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Temperature- and Tension-Induced Coil−Globule Transition of Poly(*N*-isopropylacrylamide) Chains in Water and Mixed Solvent of Water/Methanol

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ABSTRACT: The concept of cooperative dehydration, defined as the simultaneous dissociation of the water molecules bound in correlated sequences to a polymer chain, has been applied to study the collapse of a poly(*N*-isopropylacrylamide) (PNIPAM) chain upon heating in aqueous solutions. We examined the applicability of this concept in three situations: (i) PNIPAM in water (in the absence of added force), (ii) PNIPAM in water subjected to a tension applied to the chain ends, and (iii) PNIPAM in a mixed solvent of water and a second water-miscible solvent. The transition becomes sharper as the cooperativity parameter of hydration increases. The tension−elongation curve of a hydrated chain at various temperatures, calculated following an approach similar to the classical theory of coil−helix transition, presents a flat plateau corresponding to the tension for which collapsed segments reel out of the globules. The reeled-out segments are hydrated immediately upon exposure to water. The calculations suggest a possible shift to higher temperatures of the cloud points of aqueous PNIPAM solutions under shear flow. The reentrant coil−globule−coil transition in mixed solvent of water and methanol is studied from the viewpoint of competitive hydrogen bonds between polymer−water and polymer−methanol.

1. Introduction

The behavior of poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous media has attracted the interest of many researchers ever since it was first reported by Heskins and Guillet.[1] The polymer exhibits a well-defined lower critical solution temperature (LCST) in water,[1−6] and each individual chain shows a very sharp coil−globule transition[7,8] when heated to 34.5 °C. Cross-linked PNIPAM gels undergo analogous collapse transitions in aqueous solvents.[9] 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.[2]

Historically, the high-temperature collapse of a nonionic single chain[8] and gels[9] in water has been described by using the concentration-dependent interaction parameters $\chi = \chi_0 + \chi_1\phi + \chi_2\phi^2$ 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 decrease at high temperature according to such phenomenological parameters, the molecular origin of the temperature inversion can only be understood if the coefficients are described in terms of the molecular property of polymer−water interaction.

We developed earlier a description of the phase separation with closed loop miscibility gap that takes place in aqueous solutions of poly(ethylene oxide) (PEO),[10] in which we tried to include explicitly the hydration[11] in order to find the molecular origin of the high-temperature collapse. In this description, the model assumed random and independent hydrogen bonding (referred to as H-bonding) between PEO and water molecules along the chain. It was adequate to describe the experimental phase diagrams of PEO. This hydration mechanism was however unable to describe the sharp collapse of PNIPAM chains.

To elucidate the origin of the high sensitivity of PNIPAM to temperature, we recently improved 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.[12] The cooperativity in hydration is caused by a positive correlation between neighboring bound water molecules due to the presence of the large hydrophobic isopropyl side groups. If a water molecule succeeds in forming a 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).[12,13] When the chain is heated up, each sequence is dehydrated as a whole, resulting in the sharp collapse of the chain.

We recently showed that, in solutions of PNIPAM in a mixed solvent of water and methanol, the competition in forming PNIPAM−water (p−w) H-bonds and PNIPAM−methanol (p−m) H-bonds (competitive adsorption) results in cononsolvency.[14] Small differences in the composition of the mixed solvent are greatly amplified by cooperativity, and as a result, the composition of the bound molecules along the chain deviates substantially from that in the bulk (nonlinear amplification). The total coverage θ of the chain by bound molecules exhibits a minimum at the composition where the competition is strongest; hence, the chain collapses around such a composition by hydrophobic aggregation of the dehydrated chain segments.

In this paper, we apply our model of cooperative hydration to a single-chain conformational transition in water and also in a mixed solvent of water and methanol. We calculate the mean-square end-to-end distance of a chain as a function of the temperature and the composition of the mixed solvent and find that in fact the collapse transition becomes sharper with increasing cooperativity.

We also apply the model to the conformation transition of a PNIPAM chain under an external force applied to the chain

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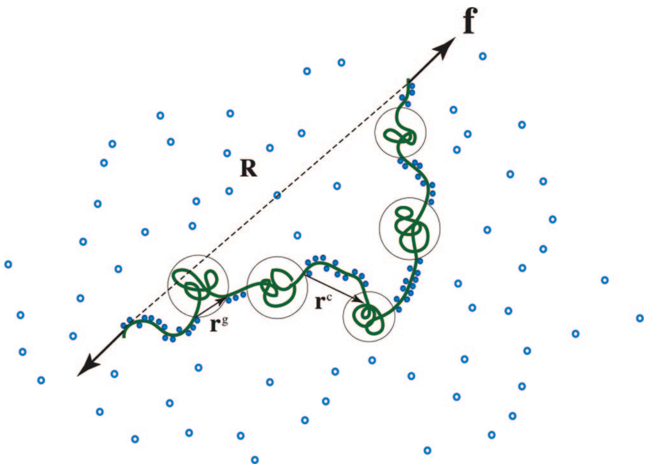

Figure 1. Sequential hydrogen bonds formed along the polymer chain, with end-to-end vector **R** under tension **f** due to the cooperative interaction between the nearest-neghboring bound water molecules. The type of globule is specified by the index $\mathbf{i} \equiv \{i_1, i_2,...\}$, where i_ζ is the number of globules of size ζ. The type of polymer−water associated complex is specified by the index $\mathbf{j} \equiv \{j_1, j_2,...\}$, where j_ζ is the number of sequences that consist of a run of H-bonded ζ consecutive water molecules. The average length of hydrated sequences sharply reduces as temperature approaches LCST from below. The vector $\mathbf{r}^g$ connects the incoming and outgoing point of a globule, while the vector $\mathbf{r}^c$ is the end-to-end vector of a hydrated coil.

ends. The tension given at the chain ends reels chain segments out of the globular aggregates. The reeled-out segments are hydrated as soon as they are exposed to water. A flat plateau in the tension−elongation curve appears during the reeling-out process. Thus, tension enhances hydration, leading eventually to highly hydrated stretched chain.

2. High-Temperature Collapse of a Free Chain

Consider a hydrated polymer chain in water assumed to take a pearl-necklace conformation (Figure 1). The pearls are the compact spherical globules formed by close-packed hydrophobic aggregates of the dehydrated chain segments. They are connected in a series by the hydrated swollen random coils. Let i_ζ be the number of pearls that consist of a number ζ of contiguous repeat units, and let j_ζ be the number of swollen coils with the length ζ connecting them. The chain conformation is specified by the indices $\mathbf{i} \equiv \{i_1,i_2,...\}$ and $\mathbf{j} \equiv \{j_1, j_2,...\}$. The partition function of a chain takes the form

$$Z_n(T) = \sum_{ij} \exp[-A(\mathbf{i},\mathbf{j})/k_BT] \tag{2.1}$$

where the statistical weight is given by

$$\exp[-A(\mathbf{i},\mathbf{j})/k_BT] \equiv \omega(\mathbf{i},\mathbf{j}) \prod_\zeta (\lambda_\zeta)^{i_\zeta} (\eta_\zeta)^{i_\zeta} \tag{2.2}$$

The combinatorial factor ω is the number of different ways to find the distribution of sequences specified by ($\mathbf{i}$, $\mathbf{j}$) and is given by

$$\omega(\mathbf{i},\mathbf{j}) = \frac{\left(\sum i_\zeta\right)! \left(\sum j_\zeta\right)!}{\prod i_\zeta! \prod j_\zeta!} \tag{2.3}$$

The statistical weight λ_ζ for a globule of size ζ can be modeled by considering its condensation free energy Δf_ζ. The cohesive energy of the globule due to hydrophobic aggregation is given by $-\epsilon\zeta$, where ϵ (>0) is the binding energy per repeat unit. The globule has a surface tension γ at the surface in contact with water, so that the total free energy is given by $\Delta f_\zeta = -\epsilon\zeta + \gamma\zeta^{2/3}$. Thus, the statistical weight takes the form

$$\lambda_\zeta(T) = e^{-\gamma\zeta^{2/3}} \lambda(T)^\zeta \tag{2.4}$$

where $\lambda(T) \equiv \exp(\epsilon/k_BT)$ is the association constant, and the dimensionless γ/k_BT from the surface free energy is simply written as γ. The formula (2.4) holds strictly for sufficiently large ζ, but here we include all possible $\zeta \geq 1$ for simplicity. The effect of the surface tension may be significant; it suppresses the nucleation of globules until they grow above a certain critical size. In what follows, however, we neglect the surface tension by fixing $\gamma = 0$. This reduces the number of material parameters and places the focus on the hydrophobic aggregation.

