Theory of solvation-induced reentrant coil–globule transition of an isolated polymer chain

Akihiko Matsuyama
Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
Fumihiko Tanaka
Department of Physics, Faculty of General Education, Tokyo University of Agriculture and Technology, Fuchu-shi, Tokyo 183, Japan

(Received 21 September 1990; accepted 12 October 1990)

This paper discusses the conformational phase change of an isolated polymer chain which is capable of forming physical bonds with solvent molecules. On the basis of the mean-field theory of Flory type, we derive a formula for the temperature dependence of the expansion factor of the chain. Our theory takes account of the extra mixing entropy change induced by the solvation. We predict that the physical-bond formation between polymer and solvent molecules causes a reentrant conformational change between coiled and globular state when temperature is varied. We also show that the polymer chain exhibits a sharp collapse near the Θ temperature as the temperature is increased to the lower critical solution temperature of the polymer solution. This behavior can be interpreted in terms of the breakup of the polymer–solvents complex. The result is compared with the observed coil–globule transition on poly (*N*-isopropylacrylalmide) in water.

I. INTRODUCTION

The conformation of an isolated polymer chain in a dilute solution depends on the temperature and the solvent conditions. In a good solvent region, a polymer is in a coiled state, while in a poor solvent region a polymer has a globular configuration. Many theoretical studies[1–5] have been concerned with the conformational change of a polymer chain in terms of the self-excluded volume interaction. The mean-field theory of Flory type has shown that the transition from an extended coil to a compact globule takes place near the Θ temperature as temperature is decreased to the upper critical solution temperature (UCST). The mechanism of the transition is similar to that of the gas–liquid transition. Such a coil–globule transition has been observed on polystyrene (PS) in cyclohexane.[6,7]

In contrast to the volume interaction, there is an important case, where a specific interaction such as hydrogen bonding plays an important role in the conformation of a polymer chain. Typical examples are a globular protein formed by intramolecular bridging[8,9] and a nonionic polymer in water.[10–19]

For poly (*N*-isopropylacrylamide) (PNIPAM) in water it has been reported that the radius of gyration of the chain sharply decreases near the Θ temperature as temperature is increased to the lower critical solution temperature (LCST).[18,19] The negative temperature dependence has also been observed on the intrinsic viscosity.[10,17] Such behavior is in contrast to the usual coil–globule transition where a chain gets swollen at high temperature.

In aqueous polymer solutions, it is obvious that the solubility of the polymer chain is enhanced due to the hydrogen-bond formation between polymer and water molecules.[13–16] The theoretical understanding of these systems, therefore, must incorporate the concept of hydrogen-bond formation between unlike molecular species.

Many theoretical studies have focused on the LCST behavior in polymer blends,[20] polymer solutions,[21,22] and mixtures of low molecular weight molecules,[23] where the hydrogen bonds between unlike molecular species play an important role for the solubility. Recently, we have presented a molecular theory for the LCST behavior in polymer solutions where solvation prevails.[22] The theory showed that the physical-bond formation, such as a hydrogen bond, between polymer and solvent molecules can be the major cause of the miscibility gaps showing closed-loop or hourglass shape.

In this paper we theoretically study the conformational change of a single-polymer chain capable of forming a physical bond with solvent molecules. On the basis of the Flory–Huggins lattice theory we incorporate the idea of hydrogen bonding. We calculate the expansion factor of the polymer chain and predict that the physical-bond formation between polymer and solvent molecules causes a reentrant conformational change when temperature is varied. We also examine a possible mechanism for the negative temperature dependence of the radius of gyration of the polymer chain. The result is compared with the experimental data on poly (*N*-isopropylacrylalmide) in water.[18]

II. FREE ENERGY OF A POLYMER–SOLVENTS COMPLEX

We consider a single-polymer chain in a solvent. The polymer chain is assumed to carry f identical functional groups which do not interact each other but are capable of forming physical bonds with the solvent molecules by reversible pairwise association. The bonding energy considered here is on the order of thermal energy, so that the bonding–unbonding equilibrium is easily attained by thermal activation. In thermal equilibrium, the polymer chain is associated with a certain number of solvent molecules. Hereafter, we

Downloaded 30 Nov 2007 to 130.54.110.22. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp

call it the "polymer–solvents complex."

