

Swelling Behavior of Submicron Gel Particles

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ABSTRACT: We prepared submicron Poly(*N*-isopropylacrylamide) gel particles. Their swelling behavior was investigated by a photon correlation spectroscopy (PCS) technique. The swelling behavior of submicron gel particles showed a continuous volume phase transition for various temperatures. We combined the extended Flory-Huggins model for mixing solvent and network with a modified Flory-Rehner theory for the elastic contribution. The proposed model agreed very well with swelling behaviors of both submicron gel particles and bulk gels. A continuous volume phase transition behavior of submicron gel particles was predicted successfully by the proposed model.

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Key words: submicron gel particles; swelling behaviors

INTRODUCTION

It is well known that the volume phase transitions 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.

The swelling equilibrium of gels free of ions is governed by both the free energy of elasticity and the free energy of mixing. In the Poly(*N*-isopropyl acrylamide) (PNIPA) gel/water system, water diffuses into the network by forces determined by the difference of chemical potential of water between the network inside and outside. The swelling gel reaches the equilibrium state at a higher concentration of water in the gel phase. Contribu-

tions of elastic forces to the chemical potential of the solvent (water) prevent the polymer from becoming completely dissolved.¹²

Numerous scientists have made great efforts, both experimental and theoretical, to describe swelling phenomena of PNIPA/water systems. Tanaka and co-workers¹³ reported that submicron gel particles show a continuous volume phase transition, while bulk gels show a discontinuous volume phase transition. In their later article,¹⁴ they explained that the continuous transition phenomenon of the submicron gels results from structural inhomogeneities in gels that were detected by dynamic light-scattering studies. Inomata et al.¹⁵ investigated the effects of copolymerization with *N*-*n*-isopropylacrylamide (NIPA) and of crosslinking density on the swelling behavior of PNIPA gels; they found that transition temperatures of copolymer gels were changed in proportion to the monomer ratio and that the crosslinking density strongly affected the swelling ratio and the transition temperatures of gels. Prausnitz et al.¹² applied an oriented quasichemical model to the swelling equilibria of gels that takes into account the strong specific interaction (e.g., hydrogen bond) between CONH group in the network and water. Cussler et al.^{16,17} applied

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the Sanchez and Lacombe's Lattice-fluid model (which considers holes in the lattice as a component) for the free energy of mixing and then compared the model with their swelling data. Moerk-erke et al.¹⁸ suggested a simple model in which the polymer-solvent interaction parameter depends not only on temperature but also on the concentration of polymer and fitted it to Inomata's swelling data. Their model has seven adjustable model parameters (fitting parameters): one related to the crosslinking density, and six related to the interaction parameter.

In this study, we propose a simple model to describe the swelling equilibria of hydrogels. We prepared submicron gel particles, not bulk gels, and investigated their continuous volume phase transition behavior by using a photon correlation spectroscopy (PCS) technique. In our model development, we combine the extended Flory-Huggins^{24,25} model in the binary polymer system with a modified Flory-Rehner theory for elastic networks.¹⁸

EXPERIMENTAL

Sample Preparation

NIPA provided by TCI Co. was used as monomer after recrystallization. *N,N'*-methylenebisacrylamide (BIS) and ammonium persulfate (APS) were used as a crosslinker and an initiator, respectively. Tween-20 was selected as a nonionic surfactant to stabilize the submicron gel particles without affecting the swelling behavior.

NIPA (0.2 g) and 0.011 g of BIS (weight ratio of monomer to crosslinker is 18.2) were dissolved in excess distilled deionized (DDI) water filtered through a 0.45- μm pore size millipore filter. After the monomer solution was poured into a batch reactor, 100 μL of APS 1% solution and 500 μL of Tween-20 1% solution were added. The reaction temperature was about 70°C. The submicron gel particles were prepared by precipitation polymerization with stirring and nitrogen blowing for 4 hs.^{19,20}

Measurements of Swelling behavior for Submicron Gel Particles by Photon Correlation Spectroscopy Technique

The hydrodynamic diameters of submicron gel particles were measured by a photon correlation spectroscopy (PCS) technique. The solution con-

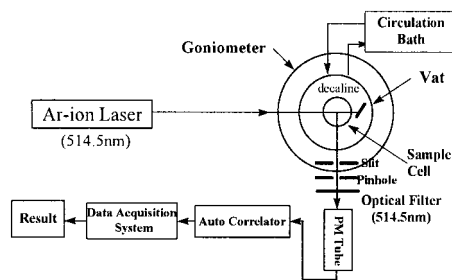


Figure 1 Schematic diagram of the photon correlation spectroscopy (PCS) apparatus.

taining gel particles was diluted with filtered DDI water to achieve an appropriate concentration for the light-scattering measurement and then poured into the glass cell.