The statistical weight η_ζ for the swollen random coil is assumed to be given by the Zimm−Bragg form[12,14−16]

$$\eta_\zeta = \sigma s(T)^\zeta \tag{2.5}$$

to include cooperativity, where $s(T) \equiv \exp[(\epsilon_H + \Delta\epsilon)/k_BT]$ is the association constant for the H-bonding of a water molecule onto a repeat unit of the polymer chain, and $\sigma \equiv \exp(-\Delta\epsilon/k_BT)$ is the cooperativity parameter of hydration due to the interaction energy $\Delta\epsilon$ of the nearest-neghboring bound water molecules. A smaller σ gives a stronger cooperativity.[17]

Instead of summing over all possible distributions, we find the most probable distribution (referred to as mpd) that minimizes the free energy $A(\mathbf{i},\mathbf{j})$ under the two conditions

$$\sum_{\zeta=1}^{n} i_\zeta = \sum_{\zeta=1}^{n} j_\zeta \tag{2.6a}$$

$$\sum_{\zeta=1}^{n} \zeta(i_\zeta + j_\zeta) = n \tag{2.6b}$$

(Small difference ±1 in eq 2.6a arising from the chain ends has been neglected.) The first condition shows the fact that a pearl and a string appear alternatively, while the second one gives a constraint that the total number of repeat units is given by n. Let us introduce two Lagrange's indeterminate multipliers α and β for these constraints and minimize

$$\begin{aligned} A(\mathbf{i},\mathbf{j})/k_BT = -\ln \omega(\mathbf{i},\mathbf{j}) - \sum_\zeta (i_\zeta \ln \lambda_\zeta + j_\zeta \ln \eta_\zeta) - \\ \alpha \sum_\zeta (i_\zeta - j_\zeta) - \beta\left[\sum_\zeta \zeta(i_\zeta + j_\zeta) - n\right] \end{aligned} \tag{2.7}$$

by changing $\mathbf{i}$ and $\mathbf{j}$. Then we find

$$i_\zeta / \sum i_\zeta = e^\alpha \lambda_\zeta z^\zeta \tag{2.8a}$$

$$j_\zeta / \sum j_\zeta = e^{-\alpha} \eta_\zeta z^\zeta \tag{2.8b}$$

where a new parameter z is introduced by the definition $z \equiv e^\beta$.

By taking the sum over $\zeta = 1,..., n$, we find that the Lagrange's multipliers must satisfy the coupled equations

$$e^\alpha U_0(z) = 1 \tag{2.9a}$$

$$e^{-\alpha} V_0(z) = 1 \tag{2.9b}$$

where

$$U_k(z) \equiv \sum_{\zeta=1}^{n} \zeta^k \lambda_\zeta z^\zeta, \quad V_k(z) \equiv \sum_{\zeta=1}^{n} \zeta^k \eta_\zeta z^\zeta \qquad (k = 0, 1, 2, ...) \tag{2.10}$$

Hence, Lagrange's constant z can be found by the equation

$$U_0(z)V_0(z) = 1 \tag{2.11}$$

This is equivalent to the Zimm−Bragg equation[15] if λ_ζ is replaced by 1 and the weight (2.5) for η_ζ is employed. In what follows, therefore, we call this ZB equation. Substituting mpd into the condition (2.6b), we find the average number ν of pearls (of coils) to be given by

$$\nu \equiv \sum_\zeta i_\zeta/n = \sum_\zeta j_\zeta/n = [U_1(z)/U_0(z) + V_1(z)/V_0(z)]^{-1} \tag{2.12}$$

By the ZB equation, it can be written as

$$\nu = [U_1(z)V_0(z) + U_0(z)V_1(z)]^{-1} \tag{2.13}$$

The fraction of the hydrated part, or the number of bound water molecules, is given by

$$\theta \equiv \sum_\zeta \zeta j_\zeta/n = U_0(z)V_1(z)/[U_1(z)V_0(z) + U_0(z)V_1(z)] \tag{2.14}$$

and hence the fraction of globules is given by $1 - \theta$. These equations can be written in more compact forms as

$$\theta = h(z)V_1(z)/[1 + h(z)V_1(z)] \tag{2.15}$$

where the function $h(z)$ is defined by

$$h(z) \equiv U_0(z)^2/U_1(z) \tag{2.16}$$

In the original ZB equation[15] with $\lambda_\zeta = 1$, $h(z)$ is reduced to z. (The upper limit of the sum is allowed to go to infinity).

The number-average size of the globules is given by

$$\bar{\zeta}_\mathrm{n} \equiv \sum_\zeta \zeta j_\zeta / \sum_\zeta j_\zeta = U_1(z)/U_0(z) = U_1(z)V_0(z) \tag{2.17}$$

Similarly, the number-average sequence length of the hydrated random coils is given by

$$\bar{\zeta}_\mathrm{n}^{(\mathrm{w})} \equiv \sum_\zeta \zeta j_\zeta / \sum_\zeta j_\zeta = V_1(z)/V_0(z) = U_0(z)V_1(z) \tag{2.18}$$

The superscript (w) indicates the swollen random coils H-bonded with water. Finally, by substituting mpd into the original partition function (2.1), we find $Z_n(T) = 1/z^n$ or

$$\ln Z_n(T) = -n \ln z \tag{2.19}$$

so that we can regard z as the partition function per repeat unit.

3. Hydrated Polymer Chain under Tension

To study the average end-to-end distance of a chain under a tension exerted at the chain ends, we next consider the partition function of the chain with a fixed end vector $\mathbf{R}$. Let $\mathbf{r}_i^\mathrm{g}$ be the vector connecting the incoming point to the outgoing point of the ith globule, and let $\mathbf{r}_j^\mathrm{c}$ be the end-to-end vector of the jth hydrated random subchain (see Figure 1). Since the end-to-end vector of the total chain is given by

$$\mathbf{R} = \sum_i \mathbf{r}_i^\mathrm{g} + \sum_j \mathbf{r}_j^\mathrm{c} \tag{3.1}$$

the partition function with a fixed $\mathbf{R}$ is written as

$$Z_n(T, \mathbf{R}) \equiv \sum_{\mathbf{i},\mathbf{j}} \omega(\mathbf{i}, \mathbf{j}) \prod_\zeta (\lambda_\zeta)^{i_\zeta} (\eta_\zeta)^{j_\zeta} \int \cdots \int \prod_i \rho_i^\mathrm{g}(\mathbf{r}_i^\mathrm{g})\, \mathrm{d}\mathbf{r}_i^\mathrm{g} \prod_j \rho_j^\mathrm{c}(\mathbf{r}_j^\mathrm{c})\, \mathrm{d}\mathbf{r}_j^\mathrm{c} \tag{3.2}$$

where $\rho(\mathbf{r})$ is the statistical distribution function of the end-to-end vector for each globule or random coil. In order to find the average end-to-end distance as a function of the tension $\mathbf{f}$ given at the chain end, we change the independent variable from $\mathbf{R}$ to $\mathbf{f}$ by carrying out the Laplace transformation

$$Q_n(T, \mathbf{f}) \equiv \int \mathrm{d}\mathbf{R}\, Z_n(T, \mathbf{R}) \mathrm{e}^{\beta \mathbf{f}\cdot\mathbf{R}} \tag{3.3}$$

with $\beta \equiv 1/k_\mathrm{B}T$. By introducing the Laplace transformation

$$g_\zeta(t) \equiv \int \rho_\zeta^\mathrm{g}(\mathbf{r}) \mathrm{e}^{\beta \mathbf{f}\cdot\mathbf{r}}\, \mathrm{d}\mathbf{r} \tag{3.4a}$$

$$h_\zeta(t) \equiv \int \rho_\zeta^\mathrm{c}(\mathbf{r}) \mathrm{e}^{\beta \mathbf{f}\cdot\mathbf{r}}\, \mathrm{d}\mathbf{r} \tag{3.4b}$$

for the distribution functions of the chain vectors, we can easily see that the partition function $Q_n(T,\mathbf{f})$ takes a form similar to Z_n as

$$Q_n(T, \mathbf{f}) = \sum_{\mathbf{i},\mathbf{j}} \omega(\mathbf{i}, \mathbf{j}) \prod_\zeta [\lambda_\zeta g_\zeta(t)]^{i_\zeta} [\eta_\zeta h_\zeta(t)]^{j_\zeta} \tag{3.5}$$

where

$$t \equiv fa/k_\mathrm{B}T \tag{3.6}$$

is the dimensionless reduced tension measured relative to the thermal energy, where a is the size of a repeat unit. The statistical weight is now renormalized by the effect of tension as

$$\lambda_\zeta \rightarrow \tilde{\lambda}_\zeta(t) \equiv \lambda_\zeta g_\zeta(t) \qquad \eta_\zeta \rightarrow \tilde{\eta}_\zeta(t) \equiv \eta_\zeta h_\zeta(t) \tag{3.7}$$

