Reentrant phase transition of Nisopropylacrylamide gels in mixed solvents

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Reentrant phase transition of *N*-isopropylacrylamide gels in mixed solvents[a)]

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Reentrant volume–phase transitions are observed in *N*-isopropyoacrylamide gels in the
methanol–water mixtures. When the solvent composition is varied systematically, the gel
undergoes two transitions: a discontinuous collapsing followed by a discontinuous swelling.
The reentrant transition defines a closed-loop instability phase boundary having both upper
and lower critical points. The closed-loop phase boundary depends on temperature and
diminishes to a point at approximately 0 °C. A simple mean field theory is presented to
describe the phenomenon, which reveals an alteration of free energy of alcohol–water
interaction by presence of polymer network. In the case of ethanol–water mixtures, there
appear two closed-loop phase boundaries, whose physico-chemical basis are not yet clear.

INTRODUCTION

N-Isopropylacrylamide gels containing ionizable groups undergo discontinuous volume–phase transitions between swollen and collapsed states in response to changes in temperature or solvent composition.[1,2] These gels are useful model systems to study the phase transition and critical phenomena. For instance, we have found that the gels underwent a reentrant phenomenon where gels, once collapsed, can swell again when the ratio of water to dimethylsulfoxide (DMSO) in mixed solvent was varied systematically.[3] This phenomenon was explained by assuming that the free energy of contact, between polymer segment and solvent, was not a monotonic function of the solvent composition. However, it was not clear why the free energy was not a linear of the solvent composition.

This paper presents another reentrant volume–phase transition in *N*-isopropylacrylamide gels in MeOH–water and EtOH–water mixed solvents. The reentrant phase transition is characterized by a closed instability region in the phase diagram. The closed instability region depends on the temperature; it shrinks as temperature decreases, and diminishes at 0 °C as two critical points merge. A three-dimensional phase diagram, having temperature, solvent composition, and gel volume as independent variables, is constructed.

THEORETICAL

In order to quantitatively interpret the reentrant phenomenon we make use of the mean field theory of phase transition of ionic gels, which was presented in detail elsewhere.[4] In the framework of this theory, the osmotic pressure of a gel is described by the Flory–Huggins' formula[5]

$$\Pi = -\frac{NkT}{v}\left[\phi + \ln(1-\phi) + \frac{\Delta F}{2kT}\phi^2\right] + vkT\left[\frac{\phi}{2\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] + fvkT\left(\frac{\phi}{\phi_0}\right), \quad (1)$$

where N is Avogadro's number, k the Boltzmann constant, T the temperature, v the molar volume of the solvent, ϕ the

volume fraction of the network, ΔF the excess free energy for the association between polymer segment and solvent, ϕ_0 the volume fraction of the network at random walk of configurations, v the number of constituent chains per unit volume at $\phi = \phi_0$, and f is the number of dissociated counterions per effective chain.

The osmotic pressure difference, between the inside and outside of a gel, must be zero in order for the gel to be in equilibrium with the surrounding solvent. The requirement of a zero osmotic pressure difference is equivalent to minimizing the free energy of the gel F, since $\Pi = \partial F/\partial V$. Here, V is the volume of the gel. From Eq. (1), this condition is expressed as

$$\tau = 1 - \frac{\Delta F}{kT} = -\frac{vv}{N\phi^2}\left[(2f+1)\left(\frac{\phi}{\phi_0}\right) - 2\left(\frac{\phi}{\phi_0}\right)^{1/3}\right] + 1 + \frac{2}{\phi} + \frac{2\ln(1-\phi)}{\phi^2}, \quad (2)$$

where τ is the reduced temperature that depends both on temperature and solvent composition. Equation (2) then determines the equilibrium network concentration as a function of the reduced temperature. For certain values of τ, however, Eq. (2) is satisfied by three values of ϕ corresponding to two minima and one maximum of the free energy.[4] The value of ϕ corresponding to the smaller minimum represents the equilibrium value. A discrete volume transition occurs when the two free energy minima are equal. The equilibrium volume of a gel is inversely proportional to its equilibrium concentration $V/V_0 = \phi_0/\phi$, where V_0 is the volume of the gel at $\phi = \phi_0$.