Let R be the average radius of the occupied region, n the number of segments on the chain, and m the number of solvents bonded on the functional groups. Figure 1 shows an equilibrium state of the chain in the solvent. The symbols ●, ○, and — show the bonded solvents, the unbonded free solvents, and functional groups on the chain, respectively. Our theory is based on the lattice theory presently by Flory–Huggings.[24] We introduce the volume a^3 of an unit lattice. The volume a^3 of a segment on the chain is assumed for simplicity to be the same for a solvent molecule. The number N_t of the total lattice cells in the sphere of radius R is given $N_t = V/a^3$, where $V = (4/3)\pi R^3$ shows the total volume of the sphere. The volume fraction ϕ of the chain in the sphere is given by $\phi = a^3 n/V$. Volume fraction of the bonded solvents and the unbonded free solvents are then expressed as

$$\phi_b = Px\phi,$$
$$\phi_0 = 1 - (1 + Px)\phi, \tag{2.1}$$

respectively, where we have defined $P \equiv f/n$ and $x \equiv m/f$. The value x $(0 \leqslant x \leqslant 1)$ equals the number fraction of solvent molecules bonded on the functional groups. Let $\alpha \equiv R/R_0$ be the expansion factor of the chain, where $R_0 = a\sqrt{n}$ is the radius of gyration under the ideal state of the chain. The volume fraction of the chain in the sphere is then given by

$$\phi = 1/\alpha^3\sqrt{n}. \tag{2.2}$$

We next consider the free-energy difference ΔF from the reference state, where pure solvent molecules and a pure single-polymer chain are prepared separately. The free energy can be constructed by three terms:

$$\Delta F = F_{\rm el} + F_{\rm rea} + \Delta F_{\rm mix}, \tag{2.3}$$

where $F_{\rm el}$ shows the free energy of the elastic restoring force due to deformation of the segment distribution from the ideal state. This free energy is given by [24,25]

$$\beta F_{\rm el} = 3[\tfrac{1}{2}(\alpha^2 - 1) - \ln\alpha], \tag{2.4}$$

where $\beta \equiv 1/k_{\rm B}T$; T is absolute temperature and $k_{\rm B}$ is the Boltzmann constant. The second term $F_{\rm rea}$ in Eq. (2.3) shows the free-energy change needed to form of a polymer–solvents complex. In our model system, $F_{\rm rea}$ is given by

$$\beta F_{\rm rea} = m\beta\delta f_0 - \ln\left[\frac{f!}{m!(f-m)!}\right], \tag{2.5}$$

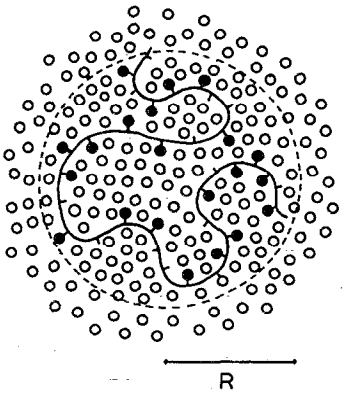

FIG. 1. Schematic drawing of a polymer–solvents complex confined in a spherical region of radius R. The symbols ●, ○ and — show bonded solvents, unbonded free solvents, and functional groups on the chain, respectively.

where δf_0 is the local free-energy change of a single-bond formation, and the second term in Eq. (2.5) is the combinatorial entropy related to the number of ways to select m sites out of f functional groups on the chain. By using Stirling's approximation, Eq. (2.5) can be expressed as

$$\beta F_{\rm rea} = nP[\beta\delta f_0 x + x\ln x + (1-x)\ln(1-x)]. \tag{2.6}$$

The third term $\Delta F_{\rm mix}$ in Eq. (2.3) describes the free-energy change required in the process of mixing the constructed polymer–solvents complex with the unbonded free-solvent molecules. According to the lattice theory of Flory–Huggins, the free energy $\Delta F_{\rm mix}$ is given by

$$\beta\Delta F_{\rm mix} = N_t[\phi_0\ln\phi_0 + \chi\phi(1-\phi)], \tag{2.7}$$

where the translational entropy of the polymer–solvents complex can be neglected.[24] The parameter χ shows the contact interaction energy related to the dispersion force and then takes a positive value.[26] The negative interaction energy between a solvent and a functional group is given through δf_0 in Eq. (2.6).

Using Eqs. (2.4), (2.6), and (2.7), the free energy ΔF of our system is expressed as

$$\begin{aligned}\beta\Delta F(\alpha,x) = {} & 3[\tfrac{1}{2}(\alpha^2-1) - \ln\alpha] \\ & + nP[\beta\delta f_0 x + x\ln x + (1-x)\ln(1-x)] \\ & + n\{(1/\phi)[1-(1+Px)\phi] \\ & \times\ln[1-(1+Px)\phi] + \chi(1-\phi)\},\end{aligned} \tag{2.8}$$

where ϕ is uniquely related to α through relation (2.2). When $P = 0$ this equation reduces to the one studied by many authors.[1–5] Next, we decide on the values of α and x in thermal equilibrium.