Multiple scattering with respect to the concentration of gel particles may occur because the detection of any light that has been scattered more than once in the sample can cause distortion of the time dependence of the measured correlation function. For a small particle, the intensity of multiple scattering relative to that of single scattering is proportional to $\langle C \rangle a^6$, where $\langle C \rangle$ is the particle number density and a is the particle radius. Brown et al.²⁸ reported that multiple scattering was small for $\langle C \rangle \approx 1.7 \times 10^9 \text{ cm}^{-3}$ and $a \approx 500 \text{ \AA}$; our value $\langle C \rangle a^6$ is much smaller than that of Brown's. Therefore, multiple scattering in this study is negligible. The schematic diagram of our PCS apparatus is shown in Figure 1. Temperature of the vat in which the cell was immersed was controlled by a circulation bath from 1°C and 80°C with the stability of $\pm 0.05^\circ\text{C}$. The source of the incident light 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 in the photomultiplier tube (PMT, Brookhaven Instruments Co., Model EMI9863) at a scattering angle of 90° . The signal from the PMT, digitized by an amplifier-discriminator, was fed into a correlator. The digital 8 bits \times 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 CONTIN method.^{21,22} Figure 2 shows the diameter distribution of a collapsed gel and a swollen gel at 50 and 10°C, respectively.

We then obtained the average hydrodynamic diameter of the equilibrium gels (D_h) at various

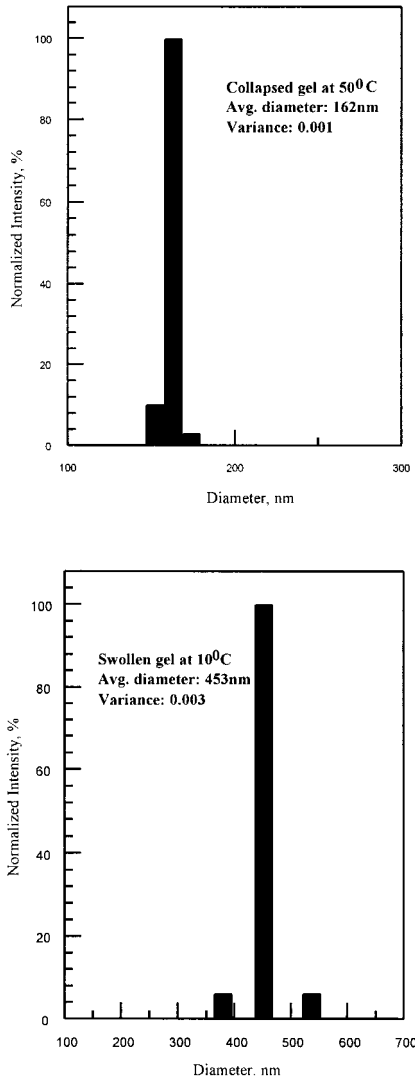


Figure 2 Distribution of the diameter of a collapsed gel and a swollen gel as calculated by the CONTIN method. The upper plot is for a collapsed gel at 50°C and the lower one for a swollen at 10°C.

temperatures and determined the degree of swelling (the ratio of the equilibrium gel volume at measurement temperature to that at a reference state) as follows:

$$V/V_0 = (D_h/D_{h,0})^3$$

where $D_{h,0}$ is the average hydrodynamic diameter of the gel at the reference state and D_h is the average hydrodynamic diameter of the gel at a given temperature. 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,

the ideal reference state is very close to that at preparation of the gel. The submicron gel particles in this work, however, are prepared in the presence of solvent and, because the polymer–solvent interaction affects the formation of the gel, we obtain a nonrandom and perturbed state. This leads to difficulties in determining the reference state. In this work, the state at preparation is arbitrarily and conveniently chosen as the reference state. In our theory, the parameter related to the reference state is determined by adjustment to experimental data for a specific system.

MODEL DEVELOPMENT

The change in Gibbs free energy of the network, ΔG_{net} due to isotropic deformation by swelling with a salt-free solvent, is given by

$$\Delta G_{\text{net}} = \Delta G_{\text{el}} + \Delta G_{\text{mix}} \quad (1)$$

where ΔG_{el} is the Gibbs free energy of elasticity and ΔG_{mix} is the Gibbs free energy of mixing.