The mpd for the globules and hydrated swollen coils under tension now takes the form

$$i_\zeta / \sum i_\zeta = \mathrm{e}^{\alpha} \tilde{\lambda}_\zeta(t) z^\zeta \tag{3.8a}$$

$$j_\zeta / \sum j_\zeta = \mathrm{e}^{-\alpha} \tilde{\eta}_\zeta(t) z^\zeta \tag{3.8b}$$

where the parameter $z(t)$, now a function of the dimensionless tension t, can be found as the solution of the ZB equation

$$U_0(t, z)V_0(t, z) = 1 \tag{3.9}$$

under tension. Functions U and V are defined by

$$U_k(t, z) \equiv \sum_{\zeta=1}^{n} \zeta^k \tilde{\lambda}_\zeta(t) z^\zeta, \quad V_k(t, z) \equiv \sum_{\zeta=1}^{n} \zeta^k \tilde{\eta}_\zeta(t) z^\zeta \qquad (k = 0, 1, 2, ...) \tag{3.10}$$

Since the free energy as a function of the tension is given by

$$G_n(T, t) \equiv -k_\mathrm{B}T \ln Q_n(T, t) = nk_\mathrm{B}T \ln z(t) \tag{3.11}$$

we can find the mean end-to-end distance by taking the derivative

$$x \equiv R/na = -\mathrm{d}\ln z/\mathrm{d}t \qquad (3.12)$$

The free energy as a function of the end-to-end distance is found by the work done by the tension

$$F_n(R, T) = \int_0^{\mathbf{R}} \mathbf{f}\cdot\mathrm{d}\mathbf{R} = nk_BT\int_0^x t\,\mathrm{d}x = nk_BT[xt(x) + \ln z(t(x))] \qquad (3.13)$$

by partial integration, where the relation (3.12) is solved for t and written as $t(x)$.

The average number of globules (coils) is now given by

$$\nu(t) = [U_1(t, z)V_0(t, z) + U_0(t, z)V_1(t, z)]^{-1} \qquad (3.14)$$

The fraction of the hydrated part, or the number of bound water molecules, is given by

$$\theta(t) = h(t, z)V_1(t, z)/[1 + h(t, z)V_1(t, z)] \qquad (3.15)$$

where

$$h(t, z) \equiv U_0(t, z)^2/U_1(t, z) \qquad (3.16)$$

The number-average sequence length of the hydrated random coils is now given by

$$\bar{\zeta}_n^{(w)} \equiv \sum_\zeta \zeta j_\zeta / \sum_\zeta j_\zeta = V_1(t, z)/V_0(t, z) \qquad (3.17)$$

To find R, we take the derivative of ZB equation with respect to the tension t and find

$$\frac{\mathrm{d}\ln z}{\mathrm{d}t} = -\nu\left[\frac{\partial U_0(t, z)}{\partial t}V_0(t, z) + U_0(t, z)\frac{\partial V_0(t, z)}{\partial t}\right] \qquad (3.18)$$

and hence we have

$$\frac{R}{na} = \frac{\partial U_0(t, z)/\partial t}{U_1(t, z)}[1 - \theta(t)] + \frac{\partial V_0(t, z)/\partial t}{V_1(t, z)}\theta(t) \qquad (3.19)$$

The physical meaning of this equation is evident; it decomposes the total length into the globule part and the swollen coil part:

$$R(t) = R^{(g)}(t)[1 - \theta(t)] + R^{(w)}(t)\theta(t) \qquad (3.20)$$

where

$$R^{(g)}(t) \equiv na\frac{\partial U_0(t, z)/\partial t}{U_1(t, z)}, \quad R^{(w)}(t) \equiv na\frac{\partial V_0(t, z)/\partial t}{V_1(t, z)} \qquad (3.21)$$

The solution $z(t)$ of ZB equation (3.9) must be used for z.

We next calculate the average square end-to-end distance $\langle R^2\rangle_0$ *in the absence of external force*. To do this, we expand the partition function $Q_n(T, t)$ in powers of the dimensionless force t. Formal expansion gives

$$Q_n(T, t)/Q_n(T, 0) = 1 + (\langle R^2\rangle_0/6a^2)t^2 + ... \qquad (3.22)$$

so that we can find $\langle R^2\rangle_0$ from the coefficient of t^2.

Let us introduce the expansion

$$z = z_0 + z_1t^2 + ... \qquad (3.23)$$

of the parameter z. Substituting this into the relation (3.11) and expanding in powers of t^2, we find

$$\langle R^2\rangle_0/na^2 = 1 - 6z_1/z_0 \qquad (3.24)$$

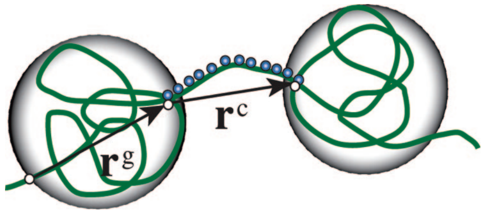

Figure 2. Local structure of a pearl-necklace chain with close-packed globules and swollen chains. The vectors $\mathbf{r}^g$ and $\mathbf{r}^c$ connecting the junction points are defined in the figure.

by comparing with (3.22). Here, z_0 is the solution of ZB equation under no force, which satisfies eq 2.11.

In order to find z_1, we expand

$$g_\zeta(t) = 1 + g_\zeta^{(1)}t^2 + ... \qquad (3.25a)$$

$$h_\zeta(t) = 1 + h_\zeta^{(1)}t^2 + ... \qquad (3.25b)$$

and substitute them into ZB equation. Then we compare the t^2 terms to find

$$\frac{z_1}{z_0} = -\frac{U^{(1)}(z_0)V_0(0, z_0) + V^{(1)}(z_0)U_0(0, z_0)}{U_1(0, z_0)V_0(0, z_0) + U_0(0, z_0)V_1(0, z_0)} \qquad (3.26)$$

and hence

$$\langle R^2\rangle_0/6na^2 = \frac{U^{(1)}(z_0)}{U_1(0, z_0)}(1 - \theta_0) + \frac{V^{(1)}(z_0)}{V_1(0, z_0)}\theta_0 \qquad (3.27)$$

where $\theta_0 \equiv \theta(0)$ is the helix content at $t = 0$, and

$$U^{(1)}(z_0) \equiv \sum_{\zeta=1}^{n} g_\zeta^{(1)}\lambda_\zeta z_0^\zeta, \quad V^{(1)}(z_0) \equiv \sum_{\zeta=1}^{n} h_\zeta^{(1)}\eta_\zeta z_0^\zeta \qquad (3.28)$$

This equation is written in a compact form as

$$\langle R^2\rangle_0 = \langle R^2\rangle_0^{(g)}(1 - \theta_0) + \langle R^2\rangle_0^{(w)}\theta_0 \qquad (3.29)$$

where

$$\langle R^2\rangle_0^{(g)} \equiv 6na^2\frac{U^{(1)}(z)}{U_1(0, z)}, \quad \langle R^2\rangle_0^{(w)} \equiv 6na^2\frac{V^{(1)}(z)}{V_1(0, z)} \qquad (3.30)$$

4. Temperature-Induced Dehydration and High-Temperature Collapse of a Free Chain

4.1. Model of the Globules. Let us introduce a simple model of the globules. A globule of size ζ (in terms of the number of repeat units) is assumed to take a spherical shape into which repeat units are close-packed (see Figure 2). The radius R is given by the condition $4\pi R^3/3 \simeq \zeta a^3$.

We then have $R \simeq \kappa a\zeta^{1/3}/2$, where $\kappa = 2(3/4\pi)^{1/3}$ is a numerical constant. We also assume that the incoming random coil goes out from the exactly opposite point of the sphere, so that the vector $\mathbf{r}^g$ has the absolute value $2R$ of the diameter. Hence, we have

$$2Rf/k_BT = \kappa\zeta^{\nu_G}t, \quad \nu_G = 1/3 \qquad (4.1)$$

The Laplace transform of the end-vector distribution for a globule then takes the form

$$g_\zeta(t) = \sinh(\kappa\zeta^{\nu_G}t)/\kappa\zeta^{\nu_G}t \equiv g(\kappa\zeta^{\nu_G}t) \qquad (4.2)$$

where

$$g(t) \equiv \sinh t/t \tag{4.3}$$

is the Laplace transform for the orientational distribution of one bond vector of the chain segment. We then find the coefficient

$$g_\zeta^{(1)} = \frac{\kappa^2}{6}\zeta^{2\nu_G} \tag{4.4}$$

by expansion of $g(t)$ in powers of t. Hence, we have

$$U_0(t, z) = \sum_{\zeta=1}^{n} g(\kappa\zeta^{\nu_G}t)\lambda_\zeta z^\zeta \tag{4.5a}$$

$$U_1(t, z) = \sum_{\zeta=1}^{n} \zeta g(\kappa\zeta^{\nu_G}t)\lambda_\zeta z^\zeta \tag{4.5b}$$

$$U^{(1)}(z_0) = \frac{\kappa^2}{6}\sum_{\zeta=1}^{n} \zeta^{2\nu_G}\lambda_\zeta z_0^\zeta \tag{4.5c}$$

with the close-packing exponent $\nu_G \equiv 1/3$. We assume the form (2.4) for the statistical weight λ_ζ.

4.2. Models of the Hydrated Segments. We next introduce a simple model for the swollen hydrated coils. The mean end-to-end distance of a chain segment with length ζ is given by

$$R = \kappa_w a\zeta^{\nu_F}, \quad \nu_F = 3/5 \tag{4.6}$$

according to Flory's law for a swollen chain with excluded-volume effect, where $\nu_F = 3/5$ is Flory's exponent, and κ_w is a numerical constant of order unity. The Laplace transform of the end-vector distribution $h_\zeta(t)$ for a hydrated coil may be derived from Pincus's picture of blobs for a chain with excluded-volume interaction under tension,[18] but here we retain the general form for a while under the condition that the coefficient of the lowest order in powers of t takes the form

$$h_\zeta^{(1)} = \frac{{\kappa_w}^2}{6}\zeta^{2\nu_F} \tag{4.7}$$

Hence, we have

$$V_0(t, z) = \sum_{\zeta=1}^{n} h_\zeta(t)\eta_\zeta z^\zeta \tag{4.8a}$$

$$V_1(t, z) = \sum_{\zeta=1}^{n} \zeta h_\zeta(t)\eta_\zeta z^\zeta \tag{4.8b}$$

$$V^{(1)}(z_0) = \frac{{\kappa_w}^2}{6}\sum_{\zeta=1}^{n} \zeta^{2\nu_F}\eta_\zeta z_0^\zeta \tag{4.8c}$$

The specific form of $h_\zeta(t)$ will be discussed when we study the finite tension. We assume ZB form (2.5) for the statistical weight η_ζ.

4.3. Coil−Globule Transition of a Free Chain. Let us calculate the degree of hydration θ_0 and the mean-square end-to-end distance $\langle R^2\rangle_0$ of a free chain as functions of the temperature and compare the result with the experimental data on PNIPAM in water. We first solve ZB equation (2.11) for specified parameters $\lambda(T)$, γ, σ, and $s(T)$ and obtain θ_0 by (2.15). The end-to-end distance can be calculated from the explicit formula

$$\langle R^2\rangle_0/na^2 = \kappa^2\overline{\zeta^{2\nu_G-1}}(1-\theta_0) + {\kappa_w}^2\overline{{\zeta_w}^{2\nu_F-1}}\theta_0 \tag{4.9}$$

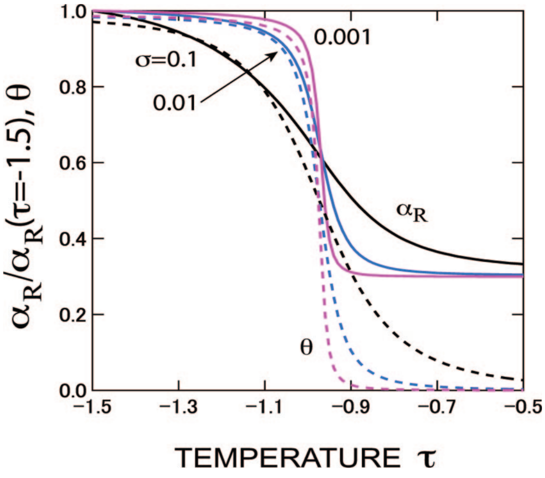

Figure 3. Theoretical calculation of the expansion factor α_R (solid lines) and the degree of hydration θ (broken lines) plotted against temperature for three different cooperativity parameters $\sigma = 10^{-1}$, 10^{-2}, and 10^{-3}. With increase in cooperativity, the coil−globule transition becomes sharper. Other parameters are fixed at $n = 100$, $\lambda_0 = 0.001$, $\gamma = 3.5$, and $\kappa_w/\kappa = 1.0$.

where

$$\overline{\zeta^{2\nu_G-1}} \equiv \sum_{\zeta=1}^{n} \zeta^{2\nu_G}\lambda_\zeta z_0^\zeta / \sum_{\zeta=1}^{n} \zeta\lambda_\zeta z_0^\zeta \tag{4.10a}$$

$$\overline{{\zeta_w}^{2\nu_F-1}} \equiv \sum_{\zeta=1}^{n} \zeta^{2\nu_F}\eta_\zeta z_0^\zeta / \sum_{\zeta=1}^{n} \zeta\eta_\zeta z_0^\zeta \tag{4.10b}$$

For the numerical calculation, we assume the form $s(T)/\lambda(T) = \lambda_0 \exp[\gamma(1-\tau)]$ for the association constant of H-bonding, where $\tau \equiv 1 - \Theta/T$ is the reduced temperature deviation from the theta temperature of the polymer solution, and $\gamma \equiv (\epsilon_H + \Delta\epsilon - \epsilon)/k_B\Theta$. ($\gamma$ here should not be confused with the surface tension.) The fraction θ and the expansion factor α_R defined below depend only upon the ratio $s(T)/\lambda(T)$. From a study of the LCST phase separation of aqueous PNIPAM solutions,[12] we know that $\Theta = 555$ K, $\lambda_0 = 0.001$, and $\gamma \simeq 3.5$ fit the experimental cloud points. In Figure 3, we consider $\tau = -1.5$ as the reference temperature where the polymer chain is fully hydrated and calculate the ratio $\alpha_R^2 \equiv \langle R^2\rangle_0/\langle R^2\rangle_0$ $(\tau = -1.5)$ (called expansion factor). Figure 3 shows how the coil−globule transition becomes sharper with cooperativity. The DP is fixed at $n = 100$, and the cooperativity parameter is varied from curve to curve. We can see clearly that the transition becomes sharper with σ. The broken lines show the fraction of hydrated parts. Sharp dehydration is evident for a small σ.

The coil−globule transition temperature τ_c can roughly be estimated from the condition $\lambda_\zeta \simeq \eta_\zeta$ for the balance between a globule and a coil consisting of the same number ζ of repeat units. This gives

$$\tau_c \simeq 1 + \frac{1}{\gamma}\left(\ln\lambda_0 + \frac{1}{\zeta}\ln\sigma\right) \tag{4.11}$$

Since the longest coil with $\zeta = n$ will be first dehydrated, we estimate the transition temperature by fixing $\zeta = n$ with other parameters being the same as in Figure 3 and find $\tau_c = -0.993$, which agrees very well with the numerical result shown in the figure.

Figure 4 shows a comparison of the theoretical curve with experimental data reported by Fujishige et al.[7] The solid line shows the expansion factor for the end-to-end distance normalized by the value at 20 °C. We have to assume a cooperativity

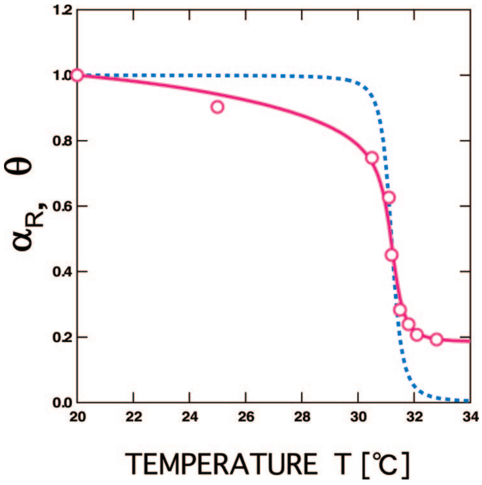

Figure 4. Comparison of the experimental data obtained by Fujishige et al. and theoretical curve. The expansion factor α_R (solid line) is defined by the ratio $\alpha_R^2 \equiv \langle R^2\rangle_0/\langle R^2\rangle_0$ (20 °C). The fraction θ of the hydrated coils (broken line) is also shown. The fitting parameters are $n = 7.0 \times 10^4$, $\lambda_0 = 0.001$, $\gamma = 3.788$, $\Theta = 555$, $\sigma = 2 \times 10^{-5}$, and $\kappa_w/\kappa = 0.31$.

as high as $\sigma = 10^{-5}$ in order to get a good fit of the sharp collapse observed in the experiments. The broken line shows the number of hydrated water molecules per repeat unit. A recent study of the phase transition of aqueous PNIPAM by dielectric measurements[26] indicates that the number of bound water molecules per repeat unit is as high as 10. This number is believed to include the water molecules participating in the hydrogen-bonded cage structure surrounding the hydrophobic isopropyl group in addition to the water molecules directly bound to a NIPAM amide group.

5. Tension-Induced Hydration

We study next the effect of tension on the coil−globule transition. When the chain is stretched by tension above a critical value, segments are reeled out from the globules and exposed to water. Hydration proceeds while the random coils grow, so that the collapse temperature is shifted to a higher value. The tension stays constant during the reeling-out process, and hence a plateau appears in the tension−elongation curve. Let us calculate the fraction $\theta(t)$ and the mean end-to-end distance $R(t)$ as functions of the tension for a given temperature.

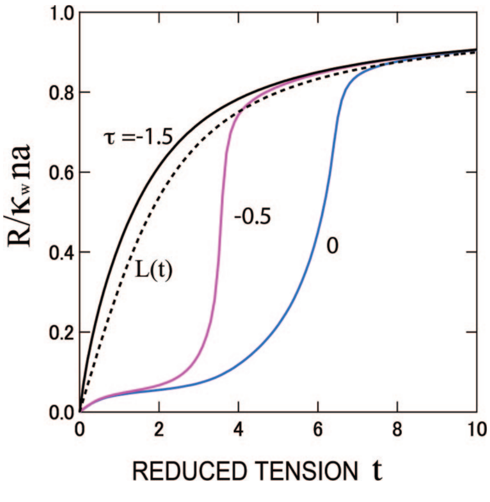

Figure 5. Mean end-to-end distance (solid lines) for three temperatures plotted against the reduced tension. The dotted line shows that of a reference Langevin chain. Parameters are fixed at $n = 100$, $\lambda_0 = 0.001$, $\gamma = 3.5$, $\sigma = 0.001$, and $\kappa_w/\kappa = 1.0$.

To find $R(t)$, we first specify the form of $h_\zeta(t)$. Considering that the excluded-volume effect becomes weaker as the chain is stretched, the end-to-end distance approaches that of a Langevin chain when the hydrated chain is fully stretched. Therefore, we can assume $h_\zeta(t) \simeq g(t)^\zeta$ in this asymptotic regime. Since the excluded-volume effect is important for the weak tension and for the transition region where segments are reeled out from the globules, we assume the form

$$h_\zeta(t) = g(\kappa_w \zeta^{(\nu_F - 1/2)/(1+t)} t)^\zeta \tag{5.1}$$

which bridges between the swollen chain at low tension and the random-flight chain at high tension. This is close to Pincus's blob picture, but we assume a constant number of blobs, each of which has the radius of a swollen repeat unit.

The end-to-end distance under tension can then be written as

$$R(t)/na = \kappa D^{(g)}(t)[1 - \theta(t)] + \kappa_w D^{(w)}(t)\theta(t) \tag{5.2}$$

where

$$D^{(g)}(t) \equiv \sum_{\zeta=1}^{n} \zeta^{\nu_G} g(\kappa\zeta^{\nu_G} t) L(\kappa\zeta^{\nu_G} t)\lambda_\zeta z^\zeta / \sum_{\zeta=1}^{n} \zeta g(\kappa\zeta^{\nu_G} t)\lambda_\zeta z^\zeta \tag{5.3a}$$

$$D^{(w)}(t) \equiv \sum_{\zeta=1}^{n} h'_\zeta(t)\eta_\zeta z^\zeta / \sum_{\zeta=1}^{n} \zeta h_\zeta(t)\eta_\zeta z^\zeta \tag{5.3b}$$

The function $L(t)$ is Langevin's function

$$L(t) \equiv \mathrm{d}\ln g(t)/\mathrm{d}t = \coth t - 1/t \tag{5.4}$$

and $h'_\zeta(t)$ is the derivative of the function (5.1) with respect to t.

Figure 5 shows the end-to-end distance $R(t)$ for three temperatures as a function of the reduced tension t. At low tension, $R(t)$ starts in the form of a Langevin chain of total length $na\theta_0$. When the tension reaches a critical value t_c, the globular parts on the chain are disentangled in a narrow region, so that $R(t)$ sharply increases to the value of the reference Langevin chain (dotted line) with a total length na. There appears a flat plateau region in the tension if we plot the tension as a function of the distance. For the lowest temperature $\tau = -1.5$ where the chain is fully hydrated and swollen, we can see an upward deviation from the reference Langevin chain due to the excluded-volume effect.

In Figure 6, the end-to-end distance $R(t)$ and the coverage θ of bound water molecules are plotted against the tension. It is evident that a sharp hydration takes place when globules are disentangled.

Let us next consider the critical tension t_c at which chain segments start to be reeled out from the globules. For the balance between a globule of the size ζ and a hydrated coil of the same size, the condition

$$g(\kappa\zeta^{\nu_G} t_c) \simeq g(\kappa_w \zeta^{(\nu_F - 1/2)/(1+t_c)} t_c)^\zeta \eta_\zeta \tag{5.5}$$

must be fulfilled. If we use the temperature deviation $\Delta\tau \equiv \tau - \tau_c$ from the transition temperature given in (4.11) instead of τ itself, this condition can be transformed into

$$\zeta \ln g(\kappa_w \zeta^{(\nu_F - 1/2)/(1+t_c)} t_c) - \zeta\gamma\Delta\tau \simeq \ln g(\kappa\zeta^{\nu_G} t_c) \tag{5.6}$$

For a small tension, we thus have

$$(\kappa_w{}^2\zeta^{2\nu_F} - \kappa^2\zeta^{2\nu_G})t_c{}^2/6 - \zeta\gamma\Delta\tau \simeq 0$$

Hence we have a scaling law

$$t_c{}^2 \simeq 6\zeta\gamma\Delta\tau/(\kappa_w{}^2\zeta^{2\nu_F} - \kappa^2\zeta^{2\nu_G}) \simeq \Delta\tau \tag{5.8}$$

It becomes smaller as the transition temperature is approached. Figure 7 shows detailed calculation of t_c from the tension−elongation profile (symbols) and a rough estimate by eq 5.8 (solid line) plotted against the temperature deviation. The agreement is good. Hence, we can expect that chain segments are easily reeled out from the globules by a small tension near the transition temperature.