III. MINIMIZATION OF THE FREE ENERGY

For the chain to be in thermal equilibrium, we need to minimize the free energy (2.8) with respect of α (or equivalently ϕ) and x:

$$(\partial\Delta F/\partial\alpha)_{x,T} = 0, \tag{3.1}$$
$$(\partial\Delta F/\partial x)_{\alpha,T} = 0. \tag{3.2}$$

The physical meanings of the above equations are obvious. Equation (3.1) keeps the balance among solvent molecules existing inside and outside of the sphere:

$$\Delta\mu_0 = \mu_0 - \mu_0^\circ = 0, \tag{3.3}$$

where μ_0 and μ_0° are the chemical potential of an unbonded free solvent in the sphere and of a solvent existing outside of the sphere, respectively. Equation (3.2) is also equivalent to the adsorption equilibrium condition:

$$\mu_0 = \mu_b, \tag{3.4}$$

where μ_b is the chemical potential of a solvent molecule bonded on the functional groups.

From Eq. (3.1) we obtain

$$\begin{aligned}\beta\Delta\mu_0 = {} & \frac{1}{n}(\alpha^2-1)\phi + \ln[1-(1+Px)\phi] \\ & + (1+Px)\phi + \chi\phi^2 = 0.\end{aligned} \tag{3.5}$$

Similarly, from Eq. (3.2) we obtain

Downloaded 30 Nov 2007 to 130.54.110.22. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp

$$Px = \frac{\lambda + 1 - (1-P)\lambda\phi - \sqrt{D}}{2\lambda\phi}, \tag{3.6}$$

where

$$D \equiv [\lambda - 1 - (1+P)\lambda\phi]^2 + 4\lambda(1-\phi), \tag{3.7}$$

and λ is defined as

$$\lambda \equiv \exp(-\beta\delta f_0 + 1). \tag{3.8}$$

We now proceed to solve the coupled equations (3.5) and (3.6). Substituting Eq. (3.6) into Eq. (3.5), we obtain a formula for the temperature dependence of the expansion factor of the polymer chain:

$$\frac{1}{n}(\alpha^2 - 1)\phi + \ln\phi_0 + 1 - \phi_0 + \chi\phi^2 = 0, \tag{3.9a}$$

where

$$\phi_0 = [\lambda - 1 - (1+P)\lambda\phi + \sqrt{D}\,]/2\lambda. \tag{3.9b}$$

Temperature T is given through λ and χ parameters, and ϕ is uniquely related to the expansion factor α through Eq. (2.2). Equations (3.9) provide complete information on the chain conformation and the number of solvent molecules bonded to the chain. Before solving them numerically, however, we will derive an approximate equation for Eqs. (3.9) which helps intuitive understanding of the underlying physics.

When ϕ is small enough, we can expand Eq. (3.9b) in power series of ϕ:

$$\phi_0 = 1 - (1 + P\tilde{\lambda})\phi\cdots, \tag{3.10a}$$

where

$$\tilde{\lambda} \equiv \lambda/(\lambda+1). \tag{3.10b}$$

From Eq. (2.1) we obtain $1 + Px = 1 + P\tilde{\lambda}$, i.e.,

$$x = \tilde{\lambda}. \tag{3.11}$$

The value $x(\equiv m/f)$ is only related to the free-energy change δf_0 of a single-bond formation and independent of n.

By substituting Eq. (3.10a) into Eq. (3.9a), the expansion of the logarithmic term yields

$$-\beta\Delta\mu_0 = \frac{1}{n}(1-\alpha^2)\phi + A_2(T)\phi^2 + A_3(T)\phi^3\cdots, \tag{3.12}$$

where the second and third virial coefficients are given by

$$A_2(T) = \tfrac{1}{2}(1 + P\tilde{\lambda})^2 - \chi, \tag{3.13}$$

$$A_3(T) = \tfrac{1}{3}(1 + P\tilde{\lambda})^3, \tag{3.14}$$

respectively. de Gennes[3] has suggested that the coefficient A_3 is increased by adding side groups on the chain. In our theory, the coefficient increases upon increasing the number fraction x of bonded solvent molecules, and x is given by Eq. (3.11) as a function of temperature. From the condition $\Delta\mu_0 = 0$, we then obtain a simple formula for the temperature dependence of the expansion factor:

$$\alpha^5 - \alpha^3 - \frac{(1+P\tilde{\lambda})^3}{3\alpha^3} = \sqrt{n}\left[\frac{1}{2}(1+P\tilde{\lambda})^2 - \chi\right]. \tag{3.15}$$

This takes the same form as the familiar equation used in the conventional theory of the coil–globule transition.[1,2] The theta temperature Θ for which $A_2 = 0$ is given by

$$\chi(\Theta) = \tfrac{1}{2}(1 + P\tilde{\lambda})^2. \tag{3.16}$$

In the following we present the results of a detailed numerical calculation of Eq. (3.9).