In Fig. 1, the reduced temperature τ is plotted as a function of the degree of swelling (V/V_0) for a series of values of f. The parameter f denotes the number of ionizable groups per effective chain incorporated into the network. As the f value increases, the magnitude of the volume change increases, and the reduced temperature of the volume transition becomes lower.

Consider now the dependence of the reduced temperature τ on the composition of a mixed solvent. If selective absorption of one of the solvent components to polymer
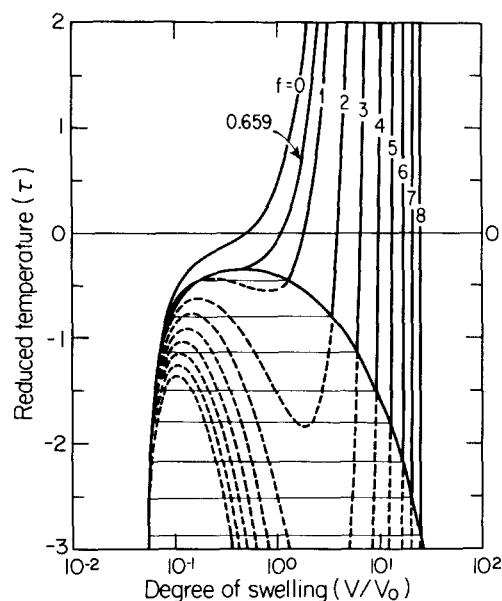
FIG. 1. Equilibrium swelling curves calculated from Eq. (2) using the parameters $(vv/N)\phi_0^3 = 10$ and $\phi_0 = 0.05$ for various values of f. This figure is adopted from Fig. 2 of Ref. 4.

network is neglected (single-liquid approximation), then the excess free energy ΔF can be described as a function of solvent composition by the equation[6]

$$\Delta F = x_1 \Delta F_1 + x_2 \Delta F_2 - x_1 x_2 \Delta F_{12} , \qquad (3)$$

where x_1 and x_2 ($x_1 + x_2 = 1$) are the mole fractions of respective solvents 1 and 2, in the mixture. ΔF_1, ΔF_2, and ΔF_{12} are parameters defining the free energy of the association between solvent 1 and polymer segment, solvent 2 and polymer segment, and solvent 1 and solvent 2, respectively. For the case

$$\Delta F_{12} < - |\Delta F_1 - \Delta F_2| , \qquad (4)$$

ΔF does not change monotonically, but has a maximum in the solvent composition in the range $0 < x_1 < 1$. Therefore, the reduced temperature $\tau(\tau = 1 - \Delta F/kT)$ has a minimum. If this minimum value is less than the critical reduced temperature, and if the reduced temperatures corresponding to both $x_1 = 0$ and $x_1 = 1$ are higher than the critical value, the reduced temperature first decreases and then increases when the solvent composition x_1 varies from 0 to 1. Then the gel will show a reentrant phase transition as a function of solvent composition. These conditions can be satisfied by choosing appropriate values for ΔF_1, ΔF_2, and ΔF_{12}. Figure 2 shows a relationship between τ and x_1, under such circumstances. Figure 3 shows how the gel volume changes with the solvent composition for various amounts of ionizable group under the same, reentrant condition. As shown in Fig. 3, the transitions are classified into five different types which are dependent on the gel composition and solvent properties. The closed coexistence curve and spinodal line are drawn by the dash–dot line and the dash–dot–dot line, respectively. Discrete reentrant phase transitions are seen for the number of counterions per chain; $f = 1$ and $f = 2$, and could be seen for $f = 5$ if the gel can exist in the metastable region, which is defined as the region between the spinodal and coexistence lines.
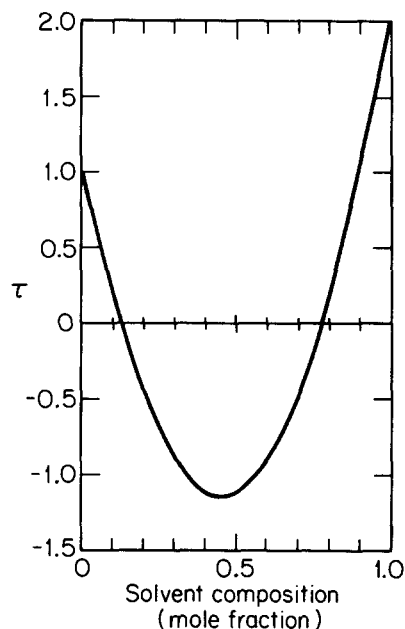

FIG. 2. Dependence of the reduced temperature on solvent composition in the mixed solvent, calculated from Eq. (3) using the parameters $\Delta F_1/kT = 1$, $\Delta F_2/kT = 2$, and $\Delta F_{12}/kT = -9.5$. Those values are chosen so that a reentrant phase transition is predicted at appropriated reduced temperature.