The elastic contribution, ΔG_{el} ,¹⁸ is expressed as:

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

where R is the gas constant, Φ_0 is the polymer volume fraction at the reference state, v_e is the number of elastically active chains in mol, and ϕ is the polymer volume fraction in the swollen network. Factors A and B are functions of ϕ :

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

$$B = \frac{2\phi}{f} \quad (3)$$

where f is the functionality of the crosslinks. The network is assumed to be perfect. If the system contains N mol of lattice sites, v_e is replaced by the number of lattice sites occupied by an average network chain, m_c ,

$$\frac{v_e}{N} = \frac{\phi}{m_c} \quad (4)$$

Then eq. (2) can be written as:

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

For an uncrosslinked polymer solution, Qian et al.,^{26,27} Koningsveld et al.,²³ and Bae et al.^{24,25} suggested the following equation where the Flory-Huggins interaction parameter χ is a function of both temperature and composition. This semi-empirical theory permits describing most observed types of binary liquid-liquid equilibria (LCST, UCST, UCST, and LCST, hourglass, closed-loop) by adjusting model parameters. The extended Flory-Huggins equation is given by

$$\begin{aligned}
\frac{\Delta G_{mix}}{NRT} &= \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \\
&\quad + \phi_2 \int_{\phi_2}^1 \chi(T, \phi) d\phi \quad (6)
\end{aligned}$$

where ϕ_1 , ϕ_2 , r_1 , and r_2 are the volume fractions and relative molar volumes of components 1 and 2, respectively. The interaction parameter, $\chi(T, \phi)$, is given by the product of two functions: one dependent on concentration, and the other on temperature.²³⁻²⁵

$$\chi(T, \phi) = \chi_T(T) \chi_\phi(\phi) \quad (7a)$$

$$\chi_T(T) = d_0 + \frac{d_1}{T} \quad (7b)$$

$$\chi_\phi(\phi) = \frac{1}{1 - b\phi} \quad (7c)$$

where d_0 , d_1 and b are adjustable model parameters obtained by fitting the swelling data.

The combinatorial term of the crosslinked hydrogels in this study is negligible, and the relative molar volume of solvent is approximately unity. Then, eq. (6) is expressed by

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

From eq. (5) and eq. (8), the total change in

Gibbs free energy of gels due to isotropic swelling deformation is given by

$$\begin{aligned}
\frac{\Delta G}{NRT} &= G_{AB} + (1 - \phi) \ln(1 - \phi) \\
&\quad + \phi \int_{\phi}^1 \chi(T, \phi) d\phi \quad (9)
\end{aligned}$$

Then, the reduced chemical potential change of a solvent in a gel phase coexisting with pure solvent is given by

$$\begin{aligned}
\frac{\Delta \mu_0}{RT} &= G_{AB} - \phi C_{AB} + [\phi + \ln(1 - \phi)] \\
&\quad + \chi_T(T) \left(\frac{\phi^2}{1 - b\phi} \right) \quad (10)
\end{aligned}$$

where

$$\begin{aligned}
C_{AB} &= \Phi_0^{2/3} \left[\left(\frac{A}{2m_c} \right) (\phi^{-2/3} - 3) \right. \\
&\quad \left. + \left(\frac{3}{fm_c} \right) (\phi^{1/3} - \phi) \right] \\
&\quad + \left(\frac{B}{m_c} \right) (\ln \phi + 1) + \left(\frac{2\phi}{fm_c} \right) \ln \phi \quad (11)
\end{aligned}$$

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

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

From the above equation, the equation of state for the swelling equilibrium of the swollen gels is given by

$$T = \frac{-d_1 \phi^2}{(1 - b\phi)[G_{AB} - \phi C_{AB} + \{\phi + \ln(1 - \phi)\}] + d_0 \phi^2} \quad (13)$$

RESULTS AND DISCUSSION

The swelling data of PNIPA submicron gel particles at various temperatures were obtained from

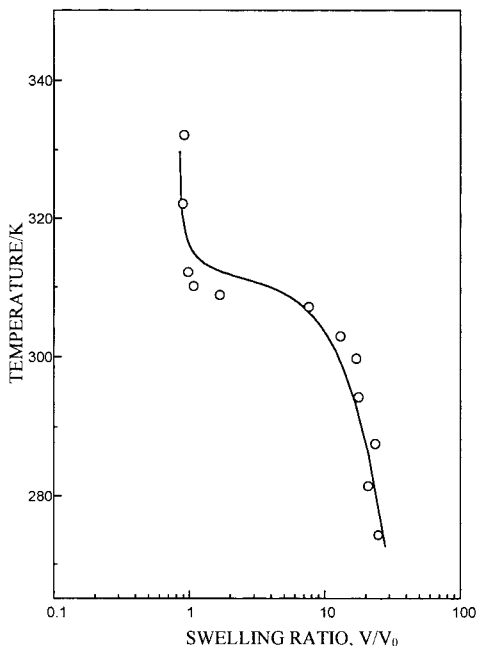


Figure 3 Swelling behavior of PNIPA submicron gel particles. Solid line demonstrates theoretical prediction from eq. (13), and open circles are experimental results.