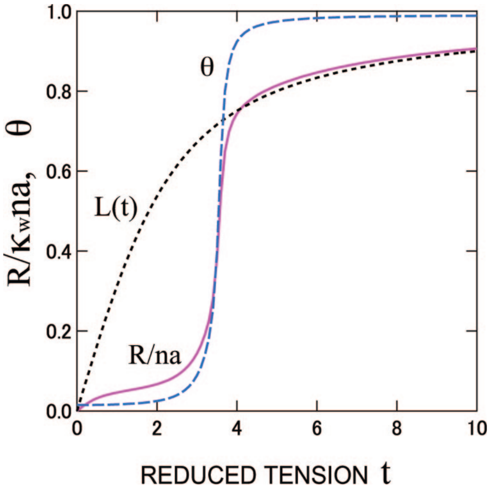

Figure 6. Mean end-to-end distance (solid line) and degree of hydration (broken line) at temperature $\tau = -0.5$ plotted against the reduced tension. The dotted line shows the mean end-to-end distance of a reference Langevin chain. Parameters are fixed at $n = 100$, $\lambda_0 = 0.001$, $\gamma = 3.5$, $\sigma = 0.001$, and $\kappa_w/\kappa = 1.0$.

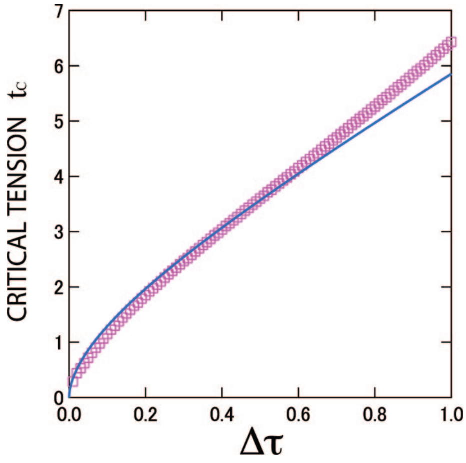

Figure 7. Critical tension t_c for reeling out a chain segment from a globule plotted against deviation of the temperature from the transition temperature. Symbols show the critical tension evaluated at the position where the slope dR/dt is the largest. The solid line shows a rough estimate by using eq 5.8. It is calculated for the largest globule $\zeta \simeq n = 100$.

6. Collapse Transition in Mixed Solvents

The PNIPAM chain exhibits peculiar conformational changes in water upon addition of a second water-miscible solvent, such as methanol, tetrahydrofuran, or dioxane. Although the second solvent is a good solvent for the polymer, the chain sharply collapses at the molar fraction $x_m \simeq 0.2$ of methanol, stays collapsed up to $x_m \simeq 0.4$, and finally recovers the swollen state at $x_m \simeq 0.6$ under majority of the second solvent.[19] The tendency for phase separation is also strongly enhanced by the presence of the second solvent. For instance, the LCST of aqueous PNIPAM solutions shifts to lower temperature when methanol is added.[20−22] The temperature drop is the largest, from 31.5 °C down to −7 °C, for a specific molar fraction of methanol $x_m = 0.35$. This enhanced phase separation in mixed good solvents is known as *cononsolvency*.[20] Cross-linked PNIPAM gels are also known to collapse sharply in water in the presence of methanol around $x_m = 0.3$ and gradually recover their swollen state with increasing methanol content.[23,24] There have been efforts to understand the phenomenon of cononsolvency by combination of three χ parameters[20] and also by invoking the formation of stoichiometric compounds between the solvent molecules.[19] Without considering direct H-bonds between polymer and solvents, however, it is difficult to explain the sharp LCST behavior. In what follows, we clarify the molecular mechanism of cononsolvency on the basis of competitive p−w and p−m H-bonds. The main result (Figure 12) was reported earlier in a short communication,[14] but here we describe the details of the analysis, focusing on the effect of the molecular volume of the second solvent and the strength of its H-bond, with the ultimate scope of applying the same idea to many other polymers and second solvents. These include PEO, polyvinylpyrrolidone (PVP), etc., in mixed systems of water and second solvents, such as ethanol, dioxane, acetone, or tetrahydrofuran.

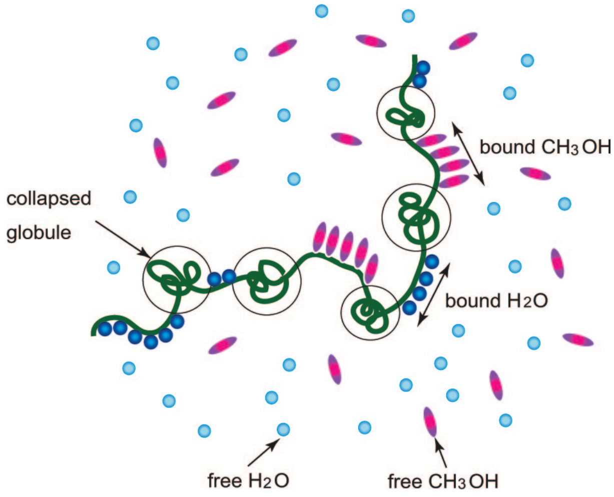

Figure 8. Competition between PNIPAM−water and PNIPAM−methanol hydrogen bonding. When there is strong cooperativity, continuous sequences of each species are exclusively formed along the chain. As a result, the chain takes a pearl-necklace conformation. (Reproduced with permission from ref 14. Copyright 2008 American Physical Society).

Considering that methanol molecules are also H-bonded onto the chain, we expect that there is a competition in forming p−w and p−m H-bonds. The statistical weight of a sequence for each is given by

$$\eta_\zeta^{(\alpha)} = \sigma_\alpha s_\alpha(T)^\zeta, \quad \alpha = \mathrm{w}, \mathrm{m} \tag{6.1}$$

In order to take into consideration the difference in molecular size of the solvents, let p be the volume of a methanol molecule relative to that of water molecule. It has a numerical value of 2−3.

Now, the number of different ways to choose such sequences from the finite total number n is given by

$$\omega(\mathbf{i},\mathbf{j}) = \frac{\left(\sum i_\zeta\right)!\left(\sum j_\zeta^{(\mathrm{w})}\right)!\left(\sum j_\zeta^{(\mathrm{m})}\right)!}{\prod_\zeta (i_\zeta! j_\zeta^{(\mathrm{w})}! j_\zeta^{(\mathrm{m})}!)} \tag{6.2}$$

We assume that the chain segments covered by bound water and bound methanol are swollen because both solvents are good, and the remaining free segments are collapsed by hydrophobic aggregation. By using this combinatorial factor in sequence selection process, we find that the canonical partition function of a chain is given by

$$Q_n(n^{(\mathrm{w})}, n^{(\mathrm{m})}, t) = \sum_{\mathbf{j}} \omega(\mathbf{i},\mathbf{j}) \prod_\zeta [\tilde{\lambda}_\zeta(t)]^{i_\zeta} [\tilde{\eta}_\zeta^{(\mathrm{w})}(t)]^{j_\zeta^{(\mathrm{w})}} [\tilde{\eta}_\zeta^{(\mathrm{m})}(t)]^{j_\zeta^{(\mathrm{m})}} \tag{6.3}$$

where $\tilde{\eta}_\zeta^{(\alpha)}(t)$ is the statistical weight of length ζ for a solvent α under the tension, and $\eta^{(\alpha)} \equiv \sum_{\zeta\geq 1}\zeta j_\zeta^{(\alpha)}$ is the total number of adsorbed molecules of the solvent α. Since the solution is a particle reservoir, we introduce the activity a_α of each type of solvent as independent variables (functions of the solvent composition) and move to the grand partition function

$$\Xi_n(\{a\}, t) \equiv \sum_{n^{(\mathrm{w})}, n^{(\mathrm{m})}=0}^{n} a_\mathrm{w}^{n^{(\mathrm{w})}} a_\mathrm{m}^{n^{(\mathrm{m})}} Q_n(n^{(\mathrm{w})}, n^{(\mathrm{m})}, t) \tag{6.4}$$

The mpd of sequences that maximizes this grand partition function (equivalent to minimizing the free energy) under the conditions

$$\sum_\zeta i_\zeta = \sum_\zeta (j_\zeta^{(\mathrm{w})} + j_\zeta^{(\mathrm{m})}) \tag{6.5}$$

and

$$\sum_\zeta \zeta(i_\zeta + j_\zeta^{(\mathrm{w})} + p j_\zeta^{(\mathrm{m})}) = n \tag{6.6}$$

are now given by

$$j_\zeta^{(\mathrm{w})}/n = (1-\theta)\eta_\zeta^{(\mathrm{w})} z (a_\mathrm{w} z)^\zeta \tag{6.7a}$$

$$j_\zeta^{(\mathrm{m})}/n = (1-\theta)\eta_\zeta^{(\mathrm{m})} z (a_\mathrm{m} z^p)^\zeta \tag{6.7b}$$

Here

$$\theta = \theta^{(\mathrm{w})} + p\theta^{(\mathrm{m})} \tag{6.8}$$

is the total coverage with $\theta^{(\alpha)} \equiv \sum_{\zeta\geq 1}\zeta j\zeta\,(\alpha)/n$ being the coverage by each solvent. Similarly

$$\nu = \nu^{(\mathrm{w})} + \nu^{(\mathrm{m})} \tag{6.9}$$

is the total number of sequences with $\nu^{(\alpha)} \equiv \sum_{\zeta\geq 1} j_\zeta^{(\alpha)}/n$ being the number of sequences of each solvent. The parameter z is defined by $z \equiv 1 - \nu/(1-\theta)$ and has the physical meaning of the probability such that an arbitralily chosen monomer belongs to the globular part. The grand partition function is given by $\Xi_n(\{a\},t) = z(t)^{-n}$.

Following the same procedure as before, we find

$$U_0(t,z)\{V_0^{(\mathrm{w})}(t, a_\mathrm{w} z) + V_0^{(\mathrm{m})}(t, a_\mathrm{m} z^p)\} = 1 \tag{6.10}$$

for the mixed solvents. This is basically the same as ZB equation in the preceding section, but here it is properly extended to describe competition in p−w and p−m H-bonding. The functions V_k are defined by

$$V_k^{(\alpha)}(t,x) \equiv \sum_{\zeta=1}^{n^*} \zeta^k \tilde{\eta}_\zeta^{(\alpha)}(t) x^\zeta \tag{6.11}$$

The upper limit of the sum is $n^* = n$ for water and $n^* = [n/p]$ for methanol, where $[k]$ means the maximum integer smaller than, or equal to k. By using the solution for z, we find that the total coverage θ is given by

$$\theta = \frac{h(t,z)[V_1^{(\mathrm{w})}(t, a_\mathrm{w} z) + pV_1^{(\mathrm{m})}(t, a_\mathrm{m} z^p)]}{1 + h(t,z)[V_1^{(\mathrm{w})}(t, a_\mathrm{w} z) + pV_1^{(\mathrm{m})}(t, a_\mathrm{m} z^p)]} \tag{6.12}$$

where

$$h(t,z) \equiv U_0(t,z)^2/U_1(t,z) \tag{6.13}$$

The end-to-end distance as a function of the tension is given in a similar way as before by

$$R(t) = \kappa D^{(\mathrm{g})}(t)[1 - \theta^{(\mathrm{w})}(t) - \theta^{(\mathrm{m})}(t)] + \kappa_\mathrm{w} D^{(\mathrm{w})}(t)\theta^{(\mathrm{w})}(t) + \kappa_\mathrm{m} D^{(\mathrm{m})}(t)\theta^{(\mathrm{m})}(t) \tag{6.14}$$

where $D^{(\mathrm{m})}$ is defined by an equation similar to that for pure water.

The mean-square average end-to-end distance of a free chain can be calculated by the equation[14,27]

$$\langle R^2\rangle_0/na^2 = \kappa^2\overline{\zeta^{2\nu_\mathrm{G}-1}}(1 - \theta_0^{(\mathrm{w})} - \theta_0^{(\mathrm{m})}) + \kappa_\mathrm{w}{}^2\overline{\zeta_\mathrm{w}^{2\nu_\mathrm{F}-1}}\theta_0^{(\mathrm{w})} + \kappa_\mathrm{m}{}^2\overline{\zeta_\mathrm{m}^{2\nu_\mathrm{F}-1}}\theta_0^{(\mathrm{m})} \tag{6.15}$$

If we employ the ZB form for the statistical weight η_ζ, the arguments of the V functions become the combined variable $a_\mathrm{w}s_\mathrm{w}t$ for water and $a_\mathrm{m}s_\mathrm{m}t^p$ for methanol. We assume that the solvent−solvent interaction is weak, compared to the solvent−polymer interaction, and neglect it. The mixed solvent is regarded as an ideal mixture.[28] Then the activity is proportional to the mole fraction of each component. We can write $a_\mathrm{w}s_\mathrm{w} = a_\mathrm{w}^\circ(T)(1 - x_\mathrm{m})$ and $a_\mathrm{m}s_\mathrm{m} = a_\mathrm{m}^\circ(T)x_\mathrm{m}$, where a°'s are functions of the temperature only.

Figure 9 shows the expansion factor for the end-to-end distance $\alpha_\mathrm{R}{}^2 \equiv \langle R^2\rangle_0/\langle R^2\rangle_0$ ($x_\mathrm{m} = 0$) (solid lines) and the total coverage θ_0 (broken lines) plotted against the molar fraction x_m of methanol. Here, $\langle R^2\rangle_0$ ($x_\mathrm{m} = 0$) is the value in pure water. The calculation was done by assuming that all parameters are symmetric and with $p = 1$. The cooperativity parameter σ varies from curve to curve. We can clearly see that the coverage takes a minimum value at $x_\mathrm{m} = 0.5$ (stoichiometric concentration) as a result of the competition, so that the end-to-end distance also takes minimum at $x_\mathrm{m} = 0.5$. As cooperativity becomes stronger, the depression of the end-to-end distance becomes narrower and deeper. In a real mixture, the association constant and cooperativity parameter are different for water and methanol, so that we expect an asymmetric behavior with respect to the molar fraction.

We first examine the effect of the ratio p of the solvent molecular volumes. With increasing p, while keeping the other parameters fixed, the composition at minimum expansion factor in Figure 9 slightly shifts toward the methanol axis, and recovery of the expansion factor become less complete (see Figure 10). This effect is caused by the occurrence of wasted H-bonding sites; the longer the adsorbed molecule, the more vacant gaps remain between the sequences. This effect is named *car parking effect*.[29,30] Longer cars waste more space along the curb when they are randomly parked on the road.

We next examine the effect of the association constant a_m° for the H-bond between polymer and the second solvent. For

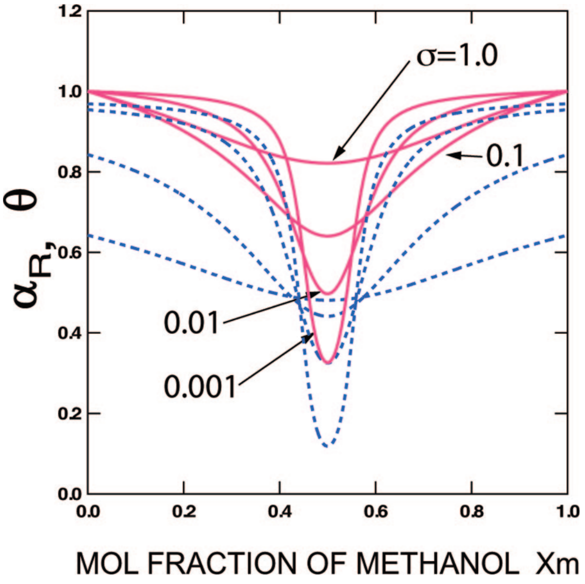

Figure 9. Normalized end-to-end distance (solid lines) and the fraction of bound water (broken lines) and of bound methanol (dotted lines) are plotted against the mole fraction of methanol. The DP of the polymer chain is fixed at $n = 100$ for a test calculation. The volume ratio of the solvents is fixed at $p = 1$. The cooperativity parameter $\sigma_w = \sigma_m$ is varied from curve to curve. The association constants are fixed at $a_w^\circ = a_m^\circ = 1.8$. The monomer expansion factors are fixed at $\kappa_w/\kappa = \kappa_m/\kappa = 2.0$.