IV. RESULTS AND DISCUSSION

For the numerical calculation of Eq. (3.9) we introduce the reduced temperature parameter τ by the definition

$$\tau \equiv 1 - \Theta_0/T. \tag{4.1}$$

In terms of τ, the χ parameter can be expressed as

$$\chi = \tfrac{1}{2} - \psi_1\tau, \tag{4.2}$$

where ψ_1 is a numerical amplitude and Θ_0 is a temperature which satisfies $\chi(\Theta_0) = 1/2$. The parameter χ shows the contact interaction energy related to the dispersion force and then takes a positive value.[26] Note that Θ_0 is not a theta temperature and $\psi_1 k_B\Theta_0$ gives the amplitude of the positive interaction energy between a polymer segment and a solvent. We further split the local free-energy change δf_0 of a hydrogen-bond formation into two parts:

$$\beta\delta f_0 = -\beta\delta\varepsilon_0 - \ln(\lambda_0/e), \tag{4.3}$$

where δs_0 is the entropy loss $\delta s_0 = k_B \ln(\lambda_0/e)$ and $\delta\varepsilon_0$ the absolute value of the bonding energy ($-\delta\varepsilon_0 < 0$).[22,27] Substituting Eq. (4.3) into Eq. (3.8), the parameter λ is expressed as

$$\lambda = \lambda_0 \exp[\gamma(1-\tau)], \tag{4.4}$$

where $\gamma \equiv \delta\varepsilon_0/k_B\Theta_0$. We then have five parameters characterizing our system: n, the number of segments on a chain; $P \equiv f/n$, the number fraction of functional groups on a chain; $\lambda_0 \equiv \exp(\delta s_0/k_B)$, the entropy parameter for a single-bond formation; $\gamma \equiv \delta\varepsilon_0/k_B\Theta_0$, the dimensionless bonding energy; and χ the unperturbed polymer–solvent interaction parameter. In Figs. 2 and 3 we have $\psi_1 = 1$ ($\chi = 1/2 - \tau$), $P = 1$, and $\gamma = 3.5$.

Figure 2 shows the expansion factor α (—) and the number fraction x (- - -) of bonded solvents plotted against the temperature parameter τ. We take $n = 10^5$ and the entropy parameter λ_0 is varied from curve to curve: (a)

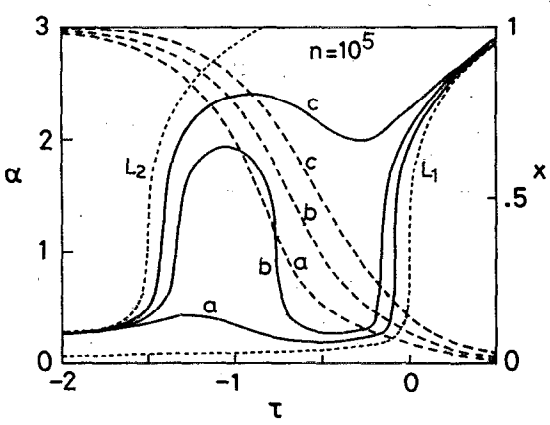

FIG. 2. Expansion factor α (—) and number fraction x (- - -) of bonded solvents are shown against the reduced temperature τ for $n = 10^5$. The entropy parameter λ_0 is varied from curve to curve: (a) $\lambda_0 = 0.002$, (b) $\lambda_0 = 0.003$, (c) $\lambda_0 = 0.005$.

Downloaded 30 Nov 2007 to 130.54.110.22. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp

$\lambda_0 = 0.002$, (b) $\lambda_0 = 0.003$, and (c) $\lambda_0 = 0.005$. The fraction x becomes larger as λ_0 is increased at a fixed τ. The calculated values of x increase from zero to unity with decreasing temperature, while the expansion factor exhibits remarkable changes. The curves L_1 and L_2 show the expansion factor α against τ when we take $x = 0$ and 1 in Eq. (3.15), respectively. The values of α saturate to the curve L_1 at high enough temperature where the chain is in a coiled state and to the curve L_2 at low enough temperature where the chain is in a globular state with bonded solvent molecules. At the intermediate temperature, the behavior of α is strongly related to the local entropy loss $\delta s_0 = k_B \ln(\lambda_0)$ for a bond formation. In this temperature region, the value of x sharply increases with decreasing temperature. When the entropy loss is large, as in the case (a), the chain remains in the globular state. As λ_0 is increased, we find that the expansion factor sharply increases with decreasing temperature, as shown in case (b). This behavior is an intrinsic character in the systems where the hydrogen-bond formation takes place between polymer segments and solvent molecules. In case (c), however, the sharp conformational change disappears.

