Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 5103–5113 **5103**
DOI: 10.1021/ma100588f

Cooperative Hydration Induces Discontinuous Volume Phase Transition of Cross-Linked Poly(*N*-isopropylacrylamide) Gels in Water

Hiroyuki Kojima and Fumihiko Tanaka*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

Received March 17, 2010; Revised Manuscript Received April 30, 2010

ABSTRACT: The concept of cooperative dehydration, defined as the simultaneous dissociation of the bound water molecules from the polymer chains in correlated sequences, is applied to study the collapse of cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) gels in aqueous solutions upon heating above the critical temperature. We examined the applicability of this concept in two situations: (i) free swelling of PNIPAM gels in water (in the absence of applied force), (ii) swelling of PNIPAM gels in water subjected to a uniaxial tension. The transition becomes sharper as the cooperativity parameter σ of hydration decreases (increasing cooperativity), and there is a critical value $\sigma_c \simeq 0.30$ of the cooperativity parameter below which the volume transition is discontinuous. Hence, the real phase transition with thermodynamic discontinuity is shown to be possible for the nonionic polymer gels if the hydration is sufficiently cooperative. The calculations of the swelling ratio and the spinodal lines are compared with the experimental data of PNIPAM gels by Hirotsu for point i and by Suzuki for point ii.

1. Introduction

Since the discovery of the volume phase transition of gels by Tanaka,[1] the swelling behavior of ionic and nonionic gels has attracted interest of researchers. In the initial study of poly(acrylamide) (PAA) gels,[1,2] it was found that their volumes discontinuously change with the temperature, or the solvent composition in the mixed solvent of water and acetone, when ionizable groups are introduced to acrylamide gels. Thereby, the osmotic pressure of dissociated free ions plays an essential role leading to a discontinuous transition. Later, it was found that discontinuous change is also possible in the cross-linked gels of poly(*N*-isopropylacrylamide) (PNIPAM) in pure water and in mixed solvent of water and dimethyl sulfoxide (DMSO).[3−7] Both PAA and PNIPAM gels collapse on heating, so that dehydration is necessary prerequisite.

Hydration of PNIPAM gel particles was recently studied by measuring ultrasonic velocity (adiabatic compressibility) as functions of temperature.[8] They estimated the hydration number (the number of water molecules per PNIPAM monomer) from the measurement of the limiting compressibility number. Annaka et al.[9] attempted to find the hydration number through the measurement of the enthalpy of hydration by DSC. In this paper, we attempt to find the necessary condition for nonionic gels to undergo discontinuous transition from the viewpoint of cooperativity in hydration of constituent polymers of the gels.

The behavior of PNIPAM in aqueous media has attracted interest of many researchers ever since it was first reported by Heskins and Guillet.[10] The polymer exhibits a well-defined lower critical solution temperature (LCST) in water,[10−15] and each individual chain shows a very sharp coil−globule transition[16,17] when heated to 32.5 °C. The flat LCST cloud point line with accompanying sharp change in polymer conformation results from a balance between hydration (direct hydrogen bonds of water onto the chain) and hydrophobic aggregation of the isopropyl groups.[11]

Historically, the high-temperature collapse of a nonionic single chain[17] and gels[7,18] in water has been described by using the concentration-dependent interaction parameters

$$\chi = \chi_0 + \chi_1\phi + \chi_2\phi^2 \tag{1.1}$$

with inverted temperature coefficient such as $\chi_0(T) = A + B/T$ with $B < 0$. Although the average radius of gyration of the chain, and also the volume of the gel, may decrease at high temperature for such phenomenological parameters, the molecular origin of the temperature inversion is difficult to identify. Understanding of the mechanism is only possible through the description of χ in terms of the molecular property of polymer−water interaction.

To elucidate the origin of the high sensitivity of PNIPAM to temperature, we recently developed the hydration model by introducing the concept of *cooperative hydration*, on the basis of which we theoretically derived the flat LCST cloud-point curves observed in aqueous PNIPAM solutions.[19−21] In this paper we apply this model to the study of the observed discontinuous volume change of cross-linked PNIPAM gels.

The cooperativity in hydration is caused by a positive correlation between neighboring bound water molecules[22] due to the presence of the large hydrophobic isopropyl side groups. If a water molecule succeeds in forming a hydrogen bond (H-bond) with an amide group on a chain, a second water molecule can form a H-bond with the chain more easily than the first one because the first molecule causes some displacement of the isopropyl group, thus creating more access space for the next molecule. As a result, consecutive sequences of bound water appear along the chain, which leads to a pearl-necklace type chain conformation (Figure 1 right).[19,23] When the chain is heated up, each sequence is dehydrated as a whole, resulting in a sharp collapse of the chain. Cooperativity in the hydration of PNIPAM chains in gels is recently studied through Raman spectroscopy[24] and molecular simulation.[25]

We start from Flory−Rhener picture[26] on swelling of polymer networks and take explicitly the free energy of cooperative hydration into consideration.

---

*To whom correspondence should be addressed.

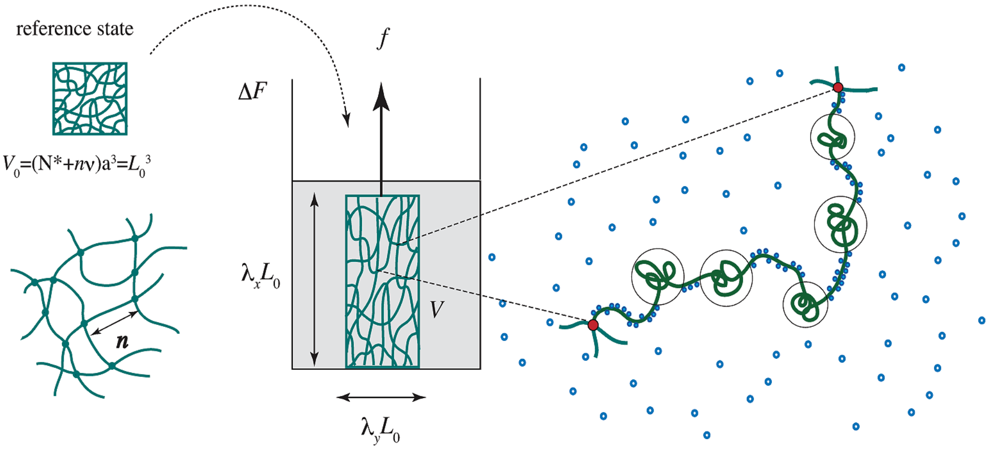

Figure 1. Swelling experiment. The state when the gel sample is cross-linked in a solvent is chosen as the reference state. The gel sample is swollen in a solvent under external force f. Polymer chains in the gel take the pearl-necklace conformation consisting of collapsed globules connected by the hydrated random coils.

2. Free Energy of Hydrated Gels

Consider a cubic sample of a gel that is immersed in a good solvent and swollen under a constant stress $\mathbf{f}$ (Figure 1). Let us choose the volume of the gel when it is prepared (cross-linked) as the reference volume V_0 of the sample. It may be synthesized in a solvent. The volume

$$V_0 \equiv L_0{}^3 = (N_0^* + nN)a^3 \tag{2.1}$$

may therefore include the number N_0^* of the solvent molecules in the preparation stage, where N is the total number of subchains, n the average number of repeat units on a subchain, a the size of a repeat unit which is for simplicity assumed to be the same as the size of a solvent molecule. The volume fraction of polymers in the reference state is $\phi_0 = nNa^3/V_0$. When the gel is immersed after dried, the reference volume is $V_{\rm dry} = nNa^3$ or $\phi_0 = 1$.

The gel adsorbs solvent molecules and swell to the volume V. If the number of solvent molecules inside the gel network is N_0, the volume is $V = (N_0 + nN)a^3$. Let $\Omega \equiv V/a^3 = N_0 + nN$ be the number of hypothetical lattice cells to place the molecules inside the volume occupied by the gel, as in the lattice theory of polymer solutions. The volume fraction of the polymers inside the gel is $\phi \equiv V_{\rm dry}/V = nN/\Omega$, and the degree of swelling is

$$Q \equiv V/V_0 = \phi_0/\phi \tag{2.2}$$

Let λ_x, λ_y, λ_z be the expansion factor of the side in each direction. The swelling ratio is then given by $Q = \lambda_x\lambda_y\lambda_z$. In particular, when the gel swells under no tension, it undergoes an isotropic free expansion, so that

$$\lambda_x = \lambda_y = \lambda_z = (\phi_0/\phi)^{1/3} \tag{2.3}$$

When the gel swells under uniaxial tension in x direction, the expansion ratios are

$$\lambda_x = \lambda, \qquad \lambda_y = \lambda_z = \left(\frac{\phi_0}{\lambda\phi}\right)^{1/2} \tag{2.4}$$

by symmetry, where λ is the elongation in the x-direction.