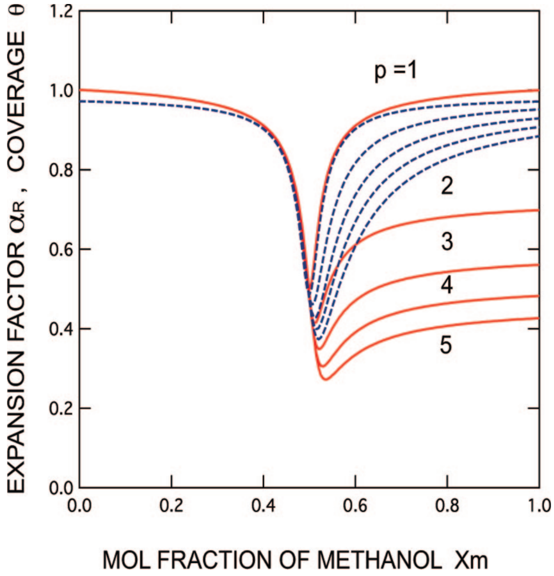

Figure 10. Expansion factor (solid lines) and the fraction of the total bound molecules (water and methanol) (broken lines) are plotted against the mole fraction of methanol. The volume ratio p is changed from 1 to 5. The position of the minimum in the expansion factor is shifted to higher mol fraction with the volume ratio. The recovery to the swollen conformation is less complete for larger volume fraction. Other parameters are fixed at $n = 100$, $\sigma = 10^{-3}$, $a_w^\circ = a_m^\circ = 2.0$, and $\kappa_w/\kappa = \kappa_m/\kappa = 1.5$.

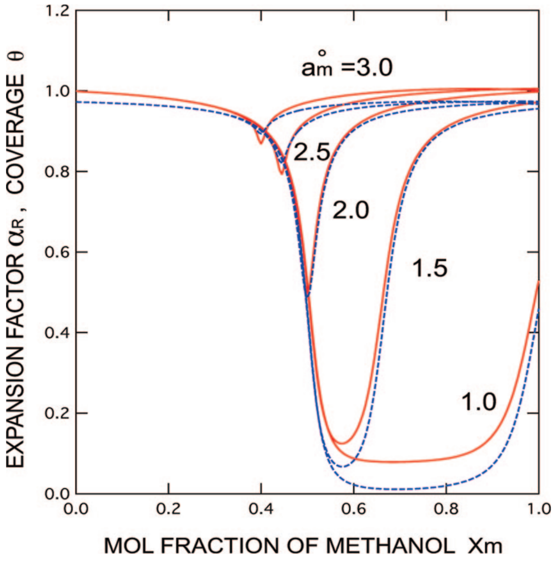

Figure 11. Expansion factor (solid lines) and the fraction of the total bound molecules (broken lines) are plotted against the mole fraction of methanol. The strength of association a_m° is changed from 1.0 to 3.0, while a_w° is fixed at 2.0. The position of the minimum in the expansion factor is shifted to higher mole fraction, and the bottom of the minimum becomes flatter with the association constant of methanol. Other parameters are fixed at $n = 100$, $\sigma = 10^{-3}$, $p = 1$, and $\kappa_w/\kappa = \kappa_m/\kappa = 1.5$.

the curve of the cooperativity $\sigma = 0.001$ in Figure 9, we consider now the region $a_m^\circ = 1.0-3.0$ with the other parameters being fixed at the same value as shown in Figure 11. With decreasing a_m°, the composition at the minimum shifts from 0.4 to 0.7, and the minimum becomes deeper with a flatter bottom. Below $a_m^\circ = 1.5$, in particular, the curves show a sharp collapse with very flat bottoms. The flat bottom seen in α_R and θ indicates that the H-bonding is highly competitive.

Figure 12 shows a comparison between the experimental mean radii of gyration (circles) obtained by laser light scattering measurements[19] and mean end-to-end distances obtained by theoretical calculations (solid line). Both are normalized by the reference value in pure water. The data obtained by light scattering measurements give the expansion factor α_S for the radius of gyration, while the theoretical curve shows α_R for the end-to-end distance. These two need not be identical but are proportional to each other. Because the calculation of the radius of gyration of the pearl-necklace conformation is not easy, we made such a comparison. The total coverage θ, including bound water and bound methanol, is also plotted (broken line). The molecular weight of the polymer used in the experiment is $M_w = 2.63 \times 10^7$ g mol^{-1}, and hence we fixed $n = 10^5$. The volume ratio is set to be $p = 2$ from the molecular structure of methanol. For larger p, it turned out that the recovery of the expansion factor at high methanol composition was not sufficient. In order to have a sharp collapse at around $x_m \simeq 0.17$, we had to fix the cooperativity as high as $\sigma_w = 10^{-4}$. Similarly, to produce the sharp recovery at around $x_m \simeq 0.4$, we used $\sigma_m = 10^{-3}$.

7. Conclusions and Discussion

We have studied the high-temperature collapse and the temperature sensitivity of a PNIPAM chain on the basis of the concepts of cooperative hydration and dehydration. Without assuming a negative temperature coefficient in Flory's interaction parameter, we succeeded in deriving the inverted coil−globule transition, and we compared the detailed results of the derivations with experimental observations. Such a new view of the interaction parameter, which is renormalized by a specific interaction such as hydrogen bonding, can directly be applied to the LCST phase separation[12] of aqueous PNIPAM solutions and also to the volume phase transition of cross-linked gels, which will be reported in our forthcoming paper. The tension−elongation curve of the hydrated chains was theoretically derived on the basis of the conventional statistical mechanical method of polymer chains. We found that, above a critical value, a tension reels out chain segments from the collapsed globules, so that one observes a flat plateau in the curve revealing the reeling-out process. Such a tension−hydration coupling may lead to significant changes in the phase separation

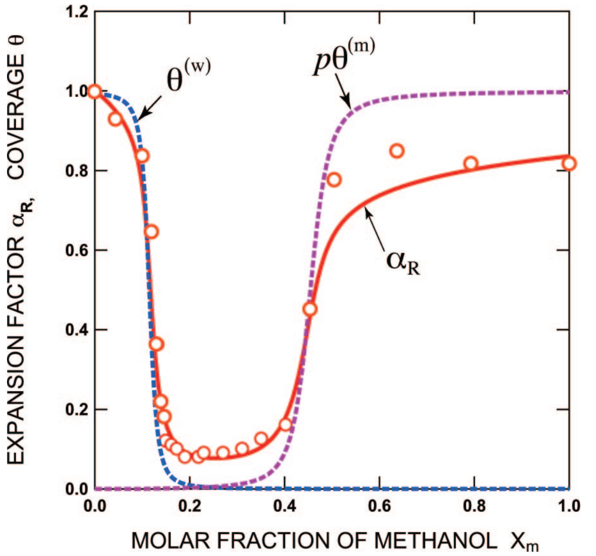

Figure 12. Comparison between the present calculation (line) of the expansion factor for the mean-square end-to-end distance for $n = 10^5$ and $p = 2$ and the experimental data of the radius of gyration by Zhang and Wu (circles).[19] The coverage by water and by methanol are also plotted (broken lines). The fitting parameters are $a_w^\circ = 1.13$, $a_m^\circ = 2.20$, $\kappa_w/\kappa = 1.15$, and $\kappa_m/\kappa = 1.06$.

of aqueous PNIPAM solutions under shear flow. An upward shift of the LCST to higher temperature is expected to be induced by shear (shear-induced mixing) if the shear stress reels out chain segments from the globules. This effect may be confirmed experimentally.

The competitive hydrogen bonding was also applied successfully to describe theoretically the molecular origin of cononsolvency in a mixed solvent of water and methanol. If there is a strong competition in forming p−w and p−m hydrogen bonds, and if both types of hydrogen bonds are cooperative, our derivation indicates that the total number of bound molecules shows a sharp minimum for a composition for which the competition is the strongest. As a result, the polymer chain undergoes a very interesting reentrant coil−globule−coil transition. Further applications of the idea of competitive hydration to solutions and gels are straightfoward. For instance, we can derive the shift to low temperatures of the LCST lines (enhanced phase separation) of PNIPAM solutions in a mixed solvent of water and methanol and of other second solvents. The details of such results will be reported in our forthcoming papers.

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References and Notes

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