Figures 3(a)–3(c) show the expansion factor α and the number fraction x plotted against τ. The entropy parameter λ_0 is changed from Fig. 3(a) to Fig. 3(c). The curves are shown for various values of the number of segments. We find the abrupt change in the behavior of α near Θ temperatures. The Θ temperatures are calculated from Eq. (3.16): (a) $\tau(\Theta) = -0.085$; (b) $\tau(\Theta) = -0.158$, -0.768, -1.328; and (c) $\tau(\Theta) = -1.42$. The second virial coefficient against τ was reported in Ref. 22. As $n \to \infty$, the temperature derivative of α becomes discontinuous at the Θ temperatures. The behavior is characteristic of a second-order phase transition. The value of α at the Θ temperatures is larger than unity.[5] Although the second virial coefficient vanishes at the Θ temperatures, the third- and all higher-order virial coefficients take positive values. In Fig. 3(a) we find an abrupt condensation from an extended coil to a compact globule takes place near the Θ temperature as temperature is decreased. At the lower-temperature side α exhibits a maximum and a minimum as a function of temperature. When $\lambda_0 = 0.002$ we have, for lower molecular weight, a closed-loop coexistence curve, and the lower coexistence curve showing an upper critical solution temperature (UCST), and for high molecular weight, an hourglass shape of phase diagram.[22] In Fig. 3(b) we find the second-order-like reentrant coil–globule transition. In the globular region at the higher-temperature side, we have a closed-loop coexistence curve on the temperature-concentration plane.[22] The value of α at the lower Θ temperature is larger than that at the higher Θ temperature. The reason is clear because the value of the third virial coefficient A_3 is increased with increasing x (or decreasing temperature). The bonded solvent molecules extend the distribution of the polymer segments. Near $\tau(\Theta_L) = -0.76$, which corresponds to the Θ_L temperature for a lower critical solution temperature (LCST) of the polymer solution, α sharply decreases with increasing temperature. This behavior has been observed on poly (N-isopropylacrylamide) in water.[18] As the entropy parameter λ_0 increases further, the sharp reentrant coil-globule phenomena disappears as shown in Fig. 3(c). At the higher-temperature side, α exhibits a maximum and a minimum as a function of temperature. As temperature is decreased further, the chain collapses into a globular state near the Θ temperature, where the χ parameter dominates the system.