EXPERIMENTAL

N-Isopropylacrylamide gels were prepared by free radical polymerization of N,N-isopropylacrylamide (major polymer component, 700–636 mM), sodium acrylate (ionized group, 0–64 mM), and N,N'-methylenebisacrylamide (cross-linking molecule) according to Hirokawa and Tanaka.[1] Gelation was carried out in cylindrical micropippets of
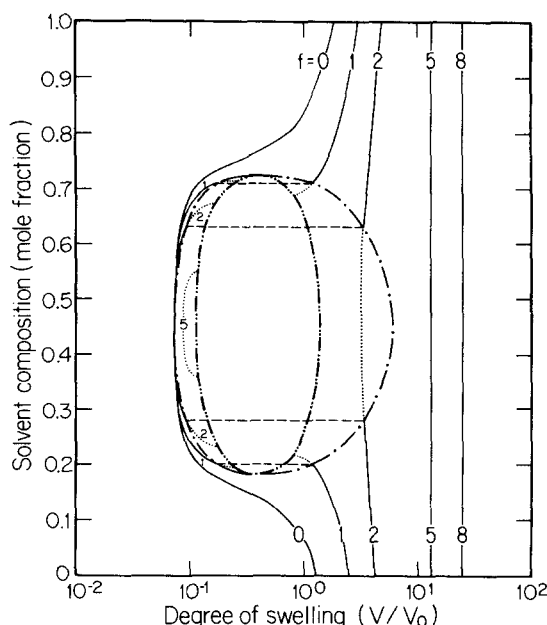

FIG. 3. Theoretical relationship between gel volume and solvent composition calculated using the parameters chosen for Fig. 2. The closed circle (–·–) indicates the phase boundary of coexistence curve. The circle line (–··–··–) denotes the spinodal line, inside of which represents the unstable phase. Between these two circles represents the metastable state.
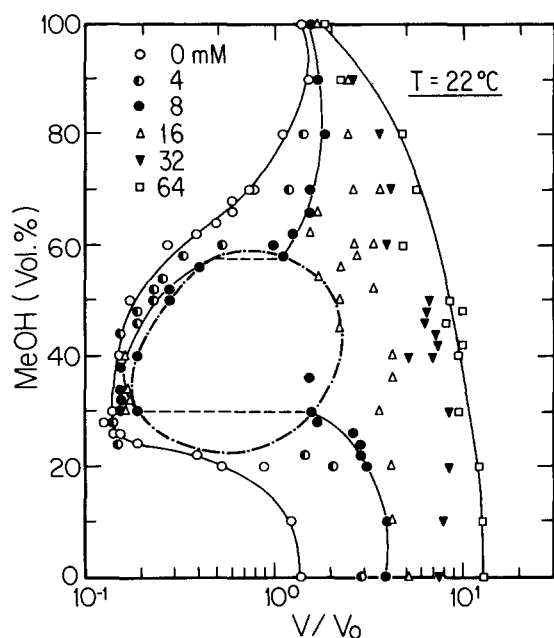
FIG. 4. Swelling ratio (final to initial equilibrium volume) of *N*-isopropyl-acrylamide gels in mixtures of MeOH and water at 22 °C. The numerical values shown in the figure indicate the concentrations of sodium acrylate incorporated within the polymer network at gelation.

FIG. 5. Swelling ratio of *N*-isopropylacrylamide gels in the mixtures of MeOH and water at 42 °C.

i.d. 1.35 mm. The gels were washed in large amount of distilled, deionized water, cut into 1 to 2 mm thick disks, and then immersed in MeOH–water or EtOH–water mixtures of various compositions. The concentrations of the mixtures shown in this paper are in the volume ratio of each pure solvent prior to mixing. The final equilibrium diameter of each gel was measured under a calibrated microscope. The initial diameter (d_0) of each gel was 1.35 mm. From the diameter we determined the degree of swelling V/V_0 = $(d/d_0)^3$, where V and V_0 are the final and initial equilibrium volumes of the gel, respectively.

