-20 solution were added. The reaction temperature was set at 70 °C. The submicrometer-sized gel particles were prepared by the precipitation polymerization with stirring and nitrogen blowing for 4 h.[21]

The hydrodynamic diameters of submicrometer gel particles were measured by the PCS technique. The solution containing gel particles was diluted with filtered DDI water to get an appropriate concentration for the light scattering measurement and then poured into the glass cell. The temperature of the vat in which the cell was immersed was controlled by a circulation bath from 1 to 80 °C with a stability of ±0.05 °C. The incident light source was an argon-ion laser (Lexel Laser Inc. Model 95-1) operated at 514.5 nm wavelength and 100 mW intensity. The scattered light was unpolarized and detected by a photomultiplier tube (PMT, Brookhaven Instruments Co. Model EMI9863) at a scattering angle of 90°. The signal from the PMT was digitized by an amplifier−discriminator and was fed into a correlator. The digital 8 bits × 256 channels (maximum) correlator (Brookhaven Instruments Co. Model BI9000AT) accumulated the time correlation function of the intensity of the scattered light. The time correlation function was calculated and analyzed by using the first cumulant method. The details of PCS technique are described elsewhere.[22,23]

Model Development

Liquid−Liquid Equilibria for the Non-cross-linked Poly(*N*-isopropylacrylamide)/Water System. Freed et al.[24,25,26] developed a complicated lattice-field theory for polymer solutions which is formally an exact mathematical solution of the Flory−Huggins lattice. Good agreement was found between predicted results and the computer simulation data by Dickman and Hall[26] for the chain insertion probability and for pressures in a system of athermal chains and voids. The general form of the Helmholtz energy of mixing based on Freed's theory can be expressed as

$$\Delta A/N_{\mathrm{r}}kT = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \sum_m\sum_n a_{mn}{\phi_1}^m{\phi_2}^m \quad (1)$$

where N_{r} is the number of lattice sites for the mixture and ϕ_i and r_i are the volume fraction and the number of segments of component i, respectively. Since the segment is defined as the portion of a chain whose volume equals that of the solvent molecules, r_1 can be set to a unity. Coefficients a_{mn} are functions of z, r_1, r_2, and energy parameters. For practical reasons, the infinite series with respect to coordination number, temperature and composition in this theory are truncated at a certain order. To obtain an analytical expression for the Helmholtz energy of mixing for the primary lattice, Hu *et al.*[18,19] employed only the first-order term multiplied by empirical coefficients. In this study, we defined Helmholtz energy of mixing as the form of the Flory−Huggins theory on the basis of Hu's expression. This expression is given by

$$\Delta A/N_{\mathrm{r}}kT = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \chi(\mathrm{T},\phi_2)\phi_1\phi_2 \quad (2)$$

where $\chi(T,\phi_2)$, a new interaction function, is defined for both temperature and composition by

$$\chi(T,\phi_2) = C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right)\tilde{\epsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + \mathrm{C}_\gamma\tilde{\epsilon}\right)\tilde{\epsilon}\phi_2 + \mathrm{C}_\gamma{\epsilon}^2{\phi_2}^2 \quad (3)$$

where C_β and C_γ are universal constants. These constants are not adjustable parameters and are determined by comparing with Monte Carlo simulation data from Madden *et al.*[28] $\tilde{\epsilon}$ is a reduced interaction parameter given by

$$\tilde{\epsilon} = \epsilon/kT = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/kT \quad (4)$$

The positive energy parameters, ϵ_{11}, ϵ_{22}, and ϵ_{12} are for the corresponding nearest-neighbor segment−segment interactions. Figure 1 shows the comparison of coexistence curves calculated from this work and Flory−Huggins model with computer simulation results. The best fitting values of C_β and C_γ are 0.141 and 1.798, respectively.

According to Freed's theory, the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\Delta A/N_{\mathrm{r}}kT = x_1\ln x_1 + x_2\ln x_2\ z\tilde{\epsilon}x_1x_2/2 - z\tilde{\epsilon}^2{x_1}^2{x_2}^2/4 + \ldots \quad (5)$$

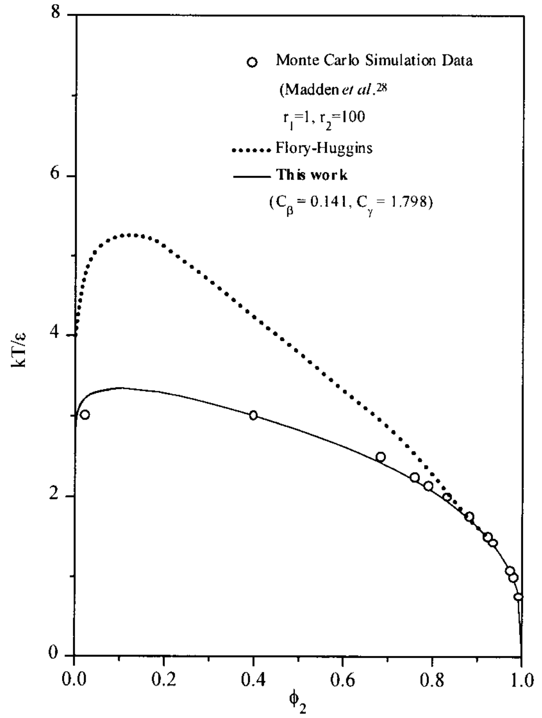

Figure 1. Comparison of coexistence curves calculated from this work and the Flory–Huggins model with computer simulation results. The dotted line is calculated from the Flory–Huggins model, and the solid line is calculated from this work with $C_\beta = 0.141$ and $C_\gamma = 1.798$. Open circles are from Madden's Monte Carlo simulation data.