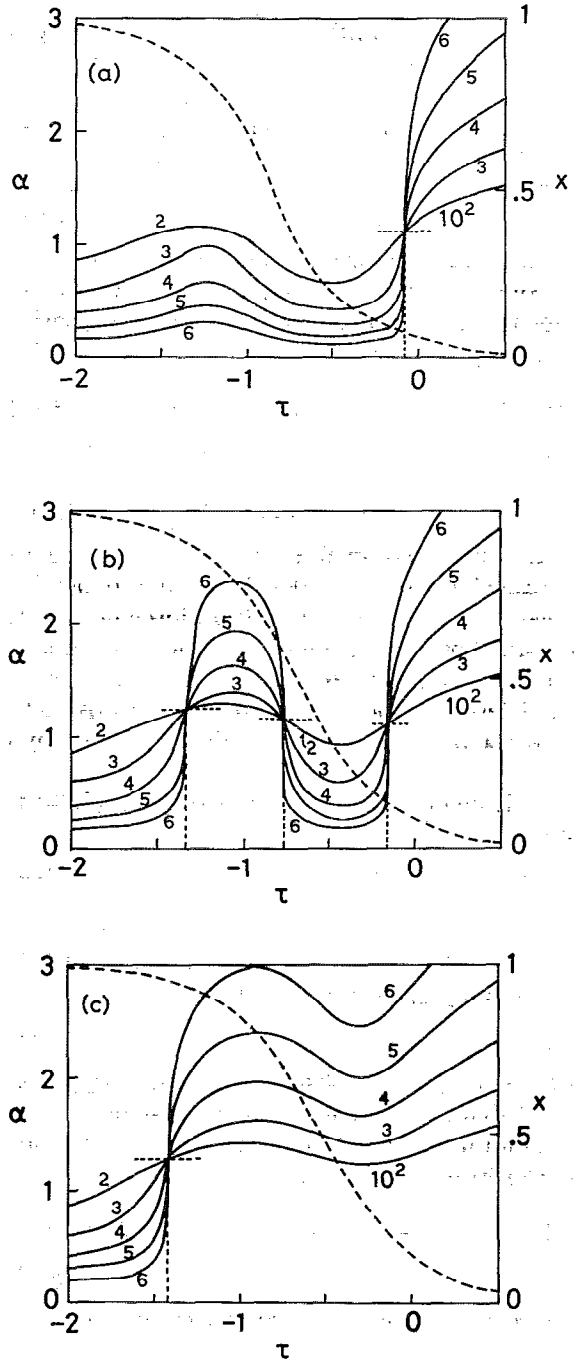

FIG. 3. Expansion factor α (—) and number fraction x (- - -) are shown against the reduced temperature τ. The entropy parameter λ_0 is changed from (a) to (c): (a) $\lambda_0 = 0.002$, (b) $\lambda_0 = 0.003$, (c) $\lambda_0 = 0.005$. The curves are shown for various values of the number of segments. The Θ temperatures are calculated from Eq. (3.16); (a) $\tau(\Theta) = -0.085$; (b) $\tau(\Theta) = -0.158$, -0.768, -1.328; and (c) $\tau(\Theta) = -1.42$. The value of α at the Θ temperatures is larger than unity. In (b), the value of α at the lower Θ temperature is larger than that at the higher Θ temperature.

In Fig. 4 we predict two possible types of reentrant coil–

Downloaded 30 Nov 2007 to 130.54.110.22. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp

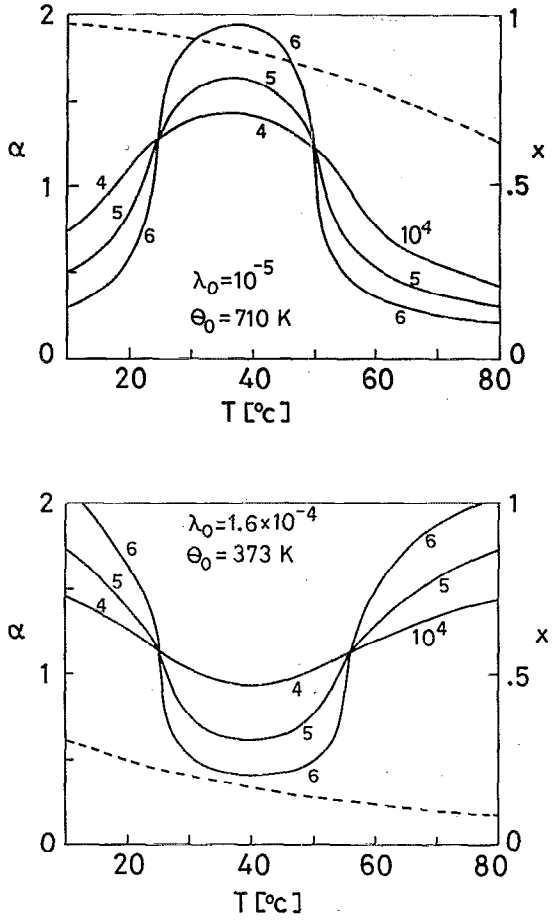

FIG. 4. Expansion factor α (—) and number fraction x (- - -) are shown against temperature for the parameters $\psi_1 = 1$, $P = 1$, $\gamma = 6$: (a) $\gamma_0 = 10^{-5}$, $\Theta_0 = 710$ K ($\chi = -0.5 + 710/T$); (b) $\lambda_0 = 1.6\times10^{-4}$, $\Theta_0 = 373$ K ($\chi = -0.5 + 373/T$). The curves are shown for various values of the number of segments. We predict two possible types of reentrant coil–globule phenomena in the realistic temperature region.

globule phenomena in the realistic temperature region for several values of n. In Fig. 4(a) the polymer chain is in a coiled state between $\Theta_U = 25$ °C and $\Theta_L = 50$ °C, where Θ_U and Θ_L are the theta temperatures for the UCST and LCST, respectively. In Fig. 4(b) the polymer chain for higher molecular weight is in a globular state between $\Theta_L = 25$ °C and $\Theta_U = 55$ °C. As n is increased, the reentrant coil–globule phenomena becomes sharper. Similar results can be derived for different values of the parameters Θ_0 and λ_0. We therefore have the possibility to observe these phenomena. The behavior of Fig. 4(b) is also similar to the reentrant phenomena of nonionic gel, where the reentrant volume transition takes place when the ratio of water to dimethyl sulfoxide in the solvent is varied.[28,29]

In Fig. 5 the expansion factor is plotted against temperature for several values of P. As the number of functional groups on a polymer chain is increased from zero to a finite value, the polymer chain becomes more swollen. When $P = 2$, we have a reentrant coil–globule phenomena. We then predict that the reentrant phenomena can be derived by adjusting the number of functional groups on a chain.