EXPERIMENTAL RESULTS

Figure 4 shows the degree of swelling of *N*-isopropyl-acrylamide gels having constant concentration of sodium acrylate in the aqueous solution of MeOH as a function of MeOH concentration. At room temperature (22 °C), the gel containing 8 mM sodium acrylate is swollen at MeOH concentrations ranging from 0% to 30%. At MeOH concentration of 30%, the gel undergoes a discrete volume collapse by 10 times. The gel volume remains collapsed under further increase of MeOH concentration up to 57%. At the concentration of 57%, the gel reswells discontinuously. The reentrant phase transition is reversible for the change in solvent composition.

A decrease in the proportion of ionizable groups incorporated in the polymer network makes the volume change at transition smaller. As a result, in the case of nonionic, the volume changes continuously, as shown in Fig. 4. In addition, with the decrease of ionizable groups, MeOH concentration required for the upper transition is raised, whereas that for the lower transition is lowered. On the contrary, with increase of ionizable groups, the volume change at tran-
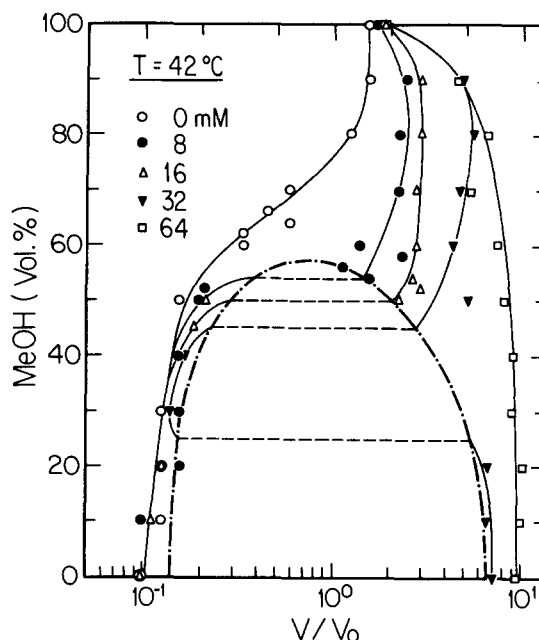
sition is larger, and MeOH concentration for the upper transition is lowered, whereas that for the lower transition is raised. Therefore, the gels containing more than 32 mM sodium acrylate no longer collapses, but is swollen for any MeOH concentrations. Based on these observations, we indicate in Fig. 4 a closed-loop phase boundary, representing a domain of instability, which has two critical points.

N-Isopropylacrylamide gel without ionizable group in water is swollen at room temperature, but collapses at temperatures higher than 34 °C.[1] At 42 °C the gel containing more than 32 mM sodium acrylate are still swollen, but gels with less ionizable groups are collapsed.[1] Figure 5 shows the degree of swelling of *N*-isopropylacrylamide gels as a function of MeOH concentration at 42 °C. The gels containing 16 mM or less sodium acrylate show only the swelling transition, since the gel is already collapsed in pure water at this temperature. On the other hand, the gel containing 32 mM sodium acrylate at 42 °C shows the reentrant phase transition which collapses at the MeOH concentration between 20% and 30%, and reswells between 40% and 50%. The gel having 64 mM sodium acrylate is always swollen for all the MeOH concentration, as shown in Fig. 4. We can indicate a semiclosed-loop phase boundary which is larger than that of 22 °C. The critical point at lower transition has gone out of the phase diagram and there is only one critical point in Fig. 5.

Figure 6 shows the degree of swelling of *N*-isopropyl-acrylamide gels at 0 °C. The phase boundary becomes smaller with decrease of temperature and finally diminishes at the temperature of 0 °C. The volumes of all gels change continuously with MeOH concentration. The phase boundary is now represented by a point at the MeOH concentration of 52%, at $V/V_0 = 0.7$, and for the sodium acrylate concentration of 8 mM. At this point the upper and lower critical points coincide and merge into one.
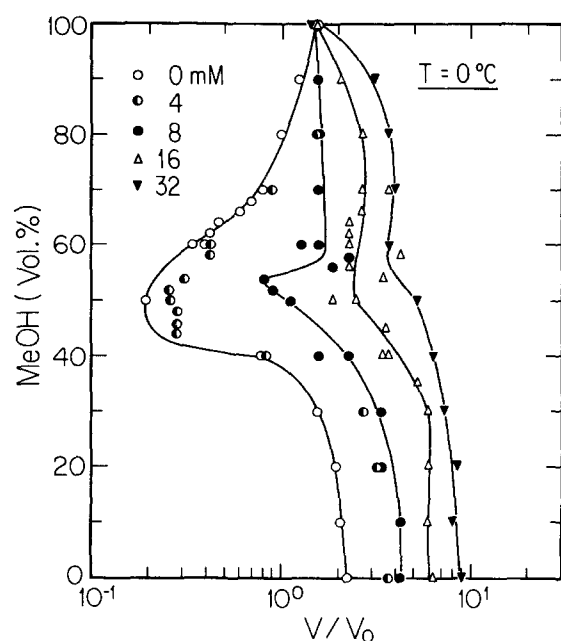
FIG. 6. Swelling ratio of *N*-isopropylacrylamide gels in the mixtures of MeOH and water at 0 °C.

FIG. 7. Swelling ratio of *N*-isopropylacrylamide gels in mixtures of EtOH and water at 22 °C.

Figure 7 shows the swelling curves of *N*-isopropylacrylamide gels as a function of EtOH concentration at 22 °C. The gel containing 8 mM sodium acrylate has two discrete collapsing transitions, and one continuous and one discrete swelling transitions. In other words, the reentrant transitions occur twice. The system of the gels in EtOH–water, consequently, have two closed phase boundary and four critical points.
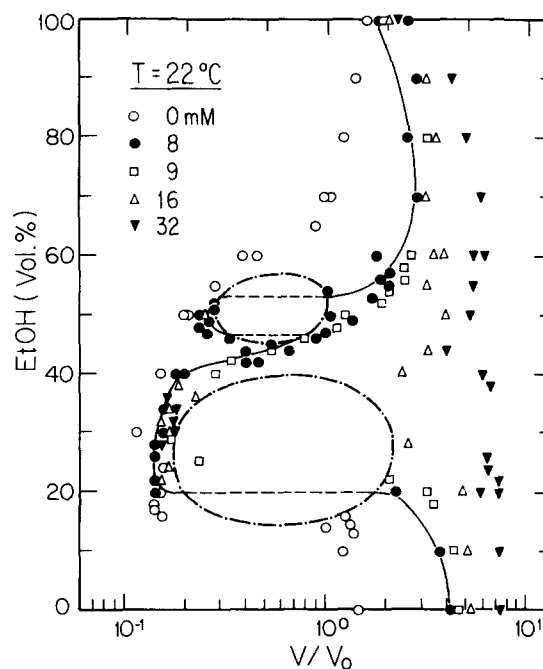
DISCUSSION

The three-dimensional representation of swelling curves of *N*-isopropylacrylamide gels in MeOH–water mixture is constructed by combining Figs. 4, 5, and 6. The results of the gels including 0, 4, 8, and 32 mM sodium acrylate are shown in Fig. 8. The phase boundary has a mountain shape, whose
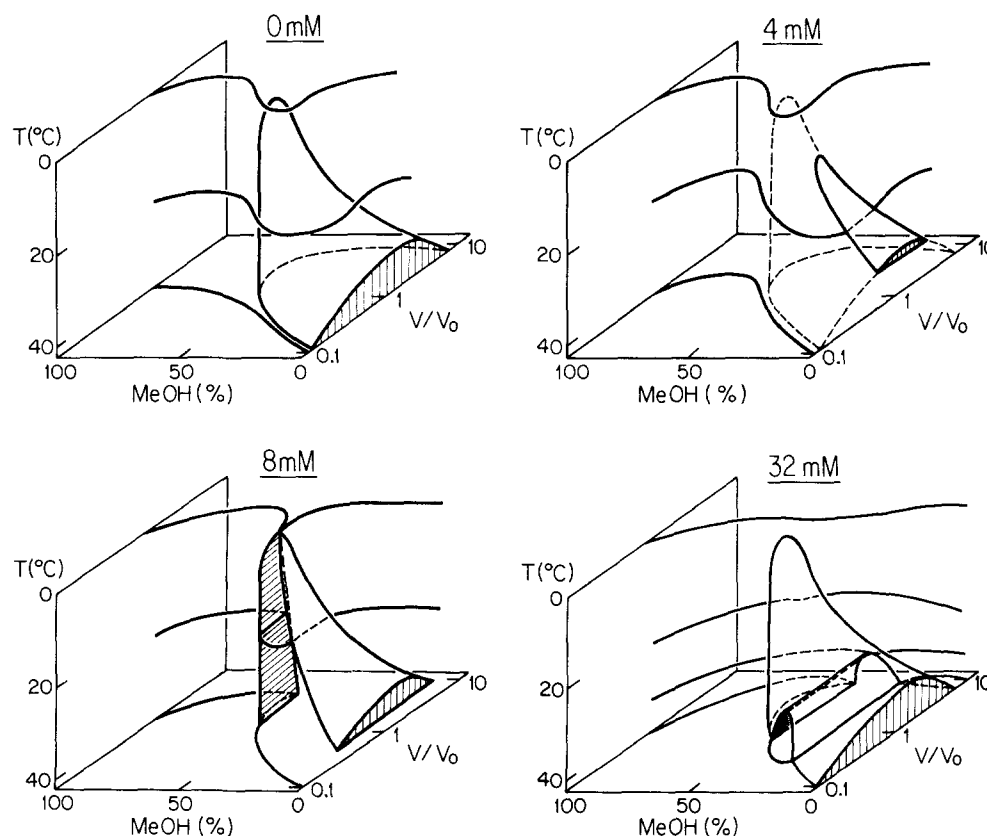