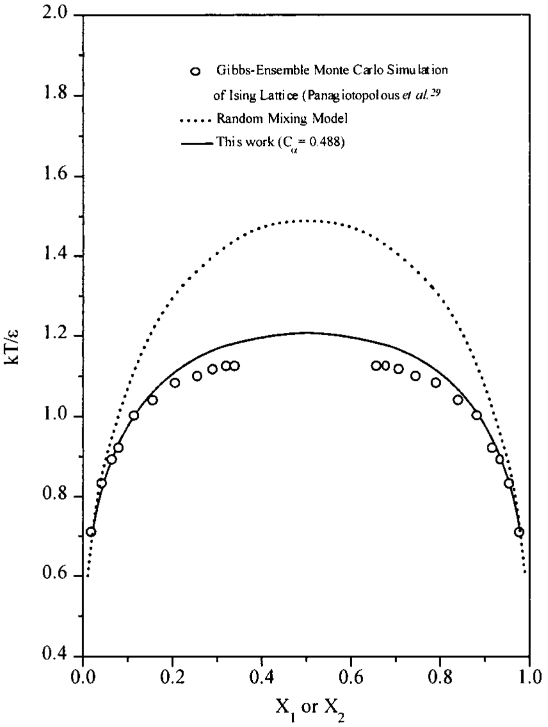

Figure 2. Comparison of Ising lattice coexistence curves calculated from this work and random mixing model with computer simulation results. The dotted line is calculated from the random mixing model, and the solid line is calculated from this work with $C_\alpha = 0.488$. Open circles are from Panagiotopolous's Gibbs-Ensemble Monte Carlo simulation data.

where z is the coordination number and x_i is the mole fraction of component i.

To obtain an analytical expression for the secondary lattice, Hu *et al.* revised the eq 5 to improve the coexistence curves by introducing two empirical coefficients and adding the additional energy of the reference state. In this study, we define a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect and to reduce the number of parameters. The expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z}\left[\eta \ln \eta + (1-\eta)\ln(1-\eta) + \frac{zC_\alpha \delta\tilde{\epsilon}_{ij}(1-\eta)\eta}{1 + C_\alpha \delta\tilde{\epsilon}_{ij}(1-\eta)\eta}\right] \quad (6)$$

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for a $i-j$ segment–segment pair and N_{ij} is the number of $i-j$ pairs, $\delta\tilde{\epsilon}$ $(=\delta\epsilon/kT)$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions. According to Hu *et al.* we arbitrarily set η to 0.3. C_α, a universal constant, also is not an adjustable parameter and is determined by comparing with Panagiotopolous *et al.*'s Gibbs-Ensemble Monte Carlo simulation data for the Ising lattice.[29] Figure 2 shows the comparison of Ising lattice coexistence curve calculated from this work and random mixing model with computer simulation results. The best fitting value of C_α is 0.488.

The secondary lattice contribution is a perturbation to the primary lattice. To incorporate the secondary lattice into the primary lattice, we replace ϵ_{ij} by $\epsilon_{ij} - \Delta A_{\text{sec},ij}/N_{ij}$ in eq 4. Following the definition of $\tilde{\epsilon}$ in eq 4, if oriented interaction occurs in $i-j$ segment–segment pairs, we replace $\tilde{\epsilon}$ by $\epsilon/\text{kT} + 2\Delta A_{\text{sec},ij}/N_{ij}kT$ in eq 4. If the oriented interaction occurs in $i-i$ segment–segment pairs, $\tilde{\epsilon}$ is replaced by $\epsilon/kT - \Delta A_{\text{sec},ii}/N_{ii}kT$. Correlation equations for calculating the binary coexistence curve are derived in the Appendix.

Swelling Equilibria for Cross-Linked NIPA Gel. Since the chemical potential given by eq A1 in the Appendix is valid only for mixtures of linear polymers, we use the Flory–Rehner expression for the random contribution to the combinatorial factor and consider the contribution of elastic forces in polymer network to the Gibbs free energy. According to Flory,[30] the chemical potential of a solvent in a gel phase coexisting with pure solvent is given by

$$\mu_1 - \mu_1^0 = \Delta\mu_1 = \Delta\mu_{1,\text{mix}} + \Delta\mu_{1,\text{ela}} \quad (7)$$