Finally, we examine a possible mechanism for the nega-

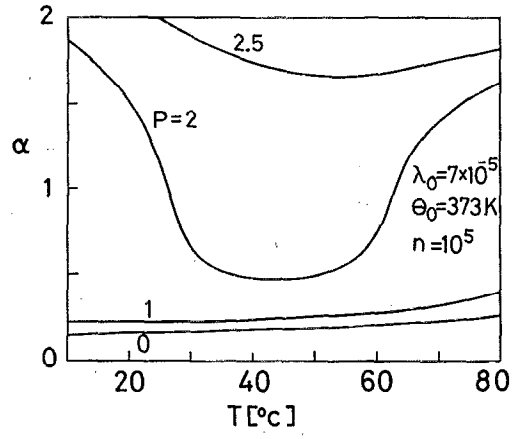

FIG. 5. Expansion factor α (—) is shown against temperature for $\psi_1 = 1$, $\gamma = 6$, $\lambda_0 = 7\times10^{-5}$, $\Theta_0 = 373$ K, and $n = 10^5$. The curves are shown for various values of the number fraction P of functional groups on the chain. When $P = 2$, we find a reentrant coil–globule phenomena.

tive temperature dependence of the radius of gyration of the polymer chain such a poly (N — isopropylacrylamide) or polymethacrylic acid in water.

Figure 6 shows the comparison of the theoretical calculations with the experimental values of α. The open circles show the data of poly (N-isoprophylacrylamide) (PNIPAM) in water.[18] The molecular weight of PNIPAM is $M_W = 8.4\times10^6$. The Θ_L temperature for the LCST is 30.5 °C. The phase diagram for $M_W = 10^6$ has the LCST at about 31 °C.[12] The parameters used the same values with Fig. 3(b). We use $R_0 = 78$ nm and $\Theta_0 = 535$ K for a best fit. We can estimate the number of segments as $n = 7.4\times10^4$ by using the molecular weight 113 of a repeating unit on the polymer. The curves are shown for various values of the number of segments. At the low-temperature side the fit of theoretical curves to the experimental data is very good. At the high-temperature side, however, the data fit the theoretical curves for larger values of n. Similar behavior can be derived for different values of the parameters. Our theory incorporates only the hydrogen-bond formation between

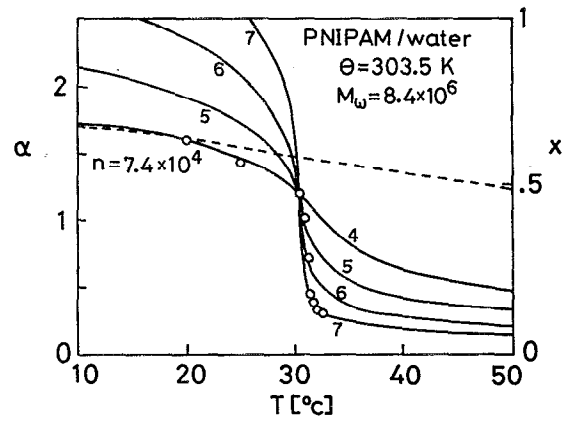

FIG. 6. A comparison of theoretical (solid curves) and experimental (open circles) values of the expansion factor α. Data were taken from Ref. 18. The curves are shown for various values of the number of segments in our numerical calculations.

Downloaded 30 Nov 2007 to 130.54.110.22. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp

polymer and solvent molecules. We must examine further the other aggregation phenomena such as the intramolecular bridging and the intermolecular aggregation of the globular chain.

Our analyses demonstrate that the chain is swollen at the low-temperature side. The entropy of the system is decreased by hydrogen-bond formation between PNIPAM and water. However, the decrease in entropy is compensated by the swelling of the chain. As a result of this, the chain is more swollen as temperature is decreased. From a theoretical point of view, the chain recollapses at low enough temperature and reswells at high enough temperature as shown in Fig. 2(b). The number of water molecules bonded on the chain is given by $m = nPx$. From Fig. 6 we obtain approximately $dx/dT = -3.75\times10^{-3}$, and can then estimate $dm/dT = -375$ for $n = 10^5$ and $P = 1$. The number of water molecules which have changed from the bonded state to the unbonded one is proportional to n. We therefore have a sharper comformational change as the number of segments is increased. The mechanism of the transition of PNIPAM in water is different from the usual one, such as PS in cyclohexane. The latter is well known as the "excluded volume-induced" coil–globule transition. The former, however, can be classified as the "solvation-induced" one.

V. CONCLUSION

We have theoretically studied the comfomational change of a single-polymer chain capable of forming a physical bond with solvent molecules. Our theory takes into account the mixing entropy change induced by solvation. Main conclusions obtained through this study are as follows:

(1) Based on the mean-filled theory we have derived a formula, Eq. (3.9), and the approximate one, Eq. (3.15), for the temperature dependence of the expansion factor of the single-polymer chain.