FIG. 8. Three-dimensional representation of swelling curves of *N*-isopropylacrylamide gels in MeOH and water mixture.

peak corresponds to the special point at which the two critical points merge. When a swelling curve encounters the phase boundary, the curve jumps to the other side of the mountain along the wall of the tunnel or the cliff as drawn in the figures.

The volumes of all the gels in pure MeOH or EtOH are the almost same and independent of the quantity of ionizable group in the network. This indicates that ionizable groups are totally neutralized yielding no counterions in pure alcohol.

The dependence of gel volume on temperature is much more conspicuous in water than in MeOH. This means that the reduced temperature τ of the N-isopropylacrylamide gels in water decreases with temperature, but that in alcohol is almost independent of temperature. Therefore, low-alcohol transition depends on temperature more strongly than high-alcohol one, which will be obviously seen in the dependence of the phase boundary on temperature in MeOH and water mixture. The low-alcohol side of the phase boundary becomes larger with temperature increase, but the other side changes little.

As indicated in the theoretical section, reentrant phenomena are a result of strong interaction between alcohol (solvent 1) and water (solvent 2). More quantitatively, the interaction parameter (the excess free energy of contact between solvents) ΔF_{12} should satisfy the condition Eq. (4). According to Butler, however, the value of the actual interaction parameter between alcohol and water is always positive, and increases with the number of carbon atoms in the alcohol chain.[7] The difference between Butler's data and the present one is in that the alcohol–water interaction is evaluated with the presence of polymer network in our case. Therefore, the term of $x_1 x_2 \Delta F_{12}$ in Eq. (3) must be affected not only by alcohol and water, but also by the presence of polymer network. For the first order approximation, ΔF_{12} may be written by the following equation:

$$\Delta F_{12} = \Delta F^0_{12} + \Delta F_{123}\phi, \tag{5}$$

where ΔF^0_{12} and ΔF_{123} are constants. Even if ΔF^0_{12} is positive, a reentrant phase transition will be seen when ΔF_{12} is negative due to a negative value of ΔF_{123}. In other words, a reentrant phase transition occurs because the attractive interaction for alcohol and water is enhanced by the presence of N-isopropylacrylamide polymers.

[1] Y. Hirokawa and T. Tanaka, J. Chem. Phys. **81**, 6379 (1985).

[2] S. Hirotsu, Y. Hirokawa, and T. Tanaka (submitted).

[3] S. Katayama, Y. Hirokawa, and T. Tanaka, Macromolecules **17**, 2641 (1984).

[4] T. Tanaka, D. J. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, Phys. Rev. Lett. **45**, 1636 (1980).

[5] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953).

[6] A. Dondos and D. Patterson, J. Polym. Sci. Part A 2 **5**, 230 (1967).

[7] J. A. V. Butler, Trans. Faraday Soc. **33**, 329 (1937).