PCS measurements. As shown in Figure 3, open circles are swelling data of submicron gel particles at various temperatures. The collapsed state of the gels at 70°C, which (reaction temperature) is set equal to the reference state ($D_0 = 149$ nm) and the maximum degree of swelling is about 25 at 1.1°C. The solid line is calculated from eq. (13). The polymer volume fraction was calculated from the swelling data:

$$\phi/\Phi_0 = V_0/V \quad (14)$$

Model parameters, using a nonlinear least-squares method, are listed in Table I. In this study, we fixed the relative molar volume of solvent to unity and assumed that $f = 4$. The polymer volume fraction at network formation, Φ_0 , can be calculated in bulk gels from their experimental condition, but not for submicron gel particles because we do not know the experimental condition when each gel particle forms. In this study, we set Φ_0 as an adjustable model parameter for fitting submicron gel particle swelling data and obtained an acceptable value of 0.87. This value is reasonable because the submicron gel particles are in a collapsed phase at the reaction temperature.

The swelling behavior of submicron gel parti-

cles shows a continuous volume phase transition that is different from that of the conventional bulk gel. The volume phase transition of the submicron gel particles occurs continuously in the temperature range 307 to 310 K. This phenomenon was extensively studied by Tanaka et al. by light-scattering studies.¹⁴ They have reported that this phenomenon results from structure inhomogeneities of the submicron gel particles, that are caused by three types of fluctuations: the fluctuation of the polymer solution at the onset of gelation, the domain formation due to the microphase separation, and the thermal dynamic concentration fluctuations after gelation.

In Figure 4, our model is compared with Inomata's swelling data¹⁵ for PNIPA bulk gels in water. The model agrees very well with experimental data. Values of adjustable model parameters obtained by fitting of our model to the swelling data for the submicron gel particles and to Inomata's swelling data of the bulk gels are listed in Table I. The predicted $m_c (=53)$ value for the bulk gels is acceptable in comparison with the one calculated from the experimental condition (~ 77); the estimated experimental value can be calculated from the molar ratio of monomer to crosslinker in feed. The $m_c (=20)$ value for the submicron gel particles, however, is smaller than that of the expected value at the experimental condition (~ 73). The adjustable model parameters for submicron gel particles show a big difference from those for bulk gels. We cannot explain this result, but we suggest that the much larger surface area of submicron gel particles relative to those of bulk gels affects the interaction parameter between gel network and solvent.

Table I Adjustable Model Parameters for the Swelling Data of Submicron Gel Particles and Bulk Gels (Inomata's¹⁵)

Adjustable Model Parameters	Swelling Data	
	Submicron Gels	Bulk Gels
b	0.7502	0.0743
d_0	14.23	2.84
d_1	-4377.9K	-641.1K
m_c	20	53
Φ_0	0.87	0.08*

* Is the value from experimental conditions.

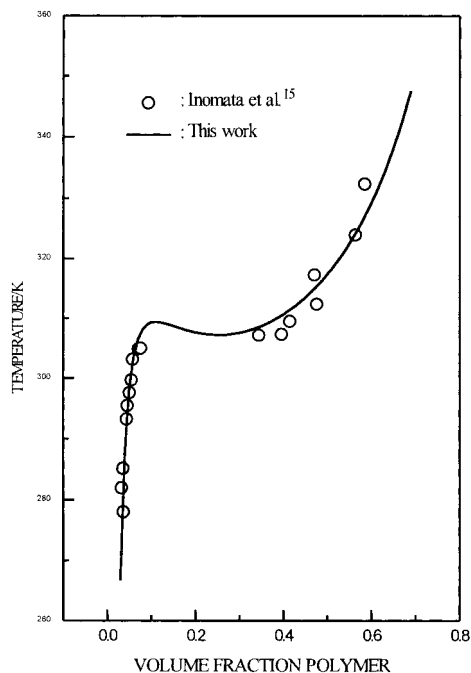


Figure 4 Theoretical predictions for the swelling behavior of bulk gels. Open circles are experimental data from Inomata et al. The solid line is calculated from eq. (13).

CONCLUSION

We have shown that the swelling behavior of submicron gel particles is successfully investigated by a PCS technique. The proposed model obtained by combination of a modified theory for the free energy of rubber elasticity and extended Flory-Huggins theory for the free energy of mixing reduced adjustable model parameters to four. The proposed model presented here has little theoretical basis; it is essentially empirical or, at best, semiempirical. Its advantage follows from its simplicity; a simple algebraic form with a few adjustable model parameters appears to be suitable for representing swelling behavior of the gel.

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