(2) The physical-bond formation between polymer and solvent molecules can be a major cause of the reentrant conformational change of the chain when temperature is varied.

(3) At the Θ temperature the chain is more swollen than the ideal state. The value of the expansion factor at the lower Θ temperature is larger than that at the higher Θ temperature.

(4) The reentrant coil-globule phenomena can be derived by adjusting the number of functional groups on the chain.

(5) The chain suddenly collapses near the Θ_L temperature as temperature is increased to the LCST. This behavior is referred to as the solvation-induced coil–globule transition.

The concept of solvation is also an important factor for other complex fluid systems, including thermal denaturation of protein and nonionic gels in water.

For nonionic PNIPAM gel in water,[29] it has been reported that the gel collapses at the high-temperature side. This behavior is in contrast to the ionic gels which swell at high temperature. The mechanism for nonionic gels will also be explained in terms of solvation along our theory.

[1] O. B. Ptitsyn, A. K. Kron, and Y. Y. Eizner, J. Polym. Sci., Part C **16**, 3509 (1968).
[2] P. G. de Gennes, Phys. Lett. A **38**, 339 (1972).
[3] P. G. de Gennes, J. Phys. (Paris) **36**, L55 (1975).
[4] I. M. Lifshitz, A. Y. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).
[5] I. C. Sanchez, Macromolecules **12**, 980 (1979).
[6] M. Nierlich, J. P. Cotton, and B. Farnoux, J. Chem. Phys. **69**, 1379 (1978).
[7] S. T. Sun, I. Nisio, G. Swislow, and T. Tanaka, J. Chem. Phys. **73**, 5971 (1980).
[8] F. Tanaka and H. Ushiki, J. Chem. Phys. **84**, 5925 (1986).
[9] J. S. Helman, A. Coniglio, and C. Tsallis, Phys. Rev. Lett. **53**, 1195 (1984).
[10] A. Silberberg, J. Eliassaf, and A. Katchalsky, J. Polym. Sci. **23**, 259 (1957).
[11] E. V. Anufrieva, T. M. Birshtein, T. N. Nekrasova, O. B. Ptitsyn, and T. V. Sheveleva, J. Polym. Sci. **16**, 3519 (1968).
[12] M. Haskin and J. E. Guillet, J. Macromol. Sci. Chem. A **2**, 1441 (1968).
[13] R. A. Horne, J. P. Almeida, A. F. Day, and N. T. Yu, J. Colloid Interface Sci. **35**, 77 (1970).
[14] R. Kjellender and E. Florin, J. Chem. Soc. Faraday Trans. 1 **77** 2053 (1981).
[15] *Physics of Amphyphiles: Micelles, Vesicles, and Microemulsion*, edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, The Netherlands, 1985), p. 303.
[16] F. M. Winnik, Macromolecules **23**, 233 (1990).
[17] S. Fujisige, Polymer J. **19**, 297 (1987).
[18] S. Fujisige, K. Kubota, and I. Ando, J. Phys. Chem. **93**, 3311 (1989).
[19] I. Yamamoto, K. Iwasaki, and S. Hirotsu, J. Phys. Soc. Jpn. **58**, 210 (1989).
[20] P. C. Painter, J. Graf, and M. M. Coleman, J. Chem. Phys. **92**, 6166 (1990); P. C. Painter, Y. Park, and M. M. Coleman, Macromolecules **22**, 580 (1989).
[21] R. E. Goldstein, J. Chem. Phys. **83**, 1246 (1985).
[22] A. Matsuyama and F. Tanaka, Phys. Rev. Lett. **65**, 341 (1990).
[23] G. R. Andersen and J. C. Wheeler, J. Chem. Phys. **69**, 2082 (1978); J. C. Wheeler and G. R. Andersen, *ibid.* **73**, 5778 (1980); J. S. Walker and C. A. Vause, Phys. Lett. A **79**, 421 (1980); J. Chem. Phys. **79**, 2660 (1983); R. E. Goldstein and J. S. Walker, J. Chem. Phys. **78**, 1492 (1983).
[24] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953), Chaps. 12 and 13.
[25] P. J. Flory, Proc. R. Soc. London, Ser. A **351**, 351 (1976).
[26] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979), Chap. 4.
[27] J. S. Walker and C. A. Vause, Sci. Am. **256** (No. 5), 90 (1987).
[28] S. Katayama, Y. Hirokawa, and T. Tanaka, Macromolecules **17**, 2641 (1984).
[29] Y. Hirokawa and T. Tanaka, J. Chem. Phys. **81**, 6379 (1984).

Downloaded 30 Nov 2007 to 130.54.110.22. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp