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Simple Scaling Rules on Swollen and Shrunken Polymer Gels

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ABSTRACT: The equilibrium swelling ratios of temperature sensitive polymer gels have been studied as a function of the initial monomer concentration at preparation in both the swollen and the shrunken states. The linear swelling ratio, d/d_0, was independent of the initial monomer concentration of *N*-isopropylacrylamide, C_0, where d and d_0 are the diameters of gels at observation and at preparation, respectively. On the other hand, d/d_0 was proportional to C_0 in the shrunken state. The swelling curves of gels with different C_0's were successfully reproduced with a modified Flory−Rehner equation, where the effective cross-link density was modified to be proportional to C_0 by taking account of the contribution of "excess cross-linking" by entanglement. Scaling rules for the polymer fractions were derived for both the swollen and the shrunken states; i.e., $\phi_{\mathrm{sw}} \sim C_0^1$ and $\phi_{\mathrm{sh}} \sim C_0^0$, where ϕ_{sw} and ϕ_{sh} are the equilibrium volume fractions of the network at the swollen and shrunken phases, respectively.

Introduction

Swelling is one of the characteristic features of polymer networks. Because of the presence of cross-links, a polymer network does not dissolve in solvent but swells. The prototype of the theory describing the swelling equilibrium, which is the so-called Flory−Rehner (FR) equation,[1] can be found in the textbook by Flory.[2] There are two important parameters to characterize polymer networks: i.e., the Flory interaction parameter and the cross-link density. On the basis of this equation, swelling experiments have been widely used to estimate the cross-link density or the interaction parameters of polymer networks, e.g., elastomers.[3]

In the case of polymer gels, the degree of swelling is one of the essential parameters to characterize a gel. Since a gel can be regarded as a piece of gigantic molecule consisting of a single macromolecule, one can investigate the molecular interaction between the network polymer and solvent by simply measuring the degree of swelling. Studies of gel swelling have been accelerated by the discovery of the volume phase transition.[4] The volume phase transition is specified as a discrete change in the gel volume with an infinitesimal change of its environmental variable, such as temperature, pH, ionic strength, etc.[5−9] In spite of a large number of studies on gel swelling, however, several basic problems of gel thermodynamics have not been fully understood. For example, though polymer gels are usually prepared from a monomer solution (or a pregel solution) in which a large amount of solvent is present, the effect of the solvent in the swelling behavior of the resultant gel remains unclear. In many cases, researchers simply employ the theory for elastomers to account for the swelling behavior of gels, where little attention is paid for the effect of the initial monomer concentration.

Several studies have been reported on the initial monomer concentration dependence of gel swelling.[10−16] Baker et al.[15] studied the effects of the total monomer concentration, cross-linker concentration, and charged monomer concentration of cationic acrylamide-based hydrogels on the swelling behavior and compression modulus. They reported that the degree of swelling decreases with increasing the initial monomer concentration. Since such a behavior cannot be predicted by the conventional theory of swelling, e.g., the FR theory, they concluded that the effect of chain interpenetration increases with increasing monomer concentration. Hino et al. reanalyzed the data of Geissler et al.[12] and Hu et al.[14] on the initial monomer concentration dependence of gel swelling and proposed a correction which takes into account the lowest bound of initial concentration to form a gel. However, these models require a set of fitting parameters to reproduce their experimental results of the degree of swelling, and the physical meaning of the parameters is not clear.

A temperature sensitive polymer gel, e.g., *N*-isopropylacrylamide (NIPA) gel in water, is one of the best systems to study the thermodynamics of polymer gels because the swelling equilibrium can be studied in both swollen and shrunken states by simply changing the temperature of the gel across the volume transition temperature, T_c (≈34 °C for NIPA gels). In addition, in the case of NIPA gels, there are a large number of studies from different aspects,[8] such as structure (small-angle neutron scattering),[17] thermal properties (differential thermal calorimetry; DSC),[18−22] and dynamics (dynamic light scattering),[23] which are particularly useful in understanding the structure and conformation change of NIPA gels between swollen and shrunken states. In this study, the equilibrium volume fraction of NIPA gels is studied in both the swollen and shrunken states. Then simple scaling rules for the volume fractions of network polymers in swollen and shrunken states are derived, and the physical meaning is discussed with an emphasis on topological constraint.

Theoretical Background

A swelling equilibrium of neutral polymer gels is attained when the net osmotic pressure, Π, becomes zero. In the context of the Flory−Rehner (FR) formalism, Π consists of two contributions, i.e., the mixing free energy, Π_{mix}, and the elastic free energy, Π_{el}, as given by

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$$\Pi = \Pi_{\mathrm{mix}} + \Pi_{\mathrm{el}} \tag{1}$$

$$\Pi_{\mathrm{mix}} = -\frac{k_B T}{V_s}[\phi + \ln(1-\phi) + \chi\phi^2] \tag{2}$$

$$\Pi_{\mathrm{el}} = \nu k_B T\left[\frac{1}{2}\left(\frac{\phi}{\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] \tag{3}$$

where k_BT is the thermal energy, V_s is the molar volume of the solvent, ν is the number of effective polymer chains per unit volume, and χ is Flory's interaction parameter. ϕ and ϕ_0 are the network volume fractions at swelling equilibrium and at the reference state, respectively. Although the volume phase transition in neutral polymer gels has been predicted by theories of Tanaka,[4,5] Khokhlov,[6] Erman and Flory,[24] Grosberg and Nechaev,[25] and others, either quantitative agreement has not been attained or a large number of parameters are required to fit the experimental data. This suggests that consensus on the theoretical description of the volume phase transition of gels has not been obtained. Therefore, we do not discuss this issue in detail and simply employ a phenomenological expression of the interaction parameter employed by Hirotsu[26] to describe the swelling curve of NIPA gels having different initial monomer concentrations. In order to account for the steep or discrete volume transition, the χ parameter is assumed to be concentration dependent and has the following form[24]

$$\chi = \chi_1 + \phi\chi_2 \tag{4}$$

where

$$\chi_1 = (\Delta H - T\Delta S)/k_B T \tag{5}$$

and χ_2 is a constant. Note that eq 4 is purely phenomenological. ΔH and ΔS are the enthalpy and entropy per monomeric unit of the network related to the volume phase transition.

Experimental Section

A series of *N*-isopropylacrylamide polymer gels (NIPA gel) were prepared by redox polymerization. The NIPA monomer concentrations were varied from 200 mM to 1000 mM. The concentration of the cross-linker, *N,N'*-methylenebisacrylamide (BIS), was also varied from 2.50 to 12.49 mM by keeping the molar ratio of NIPA/BIS = 690/8.62. The pregel solution, containing NIPA, BIS, and 1.75 mM ammonium persulfate (initiator) in distilled water, was degassed and refrigerated for about 30 min to reduce the rate of the polymerization reaction. Then, 8 mM *N,N,N',N'*-tetramethylethylenediamine (accelerator) was added, and the solution was transferred in a thermostated water bath at 5 °C to initiate the reaction. More than 1 day was allowed for completion of gelation in a micropipet with the inner diameter d_0 of 471 μm. The prepared gel of cylindrical shape was taken out from the micropipet and washed with distilled water, followed by sealing in a micropipet having a larger inner diameter with an excess amount of distilled water. The diameter of the gel, *d*, was measured as a function of temperature with an image-analyzing system consisting of an inverted microscope, a video camera, an electric scaler, and a Color Measure Unit (MC-300, Flovel, Co., Tokyo). The error of the readout was estimated to be less than a few micrometers. The temperature of the gel was regulated with a RMS-6 (Lauda, Co. Germany). Whenever the temperature was changed, the diameter was repeatedly measured until two successive readouts with an interval of 30 min to a few hours became identical. In the region of the transition, the interval was prolonged to be 12 h in order to ensure thermal equilibrium.

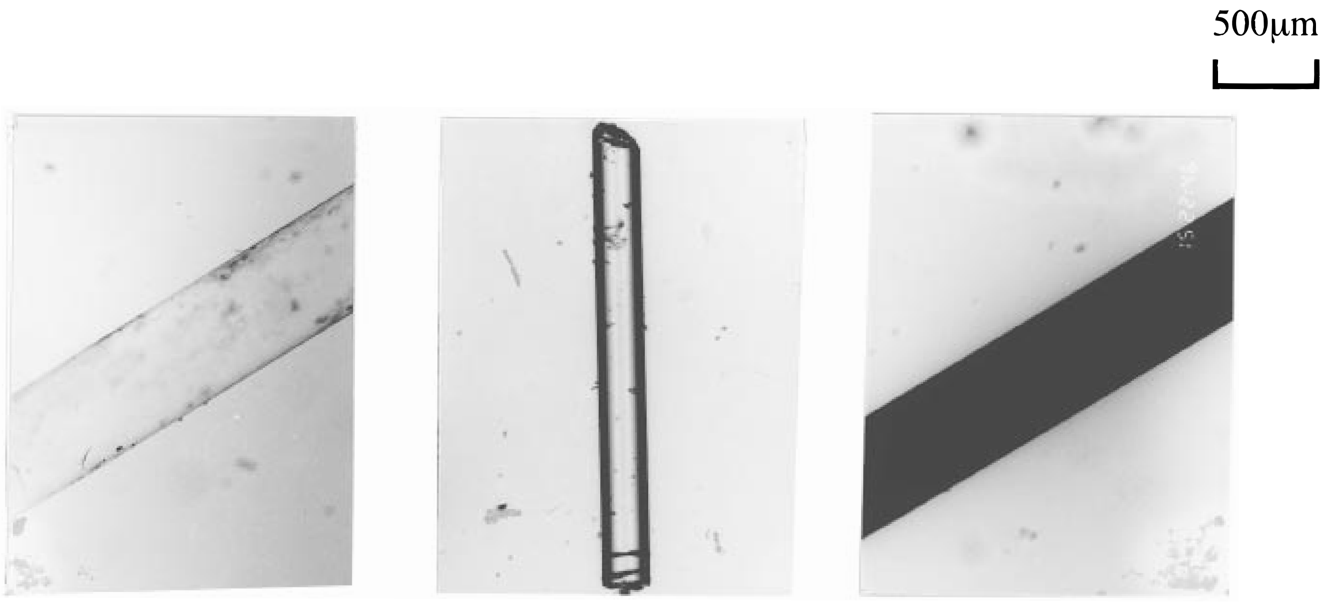
Results and Discussion

1. Swelling−Shrinking Curve. Figure 1 shows optical micrographs of cylindrical-shaped gels of NIPA (a) in the swollen state at 20 °C, (b) in the shrunken state at 36 °C, and (c) at 30 s after the temperature jump (T-jump) of the swollen gel at 20 °C, i.e. the gel shown in Figure 1a, to 45 °C. The NIPA initial monomer concentration, C_0, was 690 mM. The diameters, *d*'s, are (a) 535 and (b) 220 μm for the swollen and shrunken gel, respectively. It should be noted that both swollen and shrunken gels are transparent although several dusts are absorbed on the surface of the gels. On the other hand, the T-jumped gel, seen to be black, is completely opaque, indicating the presence of spatial inhomogeneity. It took a few tens of hours to recover transparency for the T-jumped gel. These micrographs suggest that the homogeneous shrunken state of a NIPA gel can be attained by elevating the temperature slowly enough to attain thermal equilibrium at each temperature. The following fact should also be noted here. Whenever temperature was changed stepwise in the shrunken state, a shrunken gel became hazy and it took time to recover the clarity (e.g., about 20 min and 1 h for stepwise increases of 2 and 3 °C, respectively).

Figure 2 shows the temperature dependence of the linear swelling ratio, d/d_0, for NIPA gels with different C_0's. As shown here, gels are in the swollen state at low temperatures and undergo a shrinking transition at $T_c \approx 34.0$ °C. Above T_c, the linear swelling ratio, d/d_0, seems to be invariant with temperature. This type of behavior in NIPA gels has been well-known, and a large number of investigations have been carried out.[4−9] However, two interesting facts can be drawn from the figure: (i) The value of d/d_0 does not depend on C_0 in the swollen state except for $C_0 = 200$ mM. On the other hand, (ii) d/d_0 in the shrunken state increases with C_0. We now elucidate the relationship between the swelling ratio and the initial monomer concentration in both the swollen and shrunken phases. It is more convenient to employ the volume swelling ratio, ϕ_0/ϕ, rather than d/d_0, where ϕ and ϕ_0 are the volume fractions of the polymer network at measurement and at preparation, respectively. The swelling ratio is simply given by

$$\phi_0/\phi = (d/d_0)^3 \tag{6}$$

In the original FR theory, ϕ_0 is defined at the dried network, i.e., $\phi_0 = 1$. However, it should be noted here that ϕ_0 is a controversial parameter for gels prepared in the presence of solvent, as discussed by Khokhlov.[9] Khokhlov defined ϕ_0 as the volume fraction at the reference state, which is different from that at preparation and is close to the volume fraction at the so-called Θ temperature. This means that the polymer chains between cross-links are in the unperturbed state. This situation is attained in bulk polymer chains. Most of the gels are prepared in the presence of solvent. Thus, the polymer−solvent interaction is inherently present during the gel formation, which results in a perturbed chain conformation. This leads to an ambiguity of the determination of the reference state. However, determination of such a "phantom" reference state is not practical. We believe that a gel network is formed in order to minimize the free energy of entropy elasticity and ϕ_0 is simply determined by the initial monomer



(a) 20°C; swollen **(b) 36°C; shrunken** **(c) 45°C; after T-jump**

Figure 1. Optical micrographs showing (a) swollen and (b) shrunken NIPA gels and (c) a NIPA gel after a temperature jump from the swollen state at 20 °C to 45 °C. Both swollen and shrunken gels are transparent, although the T-jumped gel, seen to be black, is opaque.

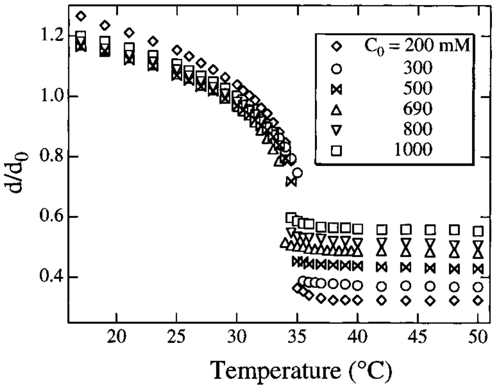


Figure 2. Temperature dependence of the linear swelling ratio, d/d_0, for NIPA gels with different initial monomer concentrations, C_0's.

concentration. Though the gels studied in this work are formed from monomer solutions, the resultant polymer network has to adjust its conformation in order to minimize its total free energy in the container. If the chains in the gel are not highly perturbed, it can be assumed that the elastic part of the free energy has its reference concentration identical to the one at its preparation condition. Obviously, this statement is incorrect for polymer chains in a good solvent cross-linked near its chain overlap concentration because the chains are highly perturbed and the Gaussian chain assumption, i.e., the FR theory, does not apply. As a matter of fact, the volume fraction at preparation is usually chosen as the reference volume fraction, for example in ref 16 and references therein. Therefore, we defined ϕ_0 as the polymer volume fraction at preparation, which leads to eq 6 and

$$\phi_0 \approx \frac{V_{\mathrm{NIPA}}}{1000} C_0 \qquad (7)$$

where V_{NIPA} is the molar volume of the NIPA monomeric unit (cm^3/mol).

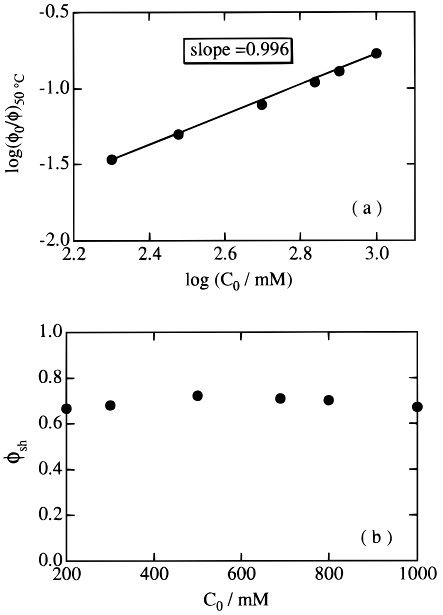


Figure 3. (a) Log−log plot of the variation of the volume swelling ratio, ϕ_0/ϕ, at 50 °C with C_0. (b) C_0 dependence of the polymer volume fraction at the shrunken state, ϕ_{sh}.

2. Shrunken State. Figure 3a shows the log−log plot of the variation of the volume swelling ratio, ϕ_0/ϕ, at 50 °C with C_0. The data collapse on to a linear line, and the slope is very close to unity. This readily leads to the invariance of ϕ_{sh} with respect to C_0, as shown in Figure 3b, because of the following relationship,

$$\phi_{\mathrm{sh}} \equiv \left(\frac{d}{d_0}\right)_{\mathrm{sh}}^{-3}\phi_0 = \left(\frac{\phi_0}{\phi}\right)_{\mathrm{sh}}^{-1}\frac{V_{\mathrm{NIPA}}}{1000}C_0 \sim C_0^{\ -1}\phi_0 \sim C_0^{\ 0} \qquad (8)$$

where the subscript sh denotes the shrunken state. The physical meaning of eq 8 is obvious. In the shrunken state, the polymer concentration is fixed irrespective of the initial monomer concentration, C_0. The value of ϕ_{sh}

is estimated to be about 0.65 from the figure. Note that a similar value of ϕ_{sh} is also obtained by differential thermal calorimetry (DSC).[22] A stoichiometric analysis with DSC on a series of NIPA gels having different polymer concentrations allowed us to estimate the polymer fraction in the shrunken state. It was found that a few water molecules per NIPA monomer are present near the NIPA monomers even in the shrunken state of NIPA gels and NIPA copolymer gels. These water molecules may be called bound water. Because of this presence, ϕ_{sh} is estimated to be around 0.6−0.8. The rather wide range of ϕ_{sh} is due to the difficulty of the quantitative analysis of ϕ_{sh} by DSC. The presence of a finite ϕ_{sh} (<1) is due to the fact that, in the shrunken state, the polymer concentration is dependent on the mixing part of the free energy but not on its elastic part. Further corrections related to this aspect were proposed by Grosberg and Nechaev (clumped globule model).[25] They introduced the concept of clumped globules in the shrunken state where every chain part on any arbitrary scale is globulized in itself and is segregated in space from all other parts of the same scale. This accounts for the nonphantomness of the network chain, which is progressively important as ϕ increases. It should be noted that the experimental finding given by eq 8 is not due to the effect of the glass transition. If the presence of a constant value of ϕ_{sh} results from a kinetic freezing of the structure by crossing the glass transition temperature, the value may change by annealing. Our DSC studies reveal a constant value of ϕ_{sh} irrespective of different thermal histories.[22] Furthermore, the gel was transparent even in the shrunken state, meaning that the thermodynamic equilibrium was attained at each temperature. A different type of correction was proposed by Cussler and co-workers.[27,28] They proposed a lattice−fluid theory which allows an expression of the lattice by incorporating holes. Though this theory is successfully used to predict the effect of hydrodynamic pressure, it does not explicitly predict the invariance of ϕ_{sh} with respect to C_0.

3. Swollen State. Contrary to the case for the shrunken state, d/d_0 in the swollen state does not depend on C_0 except for the case of $C_0 = 200$ mM. Note that $C_0 \approx 200$ mM was found to be the lowest initial monomer concentration to form a uniform gel. For $C_0 < 200$ mM, an incomplete gel, which swelled or shrank irregularly with changes in scanning temperature, was formed or no gelation took place. Therefore, it is deduced that the deviation of d/d_0 for the 200 mM gel is affected by such an incomplete gelation. A time-resolved light-scattering experiment on the gelation process of NIPA gels revealed that the critical concentration of NIPA monomers to form a gel with the same monomer to cross-link ratio lies at about 100 mM.[29] This tells one that the lowest NIPA concentration to form infinite clusters is about 100 mM. In the case of a swelling experiment, however, a well cross-linked network is required to hold the shape of the gel on swelling. Therefore, it seems to be reasonable that the value of 300 mM determined by the swelling experiment is the lower bound for gelation. If this speculation is correct, the invariance of d/d_0 with C_0 ($\geq$300 mM) is an essential feature of gel swelling. The invariance of d/d_0 with C_0 in the swollen state indicates the following scaling relation,

$$\phi_{sw} \equiv \left(\frac{d_0}{d}\right)_{sw}^{3} \phi_0 \sim {\phi_0}^{1} \tag{9}$$

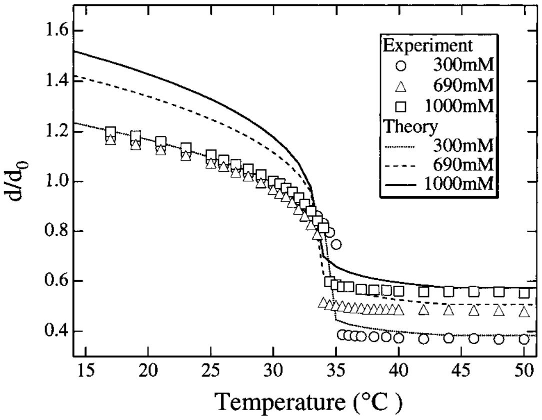


Figure 4. Comparison of the variations of d/d_0 with temperature predicted by the FR theory and obtained by the experiment.

This indicates that the volume fraction of the network in the swollen state depends on the initial monomer concentration. This is a surprising result, since the conventional theory predicts an invariance of ϕ_{sw} with respect to ϕ_0 (or C_0), as will be discussed in the next section.

4. Comparison with Theories. In order to reproduce the swelling curve with eqs 1−3, we employed the following values; $\chi_2 = 0.518$, $\Delta H = -12.46 \times 10^{-21}$ J, and $\Delta S = -4.717 \times 10^{-23}$ J/K, according to Hirotsu.[26] The value of ν was fixed to be the stoichiometric value, i.e.,

$$\nu = \frac{2C_{BIS}}{C_0}\frac{\phi_0}{V_{NIPA}} = \frac{2C_{BIS}}{1000} \tag{10}$$

where C_{BIS} is the concentration of the cross-linker, BIS. In eq 10, the molar volume of BIS is assumed to be the same as that of NIPA. Figure 4 shows the comparison of the variations of d/d_0 with temperature predicted by the FR theory and obtained by the experiment. As shown in the figure, a good agreement between the theoretical prediction (lines) and the experimental results (symbols) is attained in the shrunken phase. However, a strong deviation of the theoretical prediction of $(d/d_0)_{sw}$ from the experimental results is found in the swollen state. The theoretical value of $(d/d_0)_{sw}$ increases with C_0 while the experimental value of $(d/d_0)_{sw}$ remains constant. This comparison suggests that the theory overestimates Π_{mix} or underestimates Π_{el}. However, since Π_{mix} is not a function of ϕ_0, the strong dependence of ϕ_{sw} must result from an underestimation of Π_{el}.

In the case of gel preparation from concentrated monomer solutions or from bulk monomers, a large number of entanglements must be formed, which contribute to the swelling behavior as additional cross-links. The topological constraint may become more significant with increasing C_0 (or ϕ_0). Hooper et al. also observed a deviation of the swelling ratios between experiments and the FR theory.[13] They tried to predict the swelling behavior of NIPA gels by only using parameters for un-cross-linked polyNIPA aqueous solutions and concluded that this is due to the topological constraint.

Here, we propose a simple scaling form of the topological constraint. Figure 5 schematically shows the effect of the topological constraint, which is exhibited as additional cross-links. Suppose that we have two sheets of mesh having the same cross-link density. If we weave them together, the resultant cross-link den-

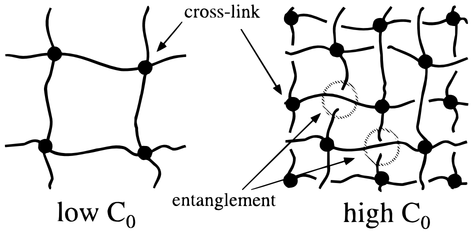


Figure 5. Schematic illustration showing the effect of the topological constraint which is exhibited as additional cross-links.

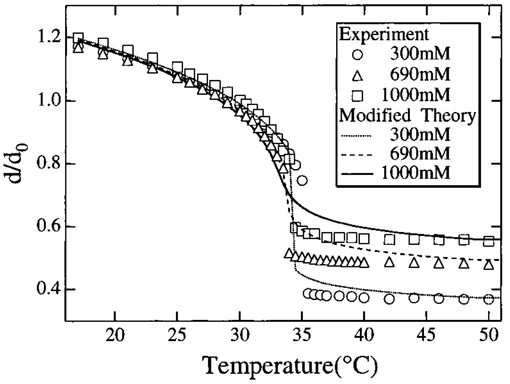


Figure 6. Comparison of the variations of d/d_0 with temperature predicted by the modified FR theory (lines; eq 12) and obtained by the experiment (symbols).

sity is expected to be twice as high as that of the previous ones. Therefore, it is reasonable to assume that the number of effective cross-links can be proportional to the initial monomer concentration. Hence, we rewrite ν by

$$\nu_e \equiv \nu_e(\phi_0) = \nu\frac{\phi_0}{\phi_{0,\mathrm{ref}}} = \nu\frac{C_0}{C_{0,\mathrm{ref}}} \qquad (11)$$

where $\phi_{0,\mathrm{ref}}$ (or $C_{0,\mathrm{ref}}$) is the lowest monomer volume fraction (or concentration) at which a uniform gel is formed. Thus the final equation for the swelling equilibrium is

$$\nu\frac{C_0}{C_{0,\mathrm{ref}}}\left[\frac{1}{2}\left(\frac{\phi}{\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] - \frac{1}{V_s}[\phi + \ln(1-\phi) + \chi\phi^2] = 0 \qquad (12)$$

Figure 6 is obtained by solving eq 12 with respect to ϕ/ϕ_0 and by plotting d/d_0 ($\equiv(\phi_0/\phi)^{1/3}$) as a function of temperature. In this case, the behavior of d/d_0 in the swollen state is successfully reproduced by choosing $C_{0,\mathrm{ref}}$ = 300 mM. Note that this is not an adjustable parameter and is the lowest concentration to form an infinite network which is responsible for swelling. We only use one adjustable parameter χ, where χ_1 and χ_2 are common parameters to reproduce all the swelling curves of gels having different C_0's. We learn from this figure that ϕ_{sw} strongly depends on C_0. The physical meaning of the strong dependence is now clarified as the topological constraint, which is exhibited as additional cross-links on swelling. In Figure 7, the volume fraction of the network in the swollen state at 20 °C, $(\phi_{sw})_{20°C}$, is plotted as a function of C_0 together with the results of the predictions by the FR (dashed line) and modified FR theories (solid line). It is clear from this figure that the experimental result, $(\phi_{sw})_{20°C}$, linearly increases with C_0 and that the modified FR theory well reproduces such a behavior.

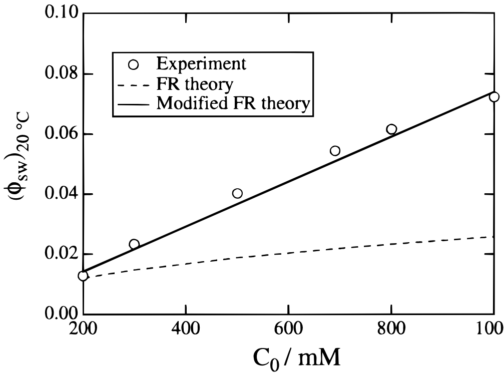


Figure 7. C_0 dependence of the polymer volume fraction in the swollen state at 20 °C, $(\phi_{sw})_{20°C}$. The solid and dashed lines are the calculated results by the modified FR and the FR theories, respectively.

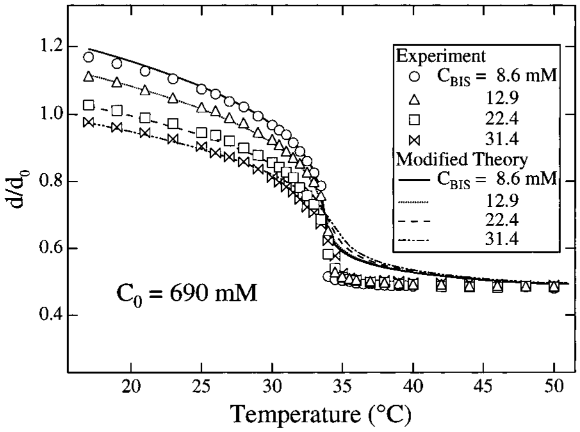


Figure 8. Temperature dependence of d/d_0 for NIPA gels (C_0 = 690 mM) with different cross-linker concentrations, C_{BIS}'s. Lines are obtained by the modified FR theory.

In order to demonstrate the effect of the cross-linking on the swelling equilibrium, a swelling curve was also measured for NIPA gels having different cross-link densities. Figure 8 shows the cross-linker concentration, C_{BIS}, dependence of the swelling curve for NIPA gels for which C_0 was fixed to be 690 mM. In this case, d/d_0 depends on C_0 in the swollen state, while it is independent of C_0 in the shrunken phase. Results of the theoretical prediction with the modified FR theory, which successfully reproduce the observed values of d/d_0 in the swollen state, are also shown in the figure. This result supports the validity of the modified theory and the concept that the entanglement effect becomes important for determination of the swelling ratio in the swollen state. A comparison of Figures 6 and 8 indicates that in the swollen state the swelling ratio depends not on C_0 but on the cross-linker concentration, C_{BIS}, whereas an opposite dependence appears in the shrunken state.

Before concluding this paper, it should be noted that a strong concentration dependence of χ is assumed in Figures 4, 7, and 8 in order to reproduce the volume phase transition of NIPA gels. The variations of χ for C_0 = 300, 690, and 1000 mM with temperature are shown as well as the variations of χ_1 and χ_2 in Figure 9. The jumpwise change in χ is ascribed to a sharp change in the network concentration, i.e., the gel volume, since χ is dependent on the network volume fraction (eq 4). Although such a treatment might be somewhat fictitious, it is beyond the scope of this paper to predict the shrinking curve of gels undergoing a discrete volume

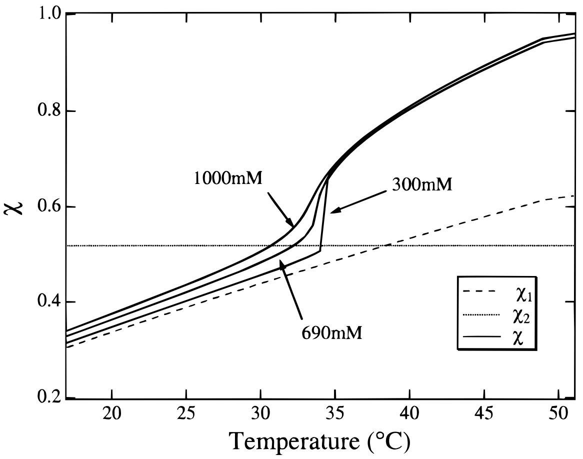


Figure 9. Temperature dependence of the χ parameter for $C_0 = 300$, 690, and 1000 mM used to calculate the temperature dependence of d/d_0. The variations of χ_1 and χ_2 are also shown.

transition. The significance of this work lies in the elucidation of the relationship between the polymer volume fraction and the initial monomer concentration in both shrunken and swollen states, as discussed with a simple scaling form.

Concluding Remarks

The swelling behavior of temperature sensitive NIPA polymer gels has been investigated as a function of the initial monomer concentration, C_0, in both the swollen and shrunken states. The polymer volume fraction in the shrunken state, ϕ_{sh}, is independent of C_0, indicating the presence of an iso-shrunken state irrespective of C_0 (i.e., $\phi_{sh} \sim C_0^0$). On the other hand, in the swollen state, the polymer volume fraction, ϕ_{sw}, is scaled as $\phi_{sw} \sim C_0^1$. This is interpreted with “additional cross-links” introduced by entanglements. A modified Flory−Rehner equation for the swelling equilibrium of gels, which successfully reproduced the experimental results on both the initial monomer and the cross-linker concentration dependencies without fitting parameters, is proposed by taking account of the topological constraints.

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