We employ the Flory–Huggins combinatorial term for random contribution to $\Delta\mu_{1,\text{mix}}$. The energy contribution to $\Delta\mu_{1,\text{mix}}$ is basically similar to those described above for systems containing non-cross-linked polymer (eq A1). In a system containing a cross-linked polymer network, the number of polymer molecules approaches zero and the $1/r_2$ term in the energetic contribution is negligible since the r_2 value is greater than r_1 and rarely influences the swelling equilibria in practical calculation. In the limits, we obtain

$$\frac{\Delta\mu_{1,\text{mix}}}{kT} = \ln(1-\phi_g) + \phi_g + r_1[(C_\beta + \tilde{\epsilon} + C_\gamma\tilde{\epsilon}^2) + 2(1 - 2C_\gamma\tilde{\epsilon})\tilde{\epsilon}\phi_g + 3C_\gamma\tilde{\epsilon}^2{\phi_g}^2]{\phi_g}^2 \quad (8)$$

where ϕ_g is the volume fraction of the gel in the gel phase. Two interaction energy parameters, i.e., ϵ/k (the interaction energy parameter between polymer and solvent in the primary lattice) and $\delta\epsilon/k$ (the interaction energy parameter due to a specific interaction in the secondary lattice), and three universal constants are the same as those obtained from LLE for the non-cross-linked polymer/solvent system.

We use an expression given by Flory and Erman[20] to obtain the contribution of elastic forces to the chemical potential. For a perfect tetrafunctional network, the chemical potential for elastic contribution is given as

$$\frac{\Delta\mu_{1,\mathrm{ela}}}{kT} = \left(\frac{\phi_g^0}{2x_c}\right)\lambda^{-1}[1 + K(\lambda)] \tag{9}$$

where

$$K(\lambda) = B[\dot{B}(1 + B)^{-1} + (\lambda/\kappa)^2(B + \lambda^2\dot{B})(1 + \lambda^2 B/\kappa)^{-1}] \tag{10}$$

with

$$\dot{\mathrm{B}} = \partial\mathrm{B}/\partial\lambda^2 = \mathrm{B}[(\lambda^2 - 1)^{-1} - 2(\lambda^2 + \kappa)^{-1}] \tag{11}$$

The linear swelling ratio λ is related to the volume fraction of polymer network

$$\lambda = \left(\frac{\mathrm{V}}{\mathrm{V}^0}\right)^{1/3} = \left(\frac{\phi_g^0}{\phi_g}\right)^{1/3} \tag{12}$$

where V and V^0 are the prevailing volume of the gel network and the volume in the reference state, respectively; ϕ_g and ϕ_g^0 are the corresponding volume fractions of the gels. The parameter κ measures the constrains on fluctuation of junctions due to the surrounding chains in which they are embedded. If constrains on fluctuation of junctions due to their embedment in the welter of surrounding randomly configured chains could be suppressed, $\kappa = 0$, and a real network approaches a “phantom network” in the limit of high degree of swelling. If fluctuations of the junctions may be considered to be suppressed totally by the constraints, $\kappa \rightarrow \infty$, and the network is called an “affine network”, a network in which the junctions are assumed to be firmly embedded in the medium. The number of segments occupied by an elastically active chain, x_c, represents the chain length of an average chain between cross-linkages (or junctions) and is inversely proportional to cross-link density or the number of active chains. According to Flory and Erman,[20] the characteristic parameter κ relates x_c and ϕ_g^0 as follows:

$$\kappa = \frac{1}{4}\mathrm{P}\phi_g^0 {x_c}^{1/2} \tag{13}$$

Here the dimensionless parameter P depends on characteristics of the generic type of polymer and on the molar volume of solvent.

If eqs 8 and 9 are substituted into eq 7, the reduced chemical potential of a solvent in gels is expressed by

$$\frac{\Delta\mu_1}{kT} = \left(\frac{\phi_g^0}{2x_c}\right)\lambda^{-1}[1 + K(\lambda)] + \ln(1 - \phi_g) + \phi_g + r_1[(C_\beta + \tilde{\epsilon} + C_\gamma\tilde{\epsilon}^2) + 2(1 - 2C_\gamma\tilde{\epsilon})\tilde{\epsilon}\phi_g + 3C_\gamma\tilde{\epsilon}^2{\phi_g}^2]{\phi_g}^2 \tag{14}$$

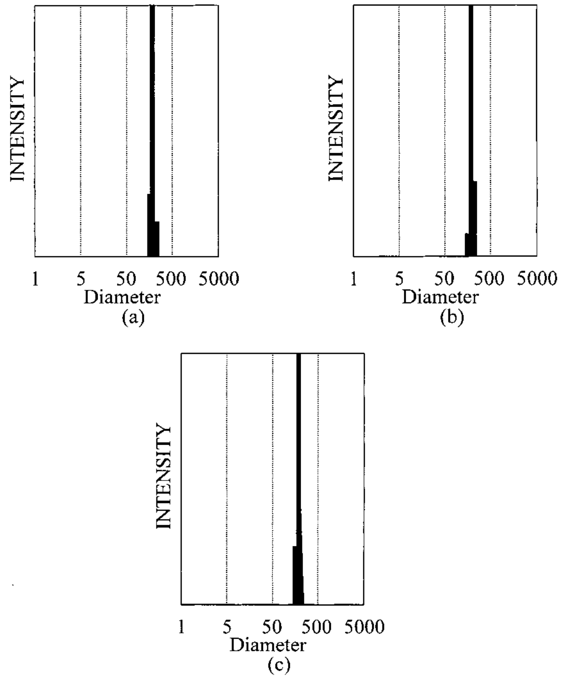

Figure 3. Particle size distribution of each sample at $T = 70$ °C: (a) C% = 1.23; (b) C% = 2.50; (c) C% = 3.88.

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

$$\frac{\Delta\mu_1}{kT} = 0 \tag{15}$$

If the swelling equilibria exhibits discontinuous volume phase transition, coexistence of two gel phases (collapse phase and swollen phase) in equilibrium in pure solvent should be considered to explain the transition. The binodal curve for the coexistence of the collapsed (denoted by C) and the swollen (denoted by S) gel phases can be determined by applying the following Maxwell condition to the chemical potential isotherms.[15]

$$\int_{\text{gel phase S}}^{\text{gel phase C}} \phi_1 \mathrm{d}(\Delta\mu_1) = 0 \tag{16}$$

The volume phase transition of gels occurs at the temperature at which eqs 15 and 16 are satisfied simultaneously.

Results and Discussion

We prepared monodispersed submicrometer-sized gel particles, whose hydrodynamic radii are smaller than 200 nm. Figure 3 shows the size distribution of gel particles: (a) 1.23 C%, 171 nm; (b) 2.5 C%, 169 nm; (c) 3.88 C%, 196 nm.

Figure 4 shows swelling behaviors of submicrometer-sized NIPA gel particles with various C%. The average hydrodynamic diameters, D_h, of equilibrium gels at various temperatures are measured by PCS technique. The volume ratio of gel particles at a given temperature to that at synthesis condition(collapsing limit) is calculated from the hydrodynamic diameter by using a simple relationship: $V/V^* = (D_h/D_h^*)^3$ where the asterisk represents the synthetic condition. The gel particles exhibit continuous volume change in the temperature range from 32 to 37 °C. As C% (cross-linking density) decreases, the volume change of gel particles is more

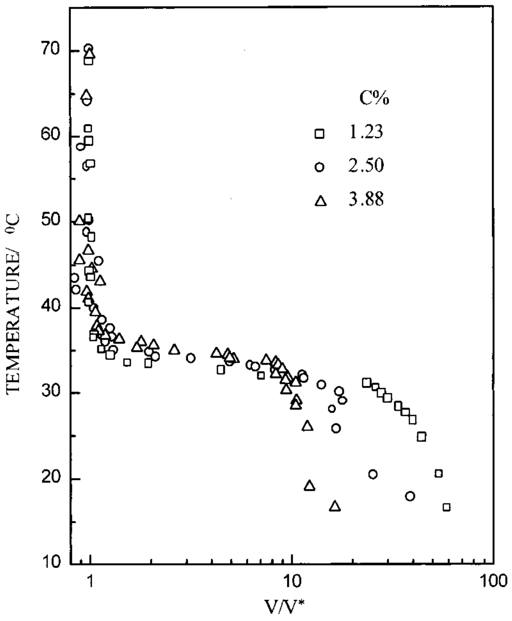

Figure 4. Swelling behaviors of submicrometer sized gel particles with various C%. The volume is calculated from the hydrodynamic diameter which is measured by PCS technique. V^* is the volume at the synthesis condition (collapsing limit).

discontinuous. This result coincides with Tanaka and Li's report[31] for a bulk gel: they have shown that the continuous volume change became a discontinuous one as the cross-linking density of a bulk NIPA gel was decreased. At 20 °C, the swelling of gel particles with smaller C% is greater than that of larger C%. The temperature at which gel particles start swelling shifts toward high temperature with increasing C%.

Figure 5 shows experimental coexistence data and the theoretical curve calculated from MDL model for linear PNIPA/water system (eqs A2 and A3 in the Appendix). Since specific interaction exists between PNIPA segment and water molecule, the system exhibits a LCST behavior and we considered $\delta\epsilon_{12}$ as an additional energy parameter in calculation; $\delta\epsilon_{11}$ and $\delta\epsilon_{22}$ are neglected in this case. The calculated curve agrees well with the experimental data although there is a slight deviation in the region of polymer rich phase. Adjustable model parameters, r_2, ϵ/k, and $\delta\epsilon_{12}/k$, are 56.0, 1643.201 K, and −1604.4 K, respectively. Two interaction energy parameters obtained from the linear PNIPA/water system are directly used in the prediction of swelling equilibria for the cross-linked NIPA gel/water system.

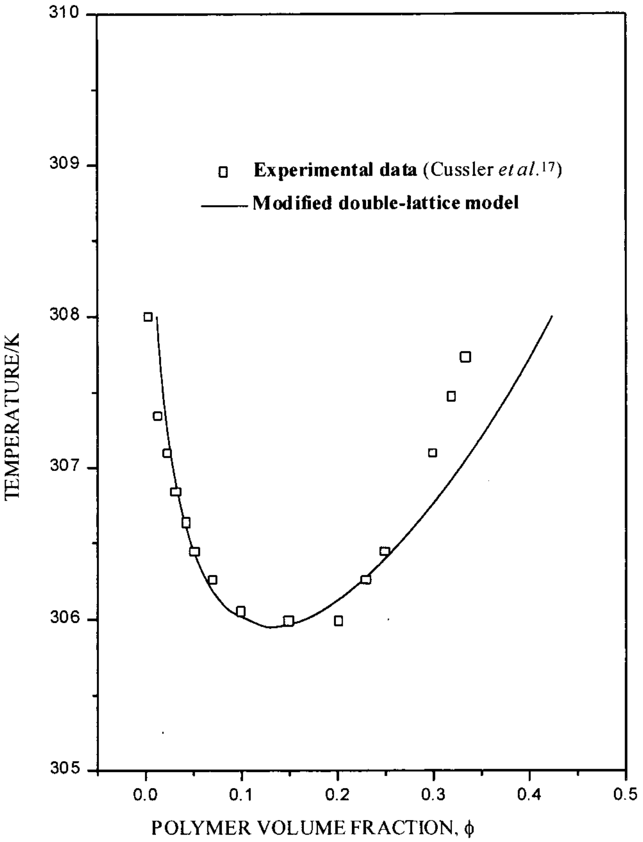

Figure 5. Cloud-point data for linear PNIPA/water system. Squares are experimental data from Cussler *et al.*[17] Solid line is calculated from the modified double-lattice model. $r_2 = 56.0$, $\epsilon/k = 1643.201$ K, $\delta\epsilon_{12}/k = -1604.4$ K.

Figure 6 shows a swelling behavior of NIPA gel particles with 1.23 for C% and the theoretical prediction from eqs 13 and 14. The gel network has a random walk configuration and an unperturbed chain conformation at the reference state. If the gel network is formed in the absence of solvent and if the change of volume of gel at the reference state, V_0, may be ignored, the ideal reference state is very close to that at the preparation condition of the gel and then $\phi_g^0 = 1$. The submicrometer gel particles in this work, however, are prepared in the presence of water, and the polymer−solvent interaction is inherently present in the formation of the gel, which results in a nonrandom and perturbed state. Furthermore, V_0 depends on temperature since NIPA gel is a representative thermo-sensitive gel. These lead to difficulties in determining the reference state. Khokhlov[32] reported that V_0 in the presence of solvent is close to that at the so-called Θ temperature. In this work, the state at the Θ temperature (~30.6 °C[14]) for the PNIPA/water system is chosen as a reference state. In this limitation of determination of the reference state, ϕ_g^0 can be estimated from the experimental asymptotic value of the swelling ratio:[33] $\phi_g^0 = 0.048$ for the gel particles with 1.23 for C%. If NIPA monomer and BIS cross-linker in the feed are completely converted into the gel network and the amount of cross-linker is much smaller than that of monomer, x_c is approximately estimated from C% as follows:

$$x_c \approx \left(\frac{1}{2\phi_J}\right)\left(\frac{v_m}{v_1}\right) \tag{17}$$

Here ϕ_J is the mole fraction of cross-linker (or junction) unit to total monomer unit in the gel network ($\phi_J \approx$ C%/100), and v_m and v_1 are the molar volumes of monomer and solvent, respectively. We assume that the fluctuation of junctions in the gel network is rarely constrained and the gel has a phantom network. In Figure 6, the dimensionless parameter P was set to a unity. As we mentioned above, two interaction energy parameters were obtained from correlating the LLE for linear PNIPA. Thus, the calculated curve shown in Figure 6 has not been fitted to experimental swelling data: this curve is a prediction based on the known gel composition at preparation and on the energy parameters obtained from independent experiment. The calculated swelling ratio at a high swollen state is greater than that of the observed one. The predicted continuous volume transition temperature is about 3 °C lower than that of the observed one. It results from our assumption that the

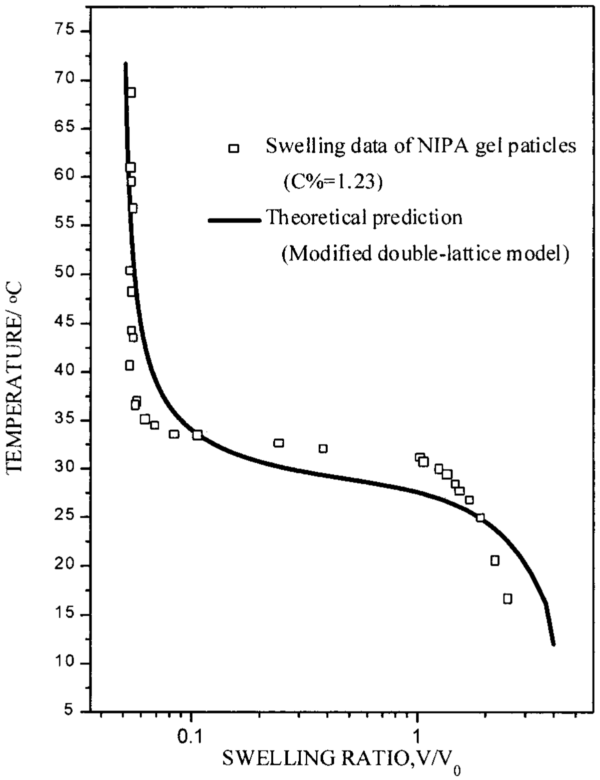

Figure 6. Swelling behavior of NIPA gel particles and their theoretical prediction from eqs 14 and 15. ϕ_g^0 and x_c are estimated from experimental conditions: 0.048 and 256.0, respectively. The characteristic parameter P is set to unity, for which the gel is near a phantom network. The energy parameters are the same as those calculated from LLE for PNIPA/water system: $\epsilon/k = 1643.201$ K; $\delta\epsilon_{12}/k = -1604.4$ K.

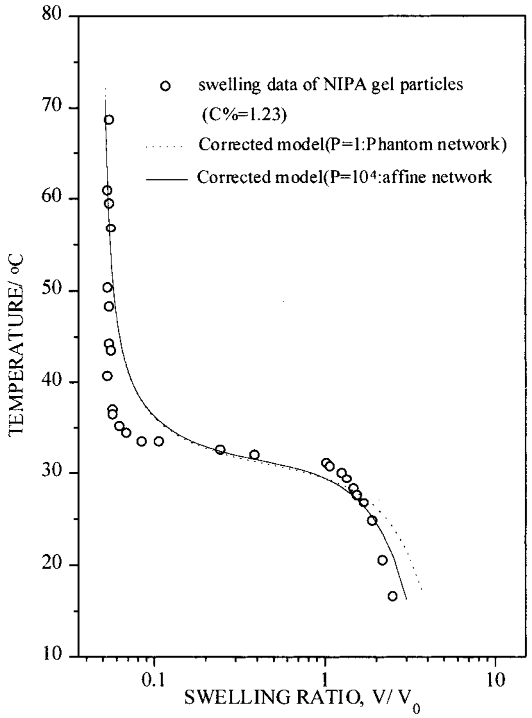

Figure 7. Swelling curve calculated from the corrected MDL model, phantom network model and affine network model. Open circles are swelling data of NIPA gel particles (C% = 1.23). The structural parameters (ϕ_g^0 and x_c) and the energy parameters are the same as those in the uncorrected model (Figure 6). The only adjustable parameter, ϵ_J/k, is −743.0 K and the mole fraction, ϕ_J, estimated from C% is 0.0123.

gel has a phantom network. Actually, fluctuation of junctions in the gel network is constrained by the surrounding junctions, especially at the high swollen state. The deviation may result from the usual assumption that the gel network contains a single type of interaction polymer segment, i.e., neglecting the existence of cross-linker in the gel. The error can be reduced if the interaction energy between cross-linker segment and solvent molecule is considered. We introduced a new interaction energy into the reduced interaction energy $\tilde{\epsilon}$ in eq 4 to correct the error. The corrected energy parameter, $\tilde{\epsilon}_c$, is expressed as

$$\tilde{\epsilon}_c = \epsilon_c/kT = (\epsilon + \phi_J\epsilon_J + 2\Delta A_{sec,12}/N_{12})/kT \quad (18)$$

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

Figure 7 shows a swelling curve calculated from the corrected MDL model and it also represents the comparison of a phantom network model and an affine network model with the swelling data of NIPA gel particles (C% = 1.23). The structural parameters and the energy parameters are the same as those in the uncorrected model as shown in Figure 6. The interaction energy, ϵ_J/k, is −743.0 K and the mole fraction, ϕ_J, estimated from C% is 0.0123. Although the value of ϵ_J/k is approximately half of the other energy parameters and ϕ_J is a very small value, the relatively small value of the correction term shifts up the predicted swelling curve by about 2 °C. The comparison of a phantom network model and an affine network model with the swelling data shows that an affine model is more appropriate than that of the phantom model for explaining the swelling behavior at a high swollen state.

In Figure 8, swelling data of NIPA gel particles with different C% are compared with the corrected MDL model in the assumption of an affine network ($P = 10^4$), parts a and b of Figure 7 exhibit swelling data and the predicted curve for NIPA gel particles with 2.50 and 3.88 for C%, respectively. The three energy parameters are the same as those in Figure 6. The structural parameters related to cross-linking density are estimated from experimental data. The predicted swelling curve actually has no adjustable or fitting parameters.

Conclusion

We have modified Hu *et al.*'s double-lattice model by introducing a new universal constant and simplifying the expression of the Helmholtz energy of mixing. This model has been used to obtain the interaction energy parameters from LLE for the linear PNIPA/water system. The modified double-lattice model describes very well the LCST behavior of the linear PNIPA/water system.

For a cross-linked NIPA gel in water, we have combined MDL theory with Flory and Erman's theory of elasticity, which takes into account the nonaffine displacements of network junctions under a high degree of swelling. The independently obtained energy parameters were directly used to predict swelling equilibria for the NIPA gel/water system. We noticed that an affine network model explains the swelling behavior of a given system at high swelling ratio more accurately than that of the phantom network model. To correct the deviation of continuous volume transition temperature, we have considered the interaction energy pa-

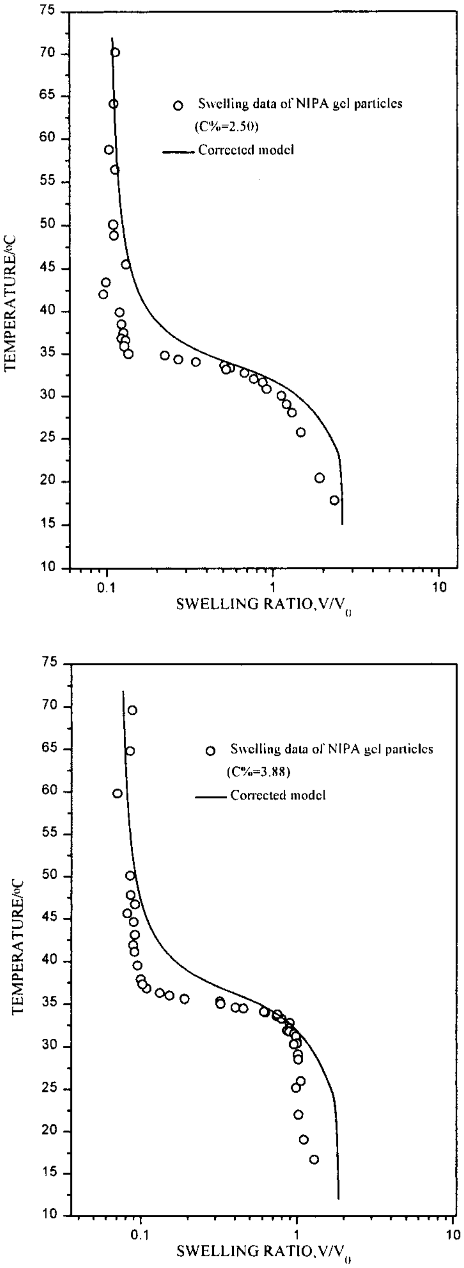

Figure 8. Comparison of the corrected MDL model with swelling data of NIPA gel particles with (a) 2.50 and (b) 3.88 for C%. Diagram a: $\phi_g^0 = 0.10$, $x_c = 126.0$, and $\phi_J = 0.025$. Diagram b: $\phi_g^0 = 0.10$, $x_c = 126.0$, $\epsilon/k = 1643.201$ K, $\delta\epsilon_{12}/k = -1604.4$ K, and $\phi_J = 0.0388$.

rameter between cross-linker segment and solvent molecule. The corrected model was applied to describe swelling equilibria of gel particles with various cross-linking density and agreed very well with their experimental data with no adjustable model parameters.

Acknowledgment. This paper was supported by Korea Science & Engineering Foundation (KOSEF) under Contract No. 96-0300-12-01-3,1996.

Appendix: Correlation Equations for LLE

For calculating the binary coexistence curve, we need a chemical potential for components 1 and 2. They are given by

$$\frac{\Delta\mu_1}{kT} = \partial(\mathrm{D}A/kT)/\partial N_1$$

$$= \ln(1-\phi_2) - \left(1 - \frac{r_1}{r_2}\right)\phi_2 + r_1\Bigg[C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon} + \left(2 + \frac{1}{r_2}\right)\tilde{\epsilon}\Bigg]{\phi_2}^2 - 2r_1\Bigg[\Bigg(\Bigg(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\Bigg)\tilde{\epsilon} + C_\gamma\tilde{\epsilon}^2\Bigg]{\phi_2}^3 + 3r_1C_\gamma\tilde{\epsilon}^2{\phi_2}^4 \quad \text{(A1)}$$

$$\frac{\Delta\mu_2}{kT} = \partial(\Delta A/kT)/\partial N_2$$

$$= \ln\phi_2 + r_2\Bigg[\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right)\tilde{\epsilon}\Bigg] - r_2\Bigg[\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + 2\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon} + 2C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + 2\left(2 + \frac{1}{r_2}\right)\tilde{\epsilon}\Bigg]\phi_2 + r_2\Bigg[4\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon} + \left(2 + \frac{1}{r_2}\right)\tilde{\epsilon} + C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + 3C_\gamma\tilde{\epsilon}^2\Bigg]{\phi_2}^2 - r_2\Bigg[6C_\gamma\tilde{\epsilon}^2 + 2\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon}\Bigg]{\phi_2}^3 + 3r_2C_\gamma\tilde{\epsilon}^2{\phi_2}^4 \quad \text{(A2)}$$

The coexistence curve is found from the following conditions:

$$\Delta{\mu_1}' = \Delta{\mu_1}'' \quad \text{(A3)}$$

$$\Delta{\mu_2}' = \Delta{\mu_2}'' \quad \text{(A4)}$$

Here primes and a double primes denote two phases at equilibrium.

For phase equilibrium calculations, we require the experimental coordinates of the critical point. We find these coordinates using

$$\frac{\partial^2(\Delta A/N_\mathrm{r}kT)}{\partial{\phi_2}^2} = 0$$

which leads to

$$\frac{\partial^2(\Delta A/N_\mathrm{r}kT)}{\partial{\phi_2}^2} = \frac{-1}{1-\phi_2} - r_1\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + 2r_1\left(C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon} + \left(2 + \frac{1}{r_2}\right)\tilde{\epsilon}\right)\phi_2 - 6r_1\Bigg(\Bigg(\Bigg(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\Bigg)\tilde{\epsilon} + C_\gamma\tilde{\epsilon}^2\Bigg){\phi_2}^2 + 12r_1C_\gamma\tilde{\epsilon}^2{\phi_2}^3 \quad \text{(A5)}$$

and

$$\frac{\partial^3(\Delta A/N_\mathrm{r}kT)}{\partial{\phi_2}^3} = 0$$

which leads to

$$\frac{\partial^3(\Delta A/N_r kT)}{\partial \phi_2{}^3} = \frac{-1}{(1-\phi_2)^2} + 2r_1\left(C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon} + \left(2+\frac{1}{r_2}\right)\tilde{\epsilon}\right) - 12r_1\left(\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right) + C_\gamma\tilde{\epsilon}\right)\tilde{\epsilon} + C_\gamma\tilde{\epsilon}^2\right)\phi_2 + 36r_1C_\gamma\tilde{\epsilon}^2\phi_2{}^2 \quad \text{(A6)}$$

References and Notes

(1) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(2) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(3) Hirokawa, Y.; Tanaka, T.; Katayama, S. *Microbial Adhesion and Aggregation*; Springer: Berlin, 1984.
(4) Tanaka, T.; Nishio, I.; Sun, S.-T.; Nishio, S. *Sci. Am.* **1982**, *218*, 467.
(5) Suzuki, A.; Tanaka, T. *Macromolecules* **1990**, *23*, 345.
(6) Mamada, A.; Tanaka, T.; Kungwatchakun, D.; Irie, M. *Macromolecules* **1990**, *23*, 1517.
(7) Katayama, Y.; Hirokawa, Y.; Tanaka, T. *Macromolecules* **1984**, *17*, 2642.
(8) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982**, *77*, 5725.
(9) Irie, M.; Misumi, Y.; Tanaka, T. *Polymer* **1993**, *34*, 4531.
(10) Kokufuta, E.; Nakaizumi, S. *Macromolecules* **1995**, *28*, 1704.
(11) Kokufuta, E.; Zhang, Y.-Q.; Tanaka, T.; Mamada, A. *Macromolecules* **1993**, *26*, 1053.
(12) Tanaka, T.; Fillore *J. Chem. Phys.* **1979**, *70*, 1214.
(13) Hirose, Y.; Amiya, T.; Hirokawa, Y.; Tanaka, T. *Macromolecules* **1987**, *20*, 1342.
(14) Wu, C.; Zhou, S. *Macromolecules* **1997**, *30*, 574.
(15) Prange, M. M.; Hooper, H. H.; Prausnitz, J. M. *AIChE J.* **1989**, *35*, 803.
(16) Marchetti, M.; Prager, S.; Cussler, E. L. *Macromolecules* **1990**, *23*, 1760.
(17) Marchetti, M.; Prager, S.; Cussler, E. L. *Macromolecules* **1990**, *23*, 3445.
(18) Hu, Y.; Lambert, S. M.; Soane, D. S.; Prausnitz, J. M. *Macromolecules* **1991**, *24*, 4356.
(19) Hu, Y., Liu, H., Soane, D. S. and Prausnitz, J. M. *Fluid Phase Equilib.* **1991**, *67*, 65.
(20) Erman, B.; Flory, P. J. *Macromolecules* **1986**, *19*, 2342.
(21) Yi, Y. D.; Oh, K. S.; Bae, Y. C., *Polymer* **1997**, *38*, 3471.
(22) Chu, B. *Laser Light Scattering*, 2nd ed.; Academic Press: New York, 1991.
(23) Schmitz, K. S. *An Introduction to Dynamic Light Scattering by Macromolecules*; Academic Press: New York, 1990.
(24) Freed, K. F. *J. Phys. A: Math. Gen.* **1985**, *18*, 871.
(25) Bawendi, M. G.; Freed, K. F.; Mohanty, U. *J. Chem. Phys.* **1988**, *87*, 5534.
(26) Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1988**, *88*, 2741.
(27) Dickman, R.; Hall, C. *J. Chem. Phys.* **1988**, *85*, 4108.
(28) Madden, W. G.; Pesci, A. I.; Freed, K. F. *Macromolecules* **1990**, *23*, 1181.
(29) Panagiotopolous, A. Z.; Quirke, N.; Stapleton, M.; Tildesley, D. J. *Mol. Phys.* **1988**, *63*, 527.
(30) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(31) Li, Y.; Tanaka, T. *J. Chem. Phys.* **1989**, *90*, 5161.
(32) Khokhlov, A. R. *Polymer* **1980**, *21*, 376.
(33) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *87*, 1392.

MA971554Y