The free energy of the gel consists of three parts

$$\Delta F = \Delta_{\rm el}F + \Delta_{\rm mix}F + \Delta_{\rm hyd}F \tag{2.5}$$

The first term $\Delta_{\rm el}F$ is the elastic free energy due to the deformation of the network. It is

$$\beta\Delta_{\rm el}F = \frac{\nu}{2}\left[\lambda_x{}^2 + \lambda_y{}^2 + \lambda_z{}^2 - 3 + \mu\ln\left(\frac{\phi}{\phi_0}\right)\right] \tag{2.6}$$

according to the affine network theory of rubber elasticity, where $\beta \equiv 1/k_BT$, and ν is the number of the elastically effective chains in the network, μ is a constant of order unity. The last term is the correction term due to the volume change of the gel. The coefficient μ depends on the cross-link density. The number ν of the elastically effective chains differes in general from the total number of chains N, so that in what follows it is written as $\nu = \eta N$ where η is the fraction of effective chains.

For free swelling, eq 2.3 leads to

$$\Delta_{\rm el}F = \frac{\eta N}{2}k_{\rm B}T\left[3\left(\frac{\phi_0}{\phi}\right)^{2/3} - 3 + \mu\ln\left(\frac{\phi}{\phi_0}\right)\right] \tag{2.7}$$

For swelling under uniaxial stretching (eq 2.4), the elastic free energy is

$$\Delta_{\rm el}F = \frac{\eta N}{2}k_{\rm B}T\left[\lambda^2 + \frac{2}{\lambda}\left(\frac{\phi_0}{\phi}\right) - 3 + \mu\ln\left(\frac{\phi}{\phi_0}\right)\right] \tag{2.8}$$

The free energy of mixing is given by

$$\Delta_{\rm mix}F = \Omega k_{\rm B}T[\phi_{\rm fw}\ln\phi_{\rm fw} + \chi(T)\phi(1-\phi)] \tag{2.9}$$

by the Flory–Huggins lattice theory,[26–29] where $\phi_{\rm fw} \equiv N_{\rm fw}/\Omega$ is the volume fraction of the free water inside the volume occupied by the gel network. There are the number $N_{\rm fw}$ of free water molecules, and $N_{\rm bw}$ of bound water molecules in the region. The mixing entropy due to the translational motion of mass centers arises only from these free water molecules inside the gel. The mixing entropy of cross-linked polymer chains has been neglected because the molecular weight of the network is infinite. The parameter $\chi(T)$ is Flory's interaction parameter which describes the effect of excluded volume interaction due to van der Waals type nonbonding interaction. It is assumed to take the conventional Schultz–Flory form[30]

$$\chi(T) = 1/2 - \psi\tau \tag{2.10}$$

where $\tau \equiv 1 - \Theta/T$ is the dimensionless temperature, ψ is the positive material parameter of order unity, and Θ is the theta temperature decided by the nonbonding excluded volume interaction in the background.

In order to incorporate specific interaction between water molecules and PNIPAM monomers, let $\mathbf{j} \equiv \{j_1, j_2, \cdots\}$ be the index specifying the polymer chain carrying the number j_ζ of sequences that consist of a run of hydrogen-bonded ζ consecutive water molecules, and let $N(\mathbf{j})$ be the number of such polymer–water complexes whose type is specified by $\mathbf{j}$ (see Figure 1). The total number of water molecules bound to a chain specified by $\mathbf{j}$ is given by $\sum \zeta j_\zeta$, and the molecular weight of a complex in terms of the number of lattice cells is given by $n(\mathbf{j}) \equiv n[1 + \theta(\mathbf{j})]$, where

$$\theta(\mathbf{j}) \equiv \sum_{\zeta=1}^{n} \zeta j_\zeta / n \tag{2.11}$$

is the fraction of the bound water molecules relative to the total number of repeat units of a polymer. The number of bound water molecules is

$$N_{\mathrm{bw}} = n \sum_{\mathbf{j}} \theta(\mathbf{j}) N(\mathbf{j}) \tag{2.12}$$

and the number of free water molecules is

$$N_{\mathrm{fw}} = N_0 - N_{\mathrm{bw}} \tag{2.13}$$

We then have the free energy of hydration

$$\Delta_{\mathrm{hyd}} F = \sum_{\mathbf{j}} [\Delta A(\mathbf{j}) + k_{\mathrm{B}} T \ln(N(\mathbf{j})/N)] N(\mathbf{j}) \tag{2.14}$$

where $\Delta A(\mathbf{j})$ is the conformational free energy required to form a complex chain of the type $\mathbf{j}$ measured relative to the reference conformation $\mathbf{j}_0 \equiv \{0, 0, \cdots\}$to which no water molecule is bound. Its specific form depends on the type of hydration, and will be given in the following sections.

From the total free energy, we find the chemical potentials by taking the partial derivatives with respect to N_{fw} and $N(\mathbf{j})$. We have

$$\Delta\mu_{\mathrm{fw}} = -\eta(\phi)\frac{\phi}{n} + 1 + \ln \phi_{\mathrm{fw}} - \phi_{\mathrm{fw}} + \chi(T)\phi^2 \tag{2.15}$$

for the free water, and

$$\beta\Delta\mu(\mathbf{j}) = \eta(\phi)\left(1 - \frac{n(\mathbf{j})}{n}\phi\right) - n(\mathbf{j})\phi_{\mathrm{fw}} + n\chi(T)[(1-\phi)^2 + \theta(\mathbf{j})\phi^2] + \beta\Delta A(\mathbf{j}) + \ln(N(\mathbf{j})/N) \tag{2.16}$$

for the subchain of type $\mathbf{j}$, where $\eta(\phi)$ is the elastic part of the chemical potential per chain. It is

$$\eta(\phi) \equiv \eta\left[\frac{\mu}{2} - \left(\frac{\phi}{\phi_0}\right)^{-2/3}\right] \tag{2.17}$$

for free swelling, and

$$\eta(\phi) \equiv \eta\left[\frac{\mu}{2} - \frac{1}{\lambda}\left(\frac{\phi}{\phi_0}\right)\right] \tag{2.18}$$

for swelling under uniaxial stretching.

3. Association Equilibrium and the Number of Bound Water Molecules in Free Swelling

We assume association equilibrium and impose the conditions

$$\Delta\mu(\mathbf{j}) = \Delta\mu(\mathbf{j}_0) + n\theta(\mathbf{j})\Delta\mu_{\mathrm{fw}} \tag{3.1}$$

to find the equilibrium distribution of associated complexes. Then, we find

$$N(\mathbf{j}) = K(\mathbf{j}) N(\mathbf{j}_0) \phi_{\mathrm{fw}}^{n\theta(\mathbf{j})} \tag{3.2}$$

for the number density of the complexes specified by $\mathbf{j}$, where

$$K(\mathbf{j}) \equiv \exp[n\theta(\mathbf{j}) - \beta\Delta A(\mathbf{j})] \tag{3.3}$$

is the association equilibrium constant. The normalization condition $\Sigma N(\mathbf{j}) = N$ leads to

$$N(\mathbf{j}_0) g_0(y) = N \tag{3.4}$$

and the total number of bound water molecules is given by

$$N_{\mathrm{bw}} = nN(\mathbf{j}_0) g_1(y) \tag{3.5}$$

where $y \equiv \phi_{\mathrm{fw}}$ is the volume fraction of the free water, and new functions $g_k(y)$ are defined by

$$g_0(y) \equiv \sum_{\mathbf{j}} K(\mathbf{j}) y^{n\theta(\mathbf{j})}, \qquad g_1(y) \equiv \sum_{\mathbf{j}} \theta(\mathbf{j}) K(\mathbf{j}) y^{n\theta(\mathbf{j})} \tag{3.6}$$

The ratio

$$g_1(y)/g_0(y) = \partial(\ln g_0(y))/n\partial(\ln y) \equiv G(y) \tag{3.7}$$

gives the thermal average of the fraction of bound water molecules when y is expressed in terms of the temperature and the volume fraction ϕ. The total polymer volume fraction ϕ is then given by

$$\phi = \phi(\mathbf{j}_0) g_0(y) \tag{3.8}$$

and the total volume fraction of water is found by the equation

$$1 - \phi = y + \phi(\mathbf{j}_0) g_1(y) \tag{3.9}$$

These coupled equations should be solved for $\phi(\mathbf{j}_0)$ and y to find the average fraction of the bound water in terms of the polymer volume fraction and the temperature. Upon eliminating $\phi(\mathbf{j}_0)$, the second equation is transformed to

$$1 - \phi = y + \phi G(y) \tag{3.10}$$

which should be solved for y with the function $G(y)$ specified by the molecular modeling of hydration.

Substituting eq 3.2 back into the starting free energy, and using the relation 3.3, we find the sum of the free energy of mixing and hydration (per lattice site) in the form

$$\beta(\Delta_{\mathrm{mix}} F + \Delta_{\mathrm{hyd}} F)/\Omega = \mathcal{F}_{\mathrm{FH}} + \mathcal{F}_{\mathrm{AS}} \tag{3.11}$$

where

$$\mathcal{F}_{\mathrm{FH}}(\phi, T) = (1-\phi)\ln(1-\phi) + \chi(T)\phi(1-\phi) \tag{3.12}$$

is the usual Flory−Huggins mixing free energy, and

$$\mathscr{F}_{\mathrm{AS}}(\phi, T) = y \ln y - (1-\phi)\ln(1-\phi) + \phi\left[-\frac{1}{n}\ln g_0(y) + (1+\ln y)G(y)\right] \qquad (3.13)$$

is the additional part due to hydrogen bonding association. Therefore, the free energy of association can be regarded as the renormalization of the χ-parameter. The original χ-parameter due to van der Waals type contact interaction is modified to $\chi + \Delta\chi$ by H-bonding association, where the renormalization part

$$\Delta\chi(\phi, T) \equiv \mathscr{F}_{\mathrm{AS}}(\phi, T)/\phi(1-\phi) \qquad (3.14)$$

depends on the polymer concentration as well as the temperature in a complex way. The appearance of peculiar-shaped phase separation regions on the phase plane of the polymer solutions originates in this effective interaction term.

Since the volume transition of PNIPAM is a reverse transition with respect to temperature, the interaction parameter must increase with the temperature. To explain discontinuous high-temparature collapse of PNIPAM gels, Hirotsu[5] introduced the concentration dependent χ parameter in the simple form

$$\chi_{\mathrm{eff}}(\phi, T) = \chi_0(T) + \chi_1(T)\phi \qquad (3.15)$$

and attempted to reproduce the discontinuous swelling curve.[6] He separated the first term into the enthalpy and entropy parts as

$$\chi_0(T) = (\Delta h - T\Delta s)/RT \qquad (3.16)$$

where both Δh, Δs are negative. If $\Delta h - T\Delta s < 0$, χ_1 increase with the temperature, leading to high temperature collapse. However, the molecular origin of these parameters for PNIPAM chains was difficult to identify by such a phenomenological study. In what follows we attempt to derive the discontinuous transition through the detailed study of hydration.

4. The Bulk Modulus and the Spinodal Condition

The osmotic pressure originates in the translational motion of the free water molecules, so that we have $\pi a^3 = -\Delta\mu_{\mathrm{fw}}$. Therefore, the swelling equilibrium condition $\pi = 0$ is given by

$$-\eta(\phi)\frac{\phi}{n} + 1 + \ln y - y + \chi(T)\phi^2 = 0 \qquad (4.1)$$

for both free swelling and swelling under stress. The bulk modulus K, or reciprocal of the osmotic compressibility κ_T, is defined by

$$K = {\kappa_T}^{-1} \equiv \phi\left(\frac{\partial\pi}{\partial\phi}\right) \qquad (4.2)$$

From the chemical potential of the free water derived above, we have

$$\beta K = \frac{1}{n}[\phi\eta'(\phi) + \eta(\phi)] - 2\chi(T)\phi + \left(1 - \frac{1}{y}\right)\frac{\mathrm{d}y}{\mathrm{d}\phi} \qquad (4.3)$$

By differentiating the relation 3.9 with respect to ϕ, we find the derivative of y is written as

$$\frac{\mathrm{d}y}{\mathrm{d}\phi} = -\frac{(1-y)}{\phi[y + \phi\Delta G(y)]} \qquad (4.4)$$

where

$$\Delta G(y) \equiv [g_0(y)g_2(y) - g_1(y)^2]/g_0(y)^2 \qquad (4.5)$$

is the mean square deviation of the number of bound water molecules from its average value. The spinodal condition $K = 0$ is then given by

$$\frac{1}{n\phi}[\phi\eta'(\phi) + \eta(\phi)] + \frac{(1-y)^2}{\phi^2[y + \phi\Delta G(y)]} - 2\chi(T) = 0 \qquad (4.6)$$

Obviously, this condition reduces to the conventional one

$$\frac{1}{n\phi}[\phi\eta'(\phi) + \eta(\phi)] + \frac{1}{1-\phi} - 2\chi(T) = 0 \qquad (4.7)$$

when there is no hydration, for which $y = 1 - \phi$ and $\Delta G(y) = 0$ hold.

5. Random Hydration

We first consider the simplest case of random hydration. Water molecules are assumed to be H-bonded onto the polymer chains randomly and independently. There is no interaction between the adjacent bound waters. The equilibrium constant is then given by

$$K(\mathbf{j}) = \frac{n!}{m!(n-m)!}\lambda(T)^m \qquad (5.1)$$

where m is the number of bound water molecules and $\lambda(T) \equiv \exp(-\beta\Delta f_{\mathrm{H}})$ is the association constant for the H-bond. Rewriting $\lambda(T)y$ as y, we find

$$g_0(y) = (1+y)^n, \qquad g_1(y) = y(1+y)^{n-1} \qquad (5.2)$$

so that the fraction $G(y) = g_1(y)/g_0(y)$ of the adsorbed sites, being identical to the degree θ of hydration, becomes of Langumuir type

$$\theta = y/(1+y) \qquad (5.3)$$

The conservation law 3.9 of water molecules becomes

$$y + \lambda(T)\phi\theta(y) = \lambda(T)(1-\phi) \qquad (5.4)$$

The solution of this equation is

$$\begin{aligned}\phi_{\mathrm{fw}} &= y/\lambda(T) \\ &= [\sqrt{1 - 4\xi^2\phi(1-\phi)} - 1 + 2\xi(1-\phi)]/2\xi \end{aligned} \qquad (5.5)$$

in terms of the effective association constant

$$\xi \equiv \lambda(T)/(1+\lambda(T)) \qquad (5.6)$$

This effective association constant agrees with the limiting value of the hydration at infinite dilution

$$\xi = \lim_{\phi \to 0} \theta(\phi) \equiv \theta_0 \qquad (5.7)$$

The swelling equilibrium condition 4.1 now takes the form

$$-\eta(\phi)\frac{\phi}{n} + 1 + \ln\frac{y}{\lambda(T)} - \frac{y}{\lambda(T)} + \chi(T)\phi^2 = 0 \qquad (5.8)$$

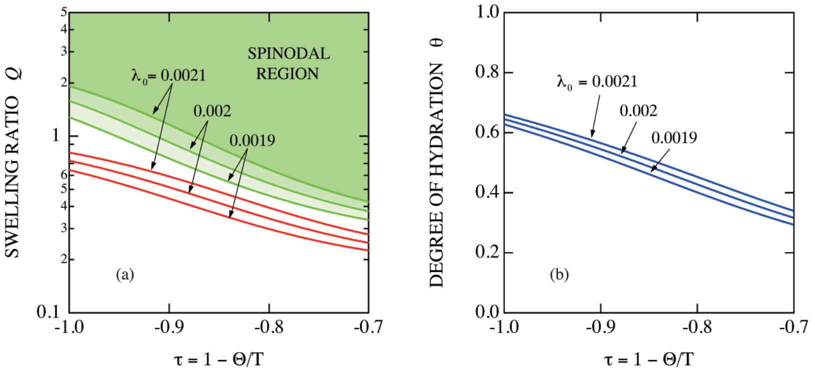

Figure 2. (a) Swelling ratio Q, and (b) the degree of hydration θ of the randomly hydrated gels, plotted against the reduced temperature. Gray area shows the spinodal region in which the gel is thermodynamically unstable. The amplitude λ_0 of the H-bonding association constant is varied from curve to curve. Other parameters used are $\eta = 1.0$, $n = 100$, $\phi_0 = 0.075$, $\mu = 1.0$, $\lambda_0 = 2.0 \times 10^{-3}$, and $\gamma = 3.5$.

5.1. Swelling Ratio and Degree of Hydration. For numerical calculation, we take the following procedure. As for the material parameters in Schultz−Flory interaction parameter, we fix $\psi = 1.0$ and $\Theta = 565$ as in our previous study of PNIPAM solutions.[19] To calculate the equilibrium swelling properties, let us introduce the free energy $\Delta f_H \equiv \Delta\epsilon_H - T\Delta s_H$ of a H-bond. The association constant takes the form

$$\lambda(T) \equiv \exp(-\beta\Delta f_H) = \lambda_0 \exp[\gamma(1-\tau)] \qquad (5.9)$$

where λ_0 is the entropy part, and $\gamma \equiv \Delta\epsilon_H/k_B\Theta$ is the H-bonding energy measured relative to the thermal energy at the theta temeperature.

Figure 2a shows the swelling ratio plotted against the reduced temperature for three different prefactors λ_0 (the entropy part of $\lambda(T)$). The gray area indicates the spinodal region whose boundary is given by the condition 4.6. Inside this area, the gel is thermodynamically unstable. Figure 2b shows the degree of hydration θ for the same parameters. As expected, the gel gradually shrinks by continuous dehydration.

5.2. Renormalization of the χ-Parameter. By expanding the solution y of eq 5.5 in powers of ϕ, we can find the coefficients of the series

$$\phi_{fw} = 1 + a_1\phi + a_2\phi^2 + \cdots \qquad (5.10)$$

as

$$a_1 = -(1+\xi) \qquad (5.11a)$$

$$a_2 = (1-\xi)\xi(1+\xi) \qquad (5.11b)$$

The effective interaction is then calculated from eq 3.14 in the form

$$\Delta\chi(T) = \chi_0(T) + \chi_1(T)\phi + \chi_2(T)\phi^2 + ... \qquad (5.12)$$

Up to the second order of the concentration, we explicity have

$$\chi_0(T) = -\ln(1+\lambda) \qquad (5.13a)$$

$$\chi_1(T) = -\ln(1+\lambda) + \xi + \frac{1}{2}\xi^2 \qquad (5.13b)$$

$$\chi_2(T) = -\ln(1+\lambda) + \xi + \frac{1}{2}\xi^2 + \frac{2}{3}\xi^3 + \frac{1}{2}\xi^4 \qquad (5.13c)$$

They are functions of the temperature through the parameter $\xi = \lambda/(1+\lambda)$. The coefficients of the effective interaction 3.15 proposed by Hirotsu have thus been explicitly calculated by using the strength of H-bonds in the case of random hydration. However, it turned out that temperature appears only through the association constant $\lambda/(T)$. If we assume $1 \ll \lambda$ and neglect 1 compared to λ in these relations, we find for instance

$$\chi_0(T) \simeq (\Delta\epsilon_H - T\Delta s_H)/k_B T \qquad (5.14)$$

and in fact we find Hirotsu's form 3.15 It may therefore be understood as the high-temperature expansion of the association constant.

6. Cooperative Hydration

Let us move onto the cooperative hydration. The equilibrium constant is most generally written as

$$K(\mathbf{j}) = \omega(\mathbf{j}) \prod_{\zeta=1}^{n} \eta_\zeta^{j_\zeta} \qquad (6.1)$$

where

$$\omega(\mathbf{j}) \equiv (n - \sum \zeta j_\zeta)!/\Pi j_\zeta![n - \sum(\zeta+1)j_\zeta]! \qquad (6.2)$$

is the number of different ways to select sequences specified by $\mathbf{j}$ from a chain, and η_ζ is the statistical weight for a single water sequence of the length ζ formed on a chain.[19,31,32] We have tacitly assumed that the correlation between adjacent bound water molecules is blocked by the cross-links. Interaction between the water molecules bound to different subchains across the cross-links can therefore be neglected. This assumption is acceptable for PNIPAM gels cross-linked by *N*,*N*′-methylenebis(acrylamide) (BIS) because the molecular volume of BIS is sufficiently large to prevent the interaction between the bound water molecules which are separated by BIS.

Because summing up all possible types $\mathbf{j}$ in the above functions is mathematically difficult, we replace the sum by the contribution from the most probable type $\mathbf{j}^*$ (*one-mode approximation*).[19] The necessary functions are then given by

$$g_0(y) = \omega(\mathbf{j}^*) \prod_{\zeta=1}^{n} (\eta_\zeta y^\zeta)^{j_\zeta} \qquad (6.3)$$

$g_1(y) = \theta(\mathbf{j}^*)g_0(y)$, and $G(y) = \theta(\mathbf{j}^*)$. The function G reduces to the degree θ of the bound water in the type $\mathbf{j}^*$.

The most probable type, or sequence distribution **j***, can be found by minimizing the free energy $\mathscr{F}_{\rm AS}$ by changing **j**. From the condition

$$\partial \mathscr{F}_{\rm AS}/\partial j_\zeta = 0$$

we find that the distribution function of the bound water molecules takes the form

$$j_\zeta/n = (1-\theta)t\eta_\zeta q^\zeta \tag{6.4}$$

where q is defined by

$$q \equiv ty \tag{6.5}$$

The parameter t is defined by

$$t \equiv 1-\nu/(1-\theta) \tag{6.6}$$

Substituting this distribution function 6.4 into the definitions of θ and ν, we find

$$\theta(q) = [1-\theta(q)]t(q)V_1(q) \tag{6.7}$$

and

$$\nu(q) = [1-\theta(q)]t(q)V_0(q) \tag{6.8}$$

and hence

$$t = t(q) = 1/[1+V_0(q)] \tag{6.9}$$

Here new functions V are defined by

$$V_0(q) \equiv \sum \eta_\zeta q^\zeta, \qquad V_1(q) \equiv \sum \zeta\eta_\zeta q^\zeta \tag{6.10}$$

By using the definition 6.6, we can express θ and ν as

$$\theta = V_1(q)/[1+V_{01}(q)] \tag{6.11a}$$

$$\nu = V_0(q)/[1+V_{01}(q)] \tag{6.11b}$$

where $V_{01}(q) \equiv V_0(q) + V_1(q)$. Now, eq 3.10 to find y as a function of the polymer volume fraction ϕ takes the form

$$1-\phi = y+\phi\theta(q) \tag{6.12}$$

Also, eq 6.5 takes the form

$$q = y/[1+V_0(q)] \tag{6.13}$$

These two relations are coupled to eq 4.1 to find q as a function of the temparature. The degree of hydration is then calculated by eq 6.11a.

Our strategy is therefore as follows. We first solve eq 6.9 for the unknown q for a given concentration ϕ and temperature T, and then find θ, ν, and t as functions of them. We then substitute the result into eq 4.1 to find the swelling ratio.

In order to complete the calculation, we have to specify the statistical weight η_ζ. To do this, we employ the simplest form

$$\eta_\zeta = \sigma\lambda(T)^\zeta \tag{6.14}$$

which was proposed by Zimm and Bragg[33,34] for the study of coil-to-helix transition of biopolymers.

The front factor σ gives the free energy penalty for a boundary between a helix and a coil (a hydrated sequence and a collapsed random coil in the present context), and is called *cooperativity parameter*. In the case of random adsorption where there is no interaction between the adsorbed water molecules, it is given by $\sigma = 1$ and the model reduces to the random hydration treated in the preceding section.

Let $\Delta f_c \equiv \Delta\epsilon_c - T\Delta s_c$ be the interaction free energy between the nearest neighboring bound water molecules. The statistical weight

$$\lambda(T) = \exp[-\beta(\Delta f_{\rm H} + \Delta f_c)] \tag{6.15}$$

includes both hydrogen-bonding free energy $\Delta f_{\rm H}$ and the free energy Δf_c of the nearest neghbor interaction. The cooperativity parameter appears from the interaction in the form

$$\sigma \equiv \exp(\beta\Delta f_c) \tag{6.16}$$

Equation 6.9 to decide q now takes the form

$$q = \lambda(T)ty \tag{6.17}$$

where λq is written as q for simplicity. The coverage θ by bound water molecules is given by

$$\theta(q) = \frac{\sigma q w_1(q)}{[1+\sigma q w_{01}(q)]} \tag{6.18}$$

Here, functions w are defined by

$$w_0(x) \equiv \sum_{\zeta=1}^{n} x^{\zeta-1}, \qquad w_1(x) \equiv \sum_{\zeta=1}^{n} \zeta x^{\zeta-1} \tag{6.19}$$

and $w_{01}(x) \equiv w_0(x) + w_1(x)$. The average sequence length of the bound water is calculated by $\bar{\zeta}_w = w_1(q)/w_0(q)$.

6.1. Hydration Curves and the Volume Phase Transition. The association constant 6.15 of H-bonding takes the same form as eq 5.9, but the dimensionless energy γ includes both factors as

$$\gamma \equiv |\Delta\epsilon_{\rm H} + \Delta\epsilon_c|/k_{\rm B}\Theta \tag{6.20}$$

The amplitude λ_0 also include both factors.

We fix them as $\lambda_0 = 0.002$ and $\gamma = 3.5$ in accordance with the result of the study on PNIPAM solutions.[19] Because the entropy part of the ineraction between the bound water molecules is usually dominant as in coil–helix transition,[33] we fix the cooperativity parameter σ at a constant value independent of the temperature. The fraction of the effective chains is fixed at $\eta = 1$, and the coefficient μ in the elastic free energy due to the volume change is fixed at $\mu = 1$ as in the conventional affine network theory. The volume fraction of the reference state (the state where the gel sample is cross-linked) is chosen as $\phi_0 = 0.075$ as in the typical experiments.[4−7]

Figure 3 shows the swelling ratio Q plotted against the reduced temperature τ with varied cooperativity (a) for weak cooperativity region of $0.3 < \sigma < 1.0$, and (b) for strong cooperativity region of $\sigma < 0.3$. In the weak cooperativity region, the swelling ratio continuously decreases with temperature, while in the strong cooperaivity region it shows a discontinuous transition. The critical value for discontinuity is $\sigma_c = 0.30$. The width of discontinuity also increases with cooperativity. Above the transition temperature, the swelling ratio takes almost the same value $Q \simeq 0.2$ independent of σ, so that the polymer fraction is $\phi = \phi_0/Q \simeq 0.375$.

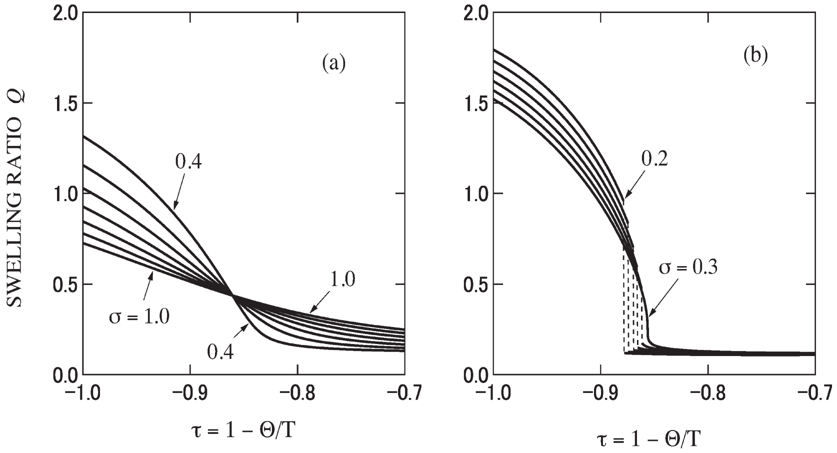

Figure 3. Swelling ratio Q plotted against the reduced temperature. The cooperativity parameter σ is varied from curve to curve. Other parameters are fixed at $\eta = 1.0$, $n = 100$, $\phi_0 = 0.075$, $\mu = 1.0$, $\lambda_0 = 2.0 \times 10^{-3}$, $\gamma = 3.5$. (a) For weakly cooperative hydration in the range of $0.3 < \sigma < 1.0$, the transition is continuous. (b) In the strongly cooperative region $\sigma < 0.3$, the transition is discontinuous.

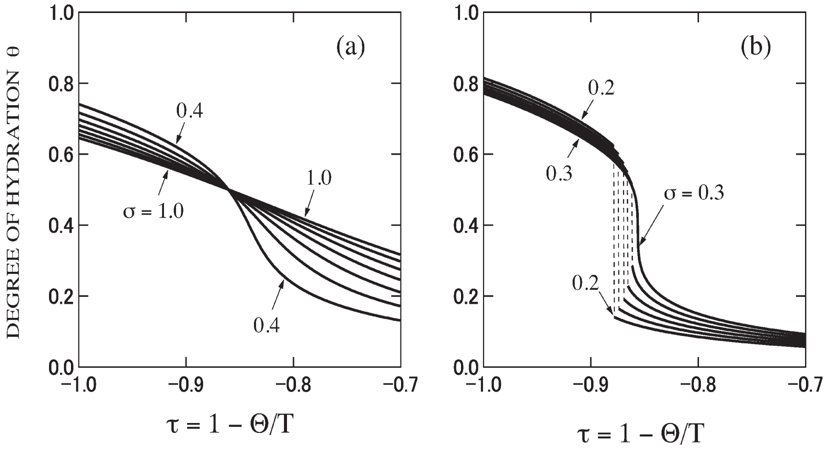

Figure 4. Degree of hydration θ plotted against the reduced temperature. The cooperativity parameter σ is varied from curve to curve. Other parameters are fixed at $\psi = 1.0$, $\lambda_0 = 2.0 \times 10^{-3}$, $\gamma = 3.5$. (a) Within the range of weak cooperativity $0.3 < \sigma < 1.0$, degree of hydration θ continuously changes as the swelling ratio. (b) In the strong cooperativity region $\sigma < 0.3$, degree of hydration changes discontinuously.

Figure 4 shows the degree of hydration θ plotted against the temperature (dehydration curve) with varied cooperativity (a) for weak cooperativity region of $0.3 < \sigma < 1.0$, and (b) for strong cooperativity region of $\sigma < 0.3$. As expected, the profile shows a discontinuity where the swelling ratio changes discontinuously. Thus, we understand that the volume change is induced by the group dissociation of bound water molecules. In our previous study on the conformational change of a singe PNIPAM chain, the collapse of the chain becomes sharper with the degree of cooperativity, but the radius of gyration changes continuously even in the limit of high cooperativity. This is due to the finiteness of the degree of freedom for internal motion of a chain because its molecular weight, or the number n of the repeat units, is finite although it might be large. However, for gels consisting of the macroscopic number N of chains, the degree of freedom is macroscopic, and hence phase transitions with finite discontinuity are possible.

Figure 5 plots the bulk modulus K as functions of the temperature. It changes discontinuously for high cooperativity region of $\sigma < \sigma_c$. In the collapsed state, K can be 3 orders of magnitude larger than in the swollen state. In the swollen state, K is almost independent of the cooperativity.

Figure 6 compares theoretical calculation with the experimental data[4] on the swelling ratio Q of PNIPAM cross-linked gels. From the study of LCST phase separation of PNIPAM solutions, we already know[19] that the association constants and the cooperativity parameter are given by $\lambda_0 = 0.0021$, $\gamma = 3.5$, $\sigma = 0.28$. The reference volume fraction of the sample used in the experiments was estimated to be $\phi_0 = 0.075$, while we find the best fit by $\phi_0 = 0.065$. Because the former is estimated from the total amount of polymers before cross-linking, this small discrepancy may be attributed to the existence of the polymer chains that are not connected to the gel when they are cross-linked.

6.2. Renormalized Interaction Parameter. As for the renormalization of the χ-parameter for cooperative hydration, we find the approximate relations

$$\chi_0(T) = -\ln[1 + V_0(q_0)] \tag{6.21a}$$

$$\chi_1(T) = -\ln[1 + V_0(q_0)] + \xi + \frac{1}{2}\xi^2 \tag{6.21b}$$

by power expansion, where the effective interaction parameter ξ is here defined by

$$\xi \equiv V_1(q_0)/[1 + V_{01}(q_0)] \tag{6.22}$$

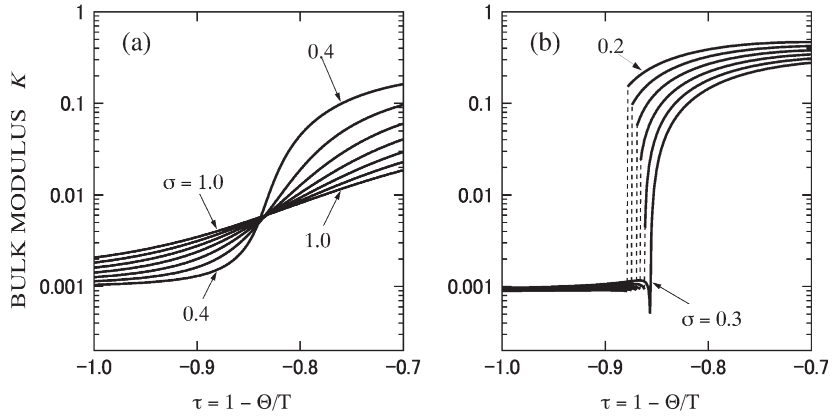

Figure 5. Bulk modulus K plotted against the reduced temperature. The cooperativity parameter σ is varied from curve to curve. Other parameters are fixed at $\psi = 1.0, \lambda_0 = 2.0 \times 10^{-3}, \gamma = 3.5$. (a) In the range $0.3 < \sigma < 1.0$, bulk modulus K changes continuously. (b) In the strongly cooperative region $\sigma < 0.3$, there is a huge discontinuity in the bulk modulus.

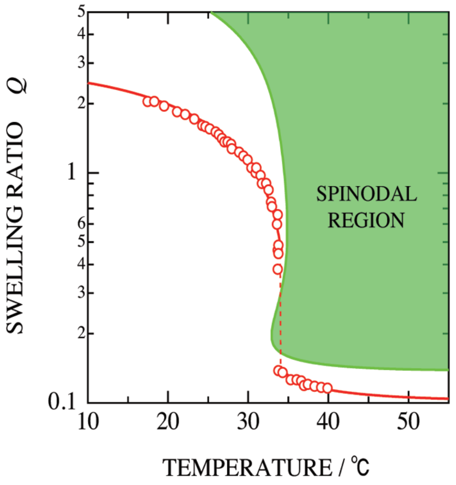

Figure 6. Fitting of the experimental data of swelling ratio (symbols) by the theoretical calculation (solid line) on the basis of cooperative hydration. The parameters used are $\sigma = 0.28$, $\lambda_0 = 0.0021$, $\gamma = 3.5$, $\eta = 0.35$, $\phi_0 = 0.065$, and $\mu = 1.0$. The shaded area shows the calculated unstable (spinodal) region.

The parameter q_0 is the solution of the equation

$$q_0[1 + V_0(q_0)] = \lambda \tag{6.23}$$

in the limit of infinite dilution. Hence, the relation

$$\xi = \lim_{\phi \to 0} \theta(\phi) = \theta_0 \tag{6.24}$$

for the single-chain hydration is retained.

For high molecular weight of the subchains, we can take the upper limit of the sum to infinity, and use the approximate form $V_0(q) \simeq \sigma q/(1 - q)$. The equation for q_0 then reduces to Zimm−Bragg equation

$$(1-\sigma)q^2 - (1+\lambda)q + 1 = 0 \tag{6.25}$$

to find the eigenvalues of the transfer matrix. We find

$$q_0 = \frac{1}{2(1-\sigma)}\{1+\lambda \pm \sqrt{(1-\lambda)^2 + 4\sigma\lambda}\} \tag{6.26}$$

In the limit of high cooperativity $\sigma \to 0$, it takes either 1 (if $\lambda > 1$), or λ (if $\lambda < 1$). Hence, the interaction parameter due to hydration sharply change as

$$\chi_0(T) \simeq \ln q_0/\lambda \simeq \begin{cases} 0 & (\lambda < 1), \\ -\ln \lambda & (\lambda > 1) \end{cases} \tag{6.27}$$

near the single chain dehydration point $\lambda = 1$.

7. Uniaxial Stretching

For the study of swelling experiments[35] under external force, we consider the intermediate state in which the sample is freely swollen from the reference size L_0 to the length $L^{(i)}$ of each side. The volume is $V_{\mathrm{i}} = L^{(i)^3}$, so that the volume ratio becomes

$$\phi_i/\phi_0 \equiv V_0/V_i \tag{7.1}$$

This is taken as the initial volume fraction of the deformation experiment.

The force **f** is then applied to the sample to bring it to the final equilibrium in the deformed state. The stress in this final state is then measured.

Let L_x, L_y, L_z be the length of each side of the sample in the final state. The macroscopic deformation tensor $\hat{\lambda}$ is defined by

$$\lambda_j \equiv \frac{L_j}{L_0} \; (j = x, y, z) \tag{7.2}$$

The deformation tensor *relative to the initial state* is then given by

$$\alpha_j \equiv \frac{L_j}{L^{(\mathrm{i})}} = \left(\frac{V_0}{V_{\mathrm{i}}}\right)^{1/3} \lambda_j \tag{7.3}$$

The difference between λ_j and α_j should be noticed in the swelling experiments.

In the case of uniaxial elongation in the x direction by an applied tension f, the deformation tensor has the elements

$$\lambda_x \equiv \lambda = \alpha\left(\frac{V_{\mathrm{i}}}{V_0}\right)^{1/3} = \alpha\left(\frac{\phi_0}{\phi_{\mathrm{i}}}\right)^{1/3} \tag{7.4a}$$

$$\lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}\left(\frac{\phi_0}{\phi}\right)^{1/2} = \frac{1}{\sqrt{\alpha}}\left(\frac{\phi_0}{\phi}\right)^{1/2}\left(\frac{V_0}{V_{\mathrm{i}}}\right)^{1/6} \tag{7.4b}$$

where $\alpha \equiv \alpha_x$ is the elongation relative to the initial state.

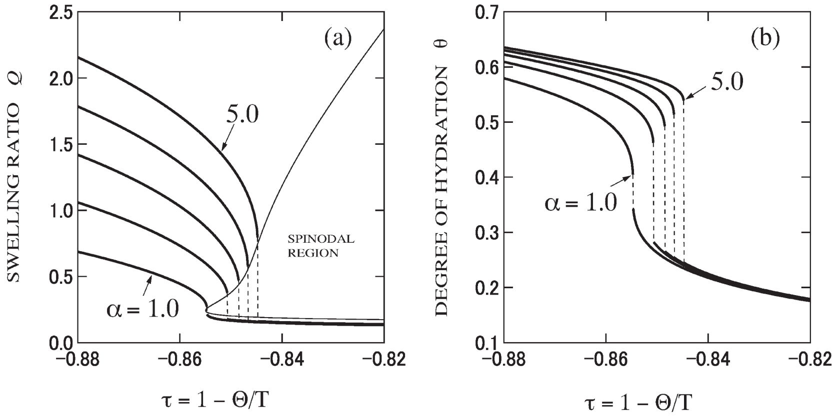

Figure 7. (a) Swelling curve (thick lines) under a fixed degree of elongation α and the spinodal line (thin line) plotted against the temperature. The elongation ratio α is varied from curve to curve. Other parameters are fixed at $\eta = 1.0, n = 100, \phi_0 = 0.1, \mu = 1.0, \psi = 1.0, \sigma = 0.3, \lambda_0 = 2.0 \times 10^{-3}$, and $\gamma = 3.5$. (b) Degree of hydration θ plotted against the temperature. The elongation ratio α is varied from curve to curve. The degree of hydration θ increases with the stretching ratio α in the swollen phase. At the transition point, it discontinuously changes as the swelling ratio.

By the derivative of the free energy $f = (\partial \Delta_{\rm def} F/\partial \lambda_x)_T/L_0$, the tension is found to be

$$f = \frac{\eta N k_{\rm B} T}{L_0}\left(\lambda - \left(\frac{\phi_0}{\phi}\right)\frac{1}{\lambda^2}\right)$$
$$= \frac{\eta N k_{\rm B} T}{L_0}\left(\frac{\phi_0}{\phi_{\rm i}}\right)^{1/3}\left[\alpha - \left(\frac{\phi_{\rm i}}{\phi}\right)\frac{1}{\alpha^2}\right] \tag{7.5}$$

The swelling ratio Q is defined by eq 2.2, as in the free swelling case. In the experiment,[35] the initial state was chosen at the temperature 30 °C (corresponding to the reduced temperature $\tau_{\rm i} = -0.865$ with $\Theta = 565$). The measured volume ratio turned out to be $V_{\rm i} \simeq V_0$.

7.1. Shift of the Phase Diagrams by Tension. For the swelling of gels under external force, measurements of the volume have been carried out in the experiments with (1) constant force, and (2) with constant stretching ratio.[35] Here, we examine the results of the latter.

Figure 7a shows a model calculation on how the swelling curve changes with the elongation ratio α. The ratio is changed from curve to curve with other parameters fixed at the values used for fitting the free swelling experiments. With increase in the deformation α, the swelling ratio in the low-temperature region goes up, and the degree of discontinuity at the transition temperature becomes larger. The spinodal line is calculated by eq 4.6, and independent of the elongation ratio. Figure 7b shows the corresponding dehydration curves. After collapse, 20% of the H-bonding sites on the chains still remain hydrated.

For the critical value $\sigma = 0.3$ of cooperativity parameter, the volume of the gel changes with finite discontinuity even for $\alpha = 1$. With increase in the stretching ratio, the collapse point moves to higher temperature, and the width of the discontinuity grows larger. The swollen state withstands up to higher temperature, and the transition becomes sharper. This is analogous to the effect of pressure on the gas−liquid phase transition. Thus, the volume transition of gels under external force serves an example of the phase transitions which are enhanced by the external field.

To demonstrate the validity of the theoretical model, we compare the theoretical calculation with experimental data of cross-liked PNIPAM gels.[35] In the experiment, the volume transition temperature is 33.45 °C. The gel is freely swollen at 30 °C. The swelling ratio turned out to be $V_{\rm i}/V_0 \simeq 1$. The sample was stretched in x-direction and kept at a constant α until it reaches equilibrium. The swelling ratio Q is then measured. Figure 8 compares the experimental data with our theoretical calculation. From the reported experimental conditions for free swelling, we estimate the parameters to be $\eta = 0.75, \phi_0 = 0.09, \lambda_0 = 0.00209, \gamma = 3.5$, and $\sigma = 0.27$. Other theoretical curves in the figure are then uniquely fixed. There is a systematic deviation from the experiment for large values of α, but, despite many assumptions used such as affine deformation, Gaussian chains etc., the tendency of the swelling curves is well described. The limiting swelling ratio 0.2 in the collapses state suggest that many bound water molecules remain inside the gel.

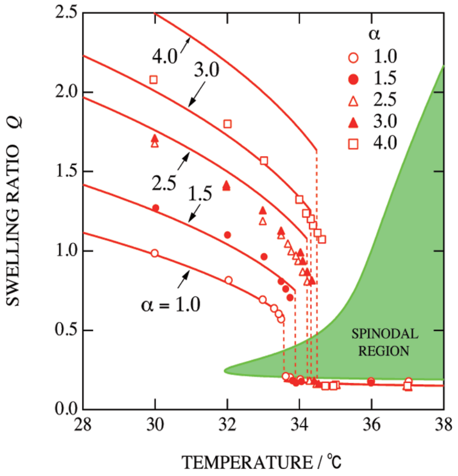

Figure 8. Experimental data (symbols) compared with the theoretical curves (solid lines) calculated on the basis of the cooperative hydration model. The elongation ratio is varied from curve to curve. Shaded area indicates the unstable region surrounded by the spinodal line. Parameters used for the theoretical calculation are $\eta = 0.75, \phi_0 = 0.09, \lambda_0 = 0.00209, \gamma = 3.5$, and $\sigma = 0.27$.

7.2. Bulk Modulus and Poisson Ratio. Let us consider a small uniaxial deformation from the equilibrium state of a matter. The Poisson ratio for a homogeneous deformation is defined by the ratio of the transverse strain relative to the longitudinal one

$$\nu \equiv -\ln \lambda_y / \ln \lambda_x \tag{7.6}$$

For homogeneous isotropic materials, it is identical to

$$\nu = \frac{3K - 2\mu}{2(3K + \mu)} \tag{7.7}$$

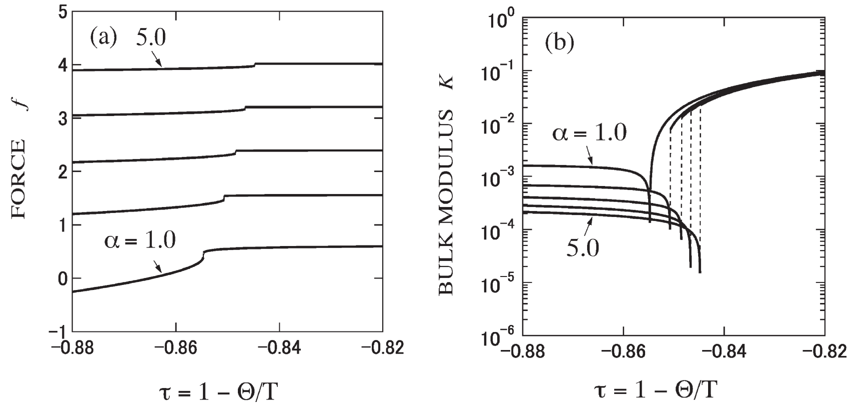

Figure 9. (a) Force *f* of PNIPAM gels for a fixed degree of elongation ratio α in water with $\tau_i = -0.865$, plotted against the temperature τ. α is varied from curve to curve. Other parameters are fixed at $\eta = 1.0$, $n = 100$, $\phi_0 = 0.075$, $\mu = 1.0$, $\psi = 1.0$, $\sigma = 0.3$, $\lambda_0 = 2.0 \times 10^{-3}$, and $\gamma = 3.5$. (b) Bulk modulus *K* of PNIPAM gels for a fixed degree of elongation α in water, plotted against the temperature τ. α is varied from curve to curve. Other parameters are fixed at the same values in Figure.7.

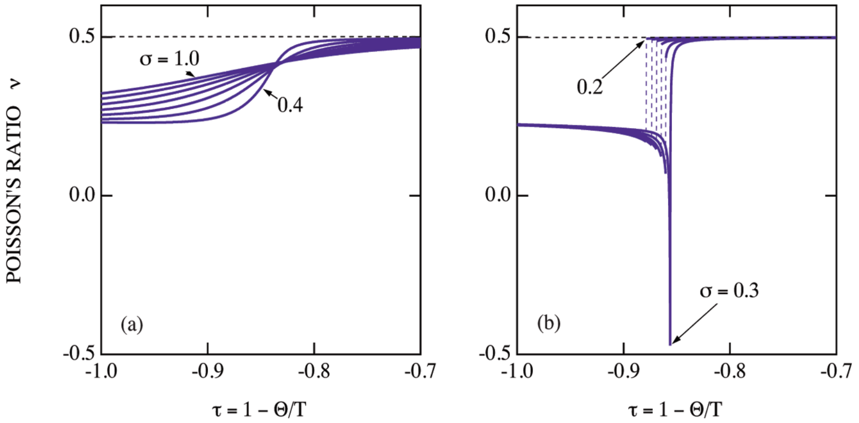

Figure 10. Poisson ratio plotted against the reduced temperature. The cooperativity parameter σ is varied from curve to curve. Other parameters are fixed at the same values in Figure.7.

where *K* is the bulk modulus and μ is the shear modulus.[36] Since *K* and μ must be positive for a stable matter, ν must take the value in the range $-1 \le \nu \le {}^{1}/_{2}$. If the material is incompressible ($K \to \infty$), then $\nu = {}^{1}/_{2}$. This is the upper limit of the ratio. For the soft limit $K \to 0$, the lower bound of the Poisson ratio $\nu = -1$ is reached.[36]

In reality, most materials have ν between 0 and ${}^{1}/_{2}$. For a single chain swollen in a good solvent, scaling argument leads to $\nu = {}^{1}/_{4}$.[37] The measurement of the ratio K/μ of the swollen polyacrylamide gels[38] showed that μ takes a value between 0.26 and 0.29 depending on the preparation condition. In the present context, the bulk modulus can be obtained by eq 4.3 for an free swelling.

We first show model calculations of the force *f* in Figure 9a and the corresponding bulk modulus in part b as functions of the temperature. The stretching ratio α is varied from curve to curve.

For the critical value $\sigma = 0.3$ of cooperativity parameter, a small step in the force and a discontinuity in the modulus appear at the collapse temperature, which moves to higher temperature, and the width of the modulus discontinuity grows larger.

For small deformation of the swollen gel under uniaxial tension, the Poisson ratio is

$$\nu = -\frac{\ln \alpha_y}{\ln \alpha_x} = \frac{1}{2}\left(1 - \frac{\ln(\phi_i/\phi)}{\ln \alpha}\right) \tag{7.8}$$

In particular, we can find the Poisson ratio for the infinitesimal deformation (initial Poisson ratio) of the freely swollen gels by taking $\alpha \to 1$ limit in this formula. Parts a and b of Figure 10 show the Poisson ratio as a function of the reduced temperature. The cooperativity parameter is changed from curve to curve. For weak cooperativity (a), it is monotonically increasing function of the temperature. However, with enhanced cooperativity in part b, it sharply decreases in the transition region. For $\sigma = 0.3$ for instance, it becomes negative, and reaches the minimum of -0.5 at the transition point. Negative Poisson ratio indicates that, when the gel is uniaxially stretched, it adsorbs water molecules and swell in the direction perpendicular to the stretched axis.

8. Conclusions and Discussion

On the basis of cooperative hydration, a new theoretical model is developed for the study the volume change of PNIPAM cross-linked gels. The results on the swelling curves for isotropic free swelling and under uniaxial deformation are compared with the experimental data. We found good agreements. The model proposed in this study has obvious advantages in describing the collapse of hydrogels in which hydration and dehydration play the crucial roles. It is found that there is a critical cooperativity parameter σ_c (0.30 for PNIPAM) below which the volume transition becomes a real first order phase transition with volume discontinuity. The molecular mechanism of such discontinuity can be understood in terms of the concentration-dependent effective interaction parameter which is the combination of the van der Waals type water-monomer interaction and the strong hydrogen-bonding interaction. The latter sharply changes near the dehydration temperature, leading to a discontinuous volume change. Thus, Hirotsu's phenomenological concentration-dependent χ-parameter is interpreted in terms of molecular parameters.

The concept of cooperative hydration is applicable to the self-assembling structures formed by hydrophobically modified PNIPAMs in water, such as flower micelles, mesoglobules, transient gels, etc. It is also related to cononsolvency of PNIPAM chains in mixed solvents of water and methanol. The chain tension is strongly coupled to the hydration as we saw in the text in the swelling of gels under deformation. Hence, when aqueous solutions of PNIPAMs are sheared, chain segments in a globular part may be reeled out by tension. Further modifications of the present theoretical model would involve all of these interesting phenomena.

Direct measurements of the hydration number (the number of water molecules per monomer) of PNIPAM chains in water across the LCST have recently been attempted by Ono and Shikata[39,40] by using high frequency dielectric techniques. They found a rather high number (10−11) compared to the one (5−6) obtained by infrared spectroscopy, and hence they proposed that there may be secondary hydration layer, such as hydrogen-bonding bridges, other than the direct hydrogen bonds. Application of such techniques to the cross-linked PNIPAM gels would lead to deeper understanding of the molecular mechanism of the phase transitions in gels.

Acknowledgment. F.T. would like to thank Professor Shikata and Professor Annaka for the discussion on the measurement of bound water molecules in PNIPAM solutions and gels. H.K. thanks Professor T. Koga for the help in numerical calculation. We also wish to acknowledge the partial support of this work by a Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science under Grant Number 19350057.

References and Notes

(1) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(2) Tanaka, T. *Sci. Am.* **1981**, *244*, 124.
(3) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(4) Hirotsu, S. *J. Phys. Soc. Jpn.* **1987**, *56*, 233.
(5) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *87*, 1392.
(6) Hirotsu, S. *J. Chem. Phys.* **1988**, *88*, 427.
(7) Hirotsu, S. *J. Chem. Phys.* **1991**, *94*, 3949.
(8) Kogure, H.; Nanami, S.; Masuda, Y.; Toyama, Y.; Kubota, K. *Colloid Polym. Sci.* **2005**, *283*, 1163.
(9) Private communication (2009).
(10) Heskins, M.; Guillet, J. E. *J. Macromol. Sci.* **1968**, *A2*, 1441.
(11) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(12) Afroze, F.; Nies, E.; Berghmans, H. *J. Mol. Struct.* **2000**, *554*, 55.
(13) de Azevedo, R. G.; Rebelo, L. P. N.; Ramos, A. M.; Szydlowski, J.; de Sousa, H. C.; Klein, J. *Fluid Phase Eq.* **2001**, *185*, 189.
(14) Rebelo, L. P. N.; Visak, Z. P.; de Sousa, H. C.; Szydlowski, J.; de Azevedo, R. G.; Ramos, A. M.; Najdanovic-Visak, V.; da Ponte, M. N.; Klein, J. *Macromolecules* **2002**, *35*, 1887.
(15) Milewska, A.; Szydlowski, J.; Rebelo, L. P. N. *J. Polym. Sci., Polym. Phys. Ed.* **2003**, *41*, 1219.
(16) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311.
(17) Wu, C.; Zhou, S. *Macromolecules* **1995**, *28*, 8381.
(18) Moerkerke, R.; Koningsveld, R.; Berghmans, H.; Dusek, K.; Solc, K. *Macromolecules* **1995**, *28*, 1103.
(19) Okada, Y.; Tanaka, F. *Macromolecules* **2005**, *38*, 4465.
(20) Tanaka, F.; Koga, T.; Winnik, F. M. *Phys. Rev. Lett.* **2008**, *101*, 028302.
(21) Tanaka, F.; Koga, T.; Kojima, H.; Winnik, F. M. *Macromolecules* **2009**, *42*, 1231.
(22) In the recent experiments by using dielectric relaxation techniques (Ono, Y.; Shikata, T. *J. Am. Chem. Soc.* **2006**, *128*, 10030. Ono, Y.; Shikata, T. *J. Phys Chem. B* **2007**, *111*, 1511), the exact number of hydrated water molecules, including directly H-bonded ones and hydrophobically hydrated ones, has been estimated. The techniques can measure the average duration time of the hydrated water molecules. It was estimated to be 23 ps. In this paper, therefore, those water molecules which stay at the polymer chains for more than 23 ps are regarded as bound. .
(23) Ye, X.; Lu, Y.; Ding, Y.; Liu, S.; Zhang, G.; Wu, C. *Macromolecules* **2007**, *40*, 4750.
(24) Ahmed, Z.; Gooding, E. A.; Pimenov, K. V.; Wang, L.; Asher, S. A. *J. Phys. Chem. B* **2009**, *113*, 4248.
(25) Deshmukh, S.; Mooney, D. A.; McDermott, T.; Kulkarni, S.; Don MacElroy, J. M. *Soft Matter* **2009**, *5*, 1514.
(26) Flory, P. J. *J. Chem. Phys.* **1950**, *18*, 108.
(27) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(28) Huggins, M. L. *J. Chem. Phys.* **1942**, *46*, 151.
(29) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter XII.
(30) Schultz, A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 4760.
(31) Tanaka, F. *Macromolecules* **2003**, *36*, 5392.
(32) Tanaka, F. *Macromolecules* **2004**, *37*, 605.
(33) Zimm, B. H.; Bragg, J. K. *J. Chem. Phys.* **1959**, *31*, 526.
(34) Poland, P.; Scheraga, H. A. *Theory of Helix-Coil Transitions in Biopolymers*; Academic Press: San Diego, CA, 1970.
(35) Suzuki, A.; Kojima, S. *J. Chem. Phys.* **1994**, *101*, 10003.
(36) Landau, L. D.; Lifshitz, E. M., *Theory of Elasticity*, Sect. 5, Pergamon Press: New York, 1981. Course of Theoretical Physics, Vol. *7*.
(37) Geissler, E.; Hecht, A. M. *Macromolecules* **1980**, *13*, 1276.
(38) Geissler, E.; Hecht, A. M.; Horkay, F.; Zrinyi, M. *Macromolecules* **1988**, *21*, 2594.
(39) Ono, Y.; Shikata, T. *J. Am. Chem. Soc.* **2006**, *128*, 10030.
(40) Ono, Y.; Shikata, T. *J. Phys. Chem. B* **2007**, *111*, 1511.