Theoretical Study of the Postgel Regime in Thermoreversible Gelation

Masahiko Ishida and Fumihiko Tanaka*

Department of Applied Physics, Faculty of Engineering, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184, Japan

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ABSTRACT: Phase diagrams of thermoreversible gels are derived by the use of two different conventional postgel treatments, *i.e.*, Flory's treatment and Stockmayer's treatment. Phase diagrams by Flory's treatment, which allows cycle formation in the gel network, often show two critical points for intermediate association constants, one in the sol region and the other in the gel region. In such a case three-phase equilibrium temperature appears. Existence of a critical solution point in the gel region suggests the possibility of phase separation into a dilute gel and a concentrated gel. One of these two critical points is a conventional type that lies on the stable coexistence curve (*binodal*), but the other one may lie on the metastable binodal. In contrast, phase diagrams by Stockmayer's treatment, which strictly excludes cycle formation in the gel network, often lead to the appearance of a tricritical point (TCP) where sol/gel transition curve intersects with the binodal line. This treatment gives no critical solution point, and hence gel/gel phase separation, in the postgel regime.

I. Introduction

Polymeric gels are roughly classified into chemical gels and physical gels. The binding energy of cross-links in chemical gels is much larger than the thermal energy due to a covalent bond, while cross-links in physical gels can be broken by thermal motion. Many natural polymers form such physical junctions. Since association and dissociation of the junctions can be in a thermal equilibrium, it is important to understand the phase behavior of physical gels.

Physical (or thermoreversible) gelation has been theoretically studied by the use of the percolation theory[1,2] and by the kinetic theory[3] based on Smoluchowski's equation. Many aspects of physical gelation, however, especially in the postgel regime are yet to be studied. In the preceding papers[4,5,6] thermoreversible gel networks are regarded as infinite aggregates of polymers in solution. This theory combines the multifunctional polycondensation theory,[7−14] especially the self-condensation of f-functional monomers, developed for chemical gels with the conventional Flory−Huggins' lattice theory[15−18] of polymer solutions. It was recently extended to include gels with multiple junctions.[19] In spite of such progress, there still remains a question regarding how best to treat the postgel regime theoretically. In the theoretical study of polycondensation by tree statistics, there have been two qualitatively different models on the postgel regime; one assumes the tree structure for a gel network as for the sol, but the other permits cycle formation within the network. The former was proposed by Stockmayer[8] and the latter by Flory.[7] Later Ziff and Stell[14] examined another possibility from a kinetic point of view. If we deal with gel formation as the limit of cluster growth and if our interest is limited to the gelation process only, both of the above-mentioned treatments in the postgel regime are acceptable. But, if our interest resides in the material properties of gels such as phase diagrams and viscoelasticity, we must carefully examine which treatment better explains the experiments.

In the preceding studies[4−6] on the phase behavior of thermoreversible gels, we have assumed the tree model for the gel network as well as the sol. In this study we shall apply the above-mentioned two treatments of the postgel regime to derive equilibrium phase diagrams of thermoreversible gels on the temperature−concentration plane and compare the results in detail. We confine ourselves for simplicity to pairwise associating systems in this paper. We obtain the extent of association, the cluster size distribution, and chemical potentials of all clusters as functions of the temperature and the polymer volume fraction by the use of multiple-equilibrium conditions for the cluster formation. We shall pay special attention to the difference in the phase diagrams derived by the two different treatments, so that we can see the effect of the network structure on the phase behavior of thermoreversible gels.

II. The Postgel Models by Flory and Stockmayer

Studies by Flory[7] and Stockmayer[8] on the basis of tree statistics provided the fundamental treatments of polymerization and gelation. Their studies start from the following two fundamental assumptions:

(i) All functional groups are equally reactive throughout the reacting process.

(ii) Reactions between functional groups on the same finite molecule (or cluster) are forbidden, *i.e.*, all finite clusters take Cayley's tree structure.

Under these assumptions, Flory[7] showed that the gel point is given by

$$\alpha^* = \frac{1}{f-1} \tag{2.1}$$

where the asterisk indicates the value at the gel point. Here α is defined as the probability that a given functional group of a branch unit (polymer in the present paper) leads via a chain of bifunctional units to another branch unit in the polyfunctional condensation polymerization. In the present paper dealing with the self-condensation of f-functional polymers, α becomes the extent of reaction. He also derived the size distribution of clusters in the pregel regime and the

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* Present address: Department of Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01, Japan.

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postgel regime. To treat the postgel regime, he introduced another assumption which allows for a specified degree of intramolecular reaction in the gel network, namely, the following:

(iii) The smaller root α' of the equation

$$x \equiv \alpha(1-\alpha)^{f-2} \tag{2.2}$$

for a given physically acceptable x corresponds to the extent of reaction with regard to the functional groups in the sol, and the larger one α'' gives the average extent of reaction for all functional groups in the system.

The relation

$$\alpha'(1-\alpha')^{f-2} = \alpha''(1-\alpha'')^{f-2} \tag{2.3}$$

holds by definition. By use of this assumption iii, he showed that the weight fraction W_S of the sol is given by

$$W_S = \frac{(1-\alpha'')^2}{\alpha''}\frac{\alpha'}{(1-\alpha')^2} \tag{2.4}$$

However, Stockmayer[8] later remarked that Flory's result in the postgel regime is inconsistent with the assumption ii, since it permits cycle formation in the gel network. To remove this inconsistency, he proposed another treatment of the postgel regime. He introduced a different assumption: (iv) The extent of reaction of functional groups in the finite clusters remains at $1/(f-1)$, its value at the gel point.

In the postgel regime the extent of reaction in the gel network takes the value $2/f$ appropriate to an infinite tree without cyclic structures. The weight fraction W_G of the gel then takes the form

$$W_G = \frac{(f-1)\alpha - 1}{1 - 2/f} \tag{2.5}$$

where α ($>\alpha^*$) is the extent of reaction with respect to all the functional groups.

In the following, we shall refer to the above two treatments as Flory's treatment and Stockmayer's treatment. In both treatments, the degree of reaction is described by a single parameter, the extent of reaction α, in the solution. Thus, it is difficult to see how the gel network reacts with floating clusters in the solution. To see this, Ziff and Stell[14] developed a kinetic theory of gelation and reinterpreted Flory's and Stockmayer's model from the time-dependent point of view. They indicated that Stockmayer's model forbids reaction between functional groups in the sol and those in the gel; thus, the gel network grows only through a limiting process of the cascade reaction among finite clusters. They also studied the asymptotic evolution of the gel fraction in the postgel regime by a new tree model which bridges the two extreme postgel models by Flory and Stockmayer. The exact analytic expression of the Ziff–Stell model was given by Yan.[20]

From a physical standpoint, the Flory model is closer to reality, since intramolecular connections are an essential feature of network structure. We elaborate this point of view in another paper.[21]

III. Definition of the Model Solution

We consider the model solution which consists of N_A polymer chains A and N_0 solvent molecules S (see Figure 1). In our series of studies we have shown such a model solution by the symbol (A•A/S). Each polymer chain consists of n statistical units and carries f functional groups which are distributed along the chain backbone. We assume that each functional group on a cluster reacts reversibly (associates) with a group on a different cluster. For simplicity we choose the volume of a unit cell, a^3, for that of both a solvent molecule and a statistical unit on a polymer chain. Let $\Omega \equiv V/a^3$ be the total number of lattice cells, where V is the total volume of the solution. The number of m-clusters which consist of m polymer chains in the solution is denoted by N_m. The total volume fraction occupied by the m-clusters is then given by

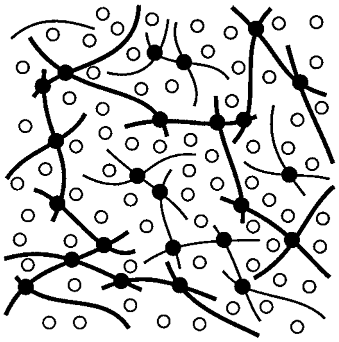

Figure 1. Illustration of the model solution with a thermoreversible gel. Thick and thin lines show polymer chains in the gel network and in finite clusters, respectively. Open and filled circles show solvent molecules and cross-links.

$$\phi_m = nm\nu_m \tag{3.1}$$

where $\nu_m \equiv N_m/\Omega$ is the number concentration of m-clusters in the solution. The volume fractions occupied by polymer chains in the sol (the sol polymer volume fraction) and in the gel (the gel polymer volume fraction) are given by

$$\phi^S = n\sum_{m\geq 1} m\nu_m \tag{3.2}$$

and

$$\phi^G = \phi - \phi^S \tag{3.3}$$

respectively, where the summation is taken over all finite clusters. Here the superscript S denotes the amount referring to the sol and G that referring to the gel. The quantities ϕ, ϕ^S, and ϕ^G show, therefore, the total volume fraction occupied by polymer chains in the solution (the total polymer volume fraction), the sol polymer volume fraction, and the gel polymer volume fraction, respectively. It is clear that the sol polymer volume fraction ϕ^S is equal to ϕ before the gel formation but becomes smaller than ϕ once a gel is formed. The volume fraction occupied by the solvent molecules in the solution is always given by

$$\phi_0 = 1 - \phi \tag{3.4}$$

if volume changes due to the association are neglected. In the following, any quantity regarding the solvent is indicated by the subscript 0.

IV. Lattice Theory of Reversibly Associating Polymer Solutions

In this section we briefly describe our theory of associating polymer solutions. It is developed by combining the Flory–Huggins' lattice theory[15–18] for polydisperse polymer solutions with the classical Flory–Stockmayer gelation theory mentioned above. The general scheme of our theory was explained in the preceding papers.[4,5]

We first consider the total free energy change ΔF to bring our system from the standard reference state to the actual solution with polydisperse associated polymers. The standard reference state is defined by the state in which N_A isolated polymer chains and N_0 isolated solvent molecules are separately prepared in a hypothetical crystalline state. The total free energy change is given by the sum of two components:

$$\Delta F = \Delta F_{\mathrm{rea}} + \Delta F_{\mathrm{mix}} \tag{4.1}$$

The first term on the right-hand side is the free energy required to bring the system from the reference state to an intermediate fictitious state in which isolated polymer chains are combined into clusters whose size distribution is exactly the same as that in the actual solution. It is expressed by the equation

$$\beta \Delta F_{\mathrm{rea}} = \sum_{m \geq 1} \Delta_m N_m + \delta_\infty N^{\mathrm{G}} \tag{4.2}$$

where $\beta \equiv 1/k_B T$ is the reciprocal temperature and N^{G} the number of polymer chains belonging to the gel network. On the right-hand side of the equation, Δ_m is the free energy to form an m-cluster in the intermediate state from m primary polymer chains:

$$\Delta_m = \beta(\mu_m^\circ - m\mu_1^\circ) \tag{4.3}$$

where μ_m° denotes the internal free energy of a cluster consisting of m polymer chains. By definition, Δ_m (<0) depends only on the temperature. In eq 4.2, δ_∞ is the free energy gain when an isolated polymer chain joins the macroscopic network. If cycle structures are completely forbidden in the macroscopic network, δ_∞ satisfies the condition

$$\delta_\infty = \lim_{m \to \infty} (\Delta_{m+1} - \Delta_m) \tag{4.4}$$

and is independent of the concentration ϕ, but, in general, it must depend on the total polymer volume fraction ϕ if cycle formation is allowed, because the average number of the cross-links per chain in the gel network increases with the concentration, and hence the absolute value of the binding free energy $|\delta_\infty|$ must also increase.

The second term on the right-hand of eq 4.1 is the free energy change produced when clusters in the intermediate state are mixed to get to the actual solution. We can obtain it by employing the conventional Flory–Huggins' lattice theory as

$$\beta \Delta F_{\mathrm{mix}} = \sum_{m \geq 1} N_m \ln \phi_m + N_0 \ln(1 - \phi) + \Omega\chi\phi(1 - \phi) \tag{4.5}$$

where $\chi = \chi(T)$ is the Flory–Huggins χ-parameter, which specifies the strength of the (net) contact interaction between a statistical unit on polymer chains and a solvent molecule.

We next consider the chemical potentials. The chemical potential $\Delta\mu_m$ of each finite-size cluster (m-cluster) in the actual solution can be found from the total free energy change ΔF by differentiation with respect to the number N_m of m-clusters under the conditions of constant temperature and constant number of solvent molecules. We are led to the result

$$\begin{aligned} \beta\Delta\mu_m \equiv \beta(\mu_m - \mu_m^\circ) &= \beta\left(\frac{\partial \Delta F}{\partial N_m}\right)_{T,N_0,N_{i\neq m},N^{\mathrm{G}}} \\ &= \Delta_m + 1 + \ln \phi_m - nm(\nu^{\mathrm{S}} + \nu_0) + \\ &\qquad nm\chi(1-\phi)^2 + \mathrm{m}\left(\frac{\partial \delta_\infty}{\partial \phi}\right)_{\mathrm{T}} \phi^{\mathrm{G}}(1-\phi) \end{aligned} \tag{4.6}$$

where $\nu^{\mathrm{S}} = \sum_m \nu_m$ is the total number concentration of finite-size clusters and $\nu_0 \equiv 1 - \phi$ the number concentration of solvent molecules. Similarly, we can obtain the chemical potentials $\Delta\mu_0$ of a solvent molecule in the solution, that of an unreacted polymer chain $\Delta\mu_1$, and that of a polymer chain belonging to a gel network $\Delta\mu_1^{\mathrm{G}}$ as

$$\begin{aligned} \beta\Delta\mu_0 \equiv \beta(\mu_0 - \mu_0^\circ) &= \beta\left(\frac{\partial \Delta F}{\partial N_0}\right)_{T,N_{\mathrm{m}},N^{\mathrm{G}}} \\ &= 1 + \ln(1-\phi) - (\nu^{\mathrm{S}} + 1 - \phi) + \\ &\qquad \chi\phi^2 - \left(\frac{\partial \delta_\infty}{\partial \phi}\right)_T \frac{\phi^{\mathrm{G}}}{n}\phi \end{aligned} \tag{4.7a}$$

$$\begin{aligned} \beta\Delta\mu_1 \equiv \beta(\mu_1 - \mu_1^\circ) &= \beta\left(\frac{\partial \Delta F}{\partial N_1}\right)_{T,N_0,N_{i\neq 1},N^{\mathrm{G}}} \\ &= 1 + \ln \phi_1 - n(\nu^{\mathrm{S}} + 1 - \phi) + n\chi(1-\phi)^2 + \\ &\qquad \left(\frac{\partial \delta_\infty}{\partial \phi}\right)_T \phi^{\mathrm{G}}(1-\phi) \end{aligned} \tag{4.7b}$$

$$\begin{aligned} \beta\Delta\mu_1^{\mathrm{G}} \equiv \beta(\mu_1^{\mathrm{G}} - \mu_1^{\mathrm{G}\circ}) &= \beta\left(\frac{\partial \Delta F}{\partial N^{\mathrm{G}}}\right)_{T,N_0,N_m} \\ &= \delta_\infty - n(\nu^{\mathrm{S}} + 1 - \phi) + n\chi(1-\phi)^2 + \\ &\qquad \left(\frac{\partial \delta_\infty}{\partial \phi}\right)_T \phi^{\mathrm{G}}(1-\phi) \end{aligned} \tag{4.7c}$$

To ensure that association in the solution is in a thermal equilibrium, we now impose the multiple-equilibrium conditions:

$$m\Delta\mu_1 = \Delta\mu_m \tag{4.8a}$$

$$\Delta\mu_1 = \Delta\mu_1^{\mathrm{G}} \tag{4.8b}$$

The condition (4.8a) gives the cluster size distribution function for finite clusters in the pregel regime in the form

$$\phi_m = K_m {\phi_1}^m \tag{4.9}$$

where

$$K_m \equiv \exp(m - 1 - \Delta_m) \tag{4.10}$$

is the equilibrium constant, which determines the strength of association between functional groups and depends only on the temperature. From the latter condition (4.8b) we find that the free energy to bind a single unreacted polymer chain into a gel network is given by

$$\delta_\infty = 1 + \ln \phi_1 \tag{4.11}$$

We next consider the Gibbs free energy Δg per lattice cell

$$\Delta g = \Delta\mu_0 \nu_0 + \sum_{m\geq 1} \Delta\mu_m \nu_m + \Delta\mu_1^{\mathrm{G}} \nu^{\mathrm{G}} \tag{4.12}$$

where $\nu^{\mathrm{G}} = N^{\mathrm{G}}/\Omega$ is the number concentration of polymer chains belonging to the gel. Under the multiple-equilibrium conditions it reduces to

$$\Delta g = (1 - \phi)\Delta\mu_0 + \frac{\phi}{n}\Delta\mu_1 \tag{4.13}$$

On substituting eqs 4.7a and 4.7b into this formula, we find

$$\beta\Delta g = \frac{\phi}{n}(1 + \ln \phi_1) + (1 - \phi)[1 + \ln(1 - \phi)] - (\nu^{\mathrm{S}} + 1 - \phi) + \chi\phi(1 - \phi) \tag{4.14}$$

V. Cluster Size Distribution

In this section we derive the cluster size distribution (4.9) as a function of the temperature and the polymer concentration. First, we consider the equilibrium constant K_m.

The free energy change Δ_m in forming an m-cluster consists of three parts:

$$\Delta_m \equiv \Delta_m^{\mathrm{comb}} + \Delta_m^{\mathrm{conf}} + \Delta_m^{\mathrm{bond}} \tag{5.1}$$

These three terms give the entropy change on combining m unreacted chains into a single m-cluster, the configurational entropy change of polymer chains caused by the constraint on the internal flexibility of cross-linked segments, and the free energy change on bonding, respectively. (In some of the preceding papers[4,6] the second term was not taken into account.)

According to the standard tree statistics,[8] the number of possible combinatorial ways to form a single m-cluster from m unreacted indistinguishable polymer chains, each carrying f identical functional groups, is given by $f^m\omega_m$, where

$$\omega_m \equiv \frac{(fm - m)!}{m!(fm - 2m + 2)!} \tag{5.2}$$

The combinatorial free energy change therefore takes the form

$$\Delta_m^{\mathrm{comb}} = -\ln(f^m \omega_m) \tag{5.3}$$

To find the configurational entropy, we employ the conventional lattice-theoretical formula for the entropy of disorientation. For a chain with chain length n, it takes the form[15,17]

$$S_1^{\mathrm{dis}} \equiv k_{\mathrm{B}} \ln\left[\frac{nz(z - 1)^{n-2}}{\sigma_1 \exp(n - 1)}\right] \tag{5.4}$$

where z is the lattice coordination number and σ_1 the symmetry number of the polymer chain. The symmetry number takes 2 if the polymer chain (or cluster) has symmetric structure and 1 if it has asymmetric structure. Therefore, for an m-cluster, we find

$$S_m^{\mathrm{dis}} \equiv k_{\mathrm{B}} \ln\left[\frac{nmz(z - 1)^{nm-2}}{\sigma_m \exp(nm - 1)}\right] \tag{5.5}$$

where σ_m is the symmetry number of the cluster. This formula gives the entropy gain to bring a cluster from the hypothetical crystalline state to a flexible amorphous state. The configurational free energy change is then given by

$$\Delta_m^{\mathrm{conf}} = -\beta T(S_m^{\mathrm{dis}} - mS_1^{\mathrm{dis}}) = -\ln\left\{m\frac{\sigma_1}{\sigma_m}\left[\frac{\sigma_1(z - 1)^2}{nze}\right]^{m-1}\right\} \tag{5.6}$$

In the following we assume for simplicity that there are very few symmetric clusters, so that we can fix $\sigma_1 = \sigma_m = 1$. Finally, the free energy change in bond formation is given by

$$\Delta_m^{\mathrm{bond}} = \beta(m - 1)\Delta f_0 \tag{5.7}$$

where Δf_0 is the standard free energy change for binding a pair of functional groups. From these three results we obtain the equilibrium constant in the form

$$K_m = fm\omega_m\left(\frac{f\lambda}{n}\right)^{m-1} \tag{5.8}$$

where the association constant

$$\lambda(T) = \frac{(z - 1)^2}{z}\exp(-\beta\Delta f_0) \tag{5.9}$$

depends on the strength of a single pairwise bond.

Substituting eq 5.8 into eq 4.9, we can find the cluster size distribution:

$$\phi_m = \frac{n}{\lambda} m\omega_m x^m \quad (m = 1, 2, ...) \tag{5.10}$$

$$\nu_m = \frac{1}{\lambda}\omega_m x^m \quad (m = 1, 2, ...) \tag{5.11}$$

where

$$x \equiv f\lambda\phi_1/n \tag{5.12}$$

is the number of functional groups $f\phi_1/n$ carried by the free polymer chains in the solution multiplied by a temperature shift factor $\lambda(T)$. From these results we can obtain the total number concentration of the finite clusters

$$\nu^{\mathrm{S}} = \sum_{m\geq 1} \nu_m = \frac{1}{\lambda}S_0(x) \tag{5.13}$$

and the polymer volume fraction of the sol

$$\phi^{\mathrm{S}} = n\sum_{m\geq 1} m\nu_m = \frac{n}{\lambda}S_1(x) \tag{5.14}$$

in the pregel regime. Here S_0 and S_1 are the 0th and the first moment of the Stockmayer distribution.[8] More generally the kth moment is defined by

$$S_k(x) \equiv \sum_{m\geq 1} m^k \omega_m x^m \tag{5.15}$$

The first three moments are[8]

$$S_0(x) = \frac{\alpha(1 - f\alpha/2)}{f(1 - \alpha)^2} \tag{5.16a}$$

$$S_1(x) = \frac{\alpha}{f(1 - \alpha)^2} \tag{5.16b}$$

$$S_2(x) = \frac{\alpha(1 + \alpha)}{f(1 - \alpha)^2[1 - (f - 1)\alpha]} \tag{5.16c}$$

Here α is a parameter defined by the root of the equation

$$x \equiv \alpha(1 - \alpha)^{f-2} \tag{5.17}$$

and gives the extent of association in the solution in the pregel regime. On the other hand, in the postgel regime we must replace α by α^S, *i.e.*, the extent of association of functional groups carried by the polymer chains in the sol. With the help of these moments, we can simply express the number- and weight-average cluster size, $\langle m\rangle_n$ and $\langle m\rangle_w$, in the sol as

$$\langle m\rangle_n \equiv \frac{\sum_m m\nu_m}{\sum_m \nu_m} = \frac{S_1(x)}{S_0(x)} = \frac{1}{1 - f\alpha^S/2} \tag{5.18}$$

and

$$\langle m\rangle_w \equiv \frac{\sum_m m^2\nu_m}{\sum_m m\nu_m} = \frac{S_2(x)}{S_1(x)} = \frac{1 + \alpha^S}{1 - (f - 1)\alpha^S} \tag{5.19}$$

respectively. The relation $\alpha^S \equiv \alpha$ holds in the pregel regime.

A. Pregel Regime and Sol/Gel Transition. The tree gelation theory assumes that finite clusters can have no cycle structure. This assumption determines the critical extent of association $\alpha^* = 1/(f - 1)$ at which gel begins to appear. This result is obtained from the divergence of the weight-average cluster size (5.19). In the pregel regime where $\alpha < \alpha^*$ holds, the volume fraction occupied by the polymer chains belonging to the sol must always equal the total polymer volume fraction, $\phi^S = \phi$, since no gel network exists. Thus, the total polymer volume fraction ϕ and the extent of association α satisfy the relation

$$\frac{\lambda}{n}\phi = \frac{\alpha}{f(1 - \alpha)^2} \tag{5.20}$$

With the help of eq 5.20, we can express ν^S as a function of ϕ and α by

$$\nu^S = \frac{\phi}{n}\left(1 - \frac{f\alpha}{2}\right) \tag{5.21}$$

On substituting the critical value of α in eq 5.20, we find the gelation threshold ϕ^* of the total polymer volume fraction and the volume fraction of the free chains just at gelation as

$$\frac{\lambda}{n}\phi^* = \frac{f - 1}{f(f - 2)^2} \tag{5.22}$$

and

$$\frac{\lambda}{n}\phi_1^* = \frac{1}{f}\alpha^*(1 - \alpha^*)^{f-2} = \frac{(f - 2)^{f-2}}{f(f - 1)^{f-1}} \tag{5.23}$$

respectively.

B. Postgel Regime. In the postgel regime, the extent of association α^S in the sol may be different from that, α^G, in the gel. The average extent α in the entire solution should be related to them through the equation

$$\alpha = \alpha^S W_S + \alpha^G W_G \tag{5.24}$$

where $W_S \equiv \phi^S/\phi$ and $W_G \equiv \phi^G/\phi$ are the weight fraction of the polymers belonging to the sol and gel, respectively.

B1. Flory's Treatment. In Flory's treatment, α' and α'' in the two relations (2.3) and (2.4) are regarded as α^S and α, respectively. On the other hand, since all the finite clusters are assumed to keep their tree structure in the postgel regime, the relation between the sol polymer volume fraction ϕ^S and the extent of association α^S in the sol must remain naturally the same as that in the pregel regime:

$$\frac{\lambda}{n}\phi^S = \frac{\alpha^S}{f(1 - \alpha^S)^2} \tag{5.25}$$

In order to satisfy both relations (2.4) and (5.25), the relationship between the total polymer volume fraction ϕ and the average extent of association α in the postgel regime must be given by

$$\frac{\lambda}{n}\phi = \frac{\alpha}{f(1 - \alpha)^2} \tag{5.26}$$

from which α is found as a function of the polymer volume fraction. By using the relation (2.3) with $\alpha' = \alpha^S$ and $\alpha'' = \alpha$, the extent of association α^S in the sol can also be found as a function of the polymer concentration. For the quantities regarding the sol, we must use α^S for the extent of reaction. For example, the volume fraction of the free polymer chains is given by

$$\frac{\lambda}{n}\phi_1 = \frac{1}{f}\alpha^S(1 - \alpha^S)^{f-2} \tag{5.27}$$

and the total number concentration of the finite clusters by

$$\nu^S = \frac{\phi^S}{n}\left(1 - \frac{f\alpha^S}{2}\right) \tag{5.28}$$

By use of this volume fraction (5.27) and the relation (4.11), we can evaluate the free energy change δ_∞ for binding an isolated polymer chain to a gel network as

$$\delta_\infty = 1 + \ln\left[\frac{n}{f\lambda}\alpha^S(1 - \alpha^S)^{f-2}\right] \tag{5.29}$$

B2. Stockmayer's Treatment. Stockmayer postulates assumption iv instead of iii in the postgel regime. We, therefore, have $\alpha^S = \alpha^*$ and $\alpha^G = 2/f$. Because of assumption iv, the volume fraction of the sol ϕ^S remains constant at $\phi^S = \phi^*$. From eq 2.5 or eq 5.24, in the postgel regime we find the following relation between the average extent of association α and the weight fraction $W_S = \phi^*/\phi$ of the sol against the total polymer weight:

$$\alpha = \frac{2}{f} - \frac{f-2}{f(f-1)} W_S = \frac{2}{f} - \frac{f-2}{f(f-1)} \frac{\phi^*}{\phi} \qquad (5.30)$$

The number concentration of the finite clusters and the volume fraction of the free polymer chains are given by

$$\nu^S = \frac{1}{2\lambda f(f-2)} \qquad (5.31)$$

and

$$\frac{\lambda}{n}\phi_1 = \frac{\lambda}{n}\phi_1^* = \frac{(f-2)^{f-2}}{f(f-1)^{f-1}} \qquad (5.32)$$

respectively. Substituting relation (5.32) into eq 4.11, we obtain

$$\delta_\infty = 1 + \ln(\phi_1^*) \qquad (5.33)$$

Thus, the free energy change δ_∞ is *independent* of the total polymer volume fraction ϕ. This result comes from assumption iv and agrees with the strict tree assumption for the gel.

VI. Numerical Calculation and Phase Diagrams

In order to see the difference between Flory's and Stockmayer's postgel models more clearly, we next proceed to the study of the phase behavior of the solution. The coexistence curve (*binodal*) for a dilute phase with polymer volume fraction ϕ' to be in a thermal equilibrium with a concentrated phase with polymer volume fraction ϕ'' is given by the coupled equations:

$$\Delta\mu_1(\phi',T) = \Delta\mu_1(\phi'',T) \qquad (6.1a)$$

$$\Delta\mu_0(\phi',T) = \Delta\mu_0(\phi'',T) \qquad (6.1b)$$

On the other hand, we can find the thermodynamic stability limit (*spinodal*) by the condition

$$\frac{\partial^2 \Delta g}{\partial \phi^2} = 0 \qquad (6.2)$$

From eqs 4.14 and 6.2, the spinodal is given by

$$\frac{\kappa(\phi)}{n\phi} + \frac{1}{1-\phi} - 2\chi = 0 \qquad (6.3)$$

with a new function $\kappa(\phi)$ defined by[4,5]

$$\kappa(\phi) \equiv \phi \frac{\partial}{\partial \phi}\left[1 + \phi^G \frac{\partial}{\partial \phi}\right] \ln \phi_1 = \phi\left\{\left[1 + \frac{\partial \phi^G}{\partial \phi}\right]\frac{\partial \delta_\infty}{\partial \phi} + \phi^G \frac{\partial^2 \delta_\infty}{\partial \phi^2}\right\} \qquad (6.4)$$

The κ-function shows that, while the spinodal depends on the cluster size distribution in the pregel regime, in the postgel regime the free energy change for binding an isolated polymer chain to a gel network plays an important role in the stability.

From these equations and above-mentioned relationships in each postgel treatment, we can show the phase behavior of reversibly associating polymer solutions on the basis of Flory's or Stockmayer's postgel treatment. For example, the κ-function is explicitly given by

$$\kappa(\phi) = \frac{1-(f-1)\alpha^S}{1+\alpha^S} = \frac{1}{\langle m \rangle_w} \qquad (6.5)$$

in Stockmayer's treatment. This function is similar to that in the pregel regime. That is, the extent of association in the sol α^S is given by the relation $\alpha^S = \alpha$ in the pregel regime, while it is $\alpha^S = \alpha^*$ in the postgel regime. Thus, in the postgel regime this function vanishes since the weight-average cluster size is always infinite. In the case of Stockmayer's treatment, the *spinodal* is determined only by the degree of association in the sol and the total polymer volume fraction.

On the other hand, the κ-function in the postgel regime on the basis of Flory's treatment can be explicitly given by the use of eq 5.27:

$$\kappa(\phi) = \frac{1-(f-1)\alpha}{1+\alpha}\left[2 - \frac{\phi^S}{\phi}\frac{1-(f-1)\alpha}{1+\alpha}\langle m \rangle_w\right] + \frac{\phi^G}{\phi}\frac{(f-1)\alpha^2(\alpha+3) - 3\alpha - 1}{(1+\alpha)^3} \qquad (6.6)$$

For the numerical calculation we take the temperature and the total polymer volume fraction as independent variables. As the temperature variable, we introduce the familiar reduced temperature $\tau \equiv 1 - \Theta/T$ measured relative to the Θ-temperature. We then assume the form

$$\chi = 1/2 - \psi_1 \tau \qquad (6.7)$$

for the χ-parameter, where ψ_1 is the entropy parameter of order unity which is related to the entropy part of the nonassociative molecular interaction. The association constant (5.9) can be rewritten as

$$\lambda(T) = \frac{(z-1)^2}{z} \exp(\Delta s_0/k_B) \exp(-\beta\Delta\epsilon) \qquad (6.8)$$

where Δs_0 and $\Delta\epsilon$ (<0) are the entropy and energy contributions to Δf_0. For convenience of numerical calculation we here express this factor $\lambda(T)$ as

$$\lambda(T) = \lambda_0 \exp[\gamma(1-\tau)] \qquad (6.9)$$

with

$$\lambda_0 \equiv \frac{(z-1)^2}{z} \exp(\Delta s_0/k_B) \qquad (6.10)$$

and

$$\gamma \equiv \frac{-\Delta\epsilon}{k_B\Theta} \qquad (6.11)$$

Thus, we have three material parameters ψ_1, λ_0, and γ. In addition to these three, we must specify the number n of statistical units on a primary polymer chain and its functionality f. In the following, we shall fix these parameters at $n = 100$, $f = 10$, $\gamma = 1.0$, and $\psi_1 = 1.0$ as an example.

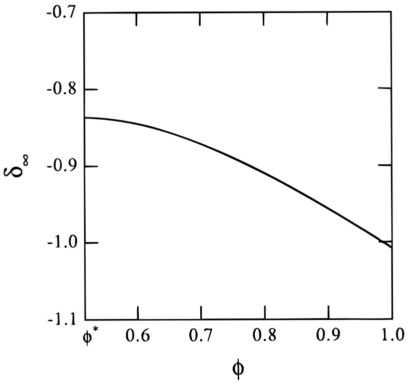

Figure 2. Free energy gain δ_∞, in Flory's treatment, produced when an isolated polymer chain is connected to a gel network. It is shown as a function of the total volume fraction ϕ of the polymer under the conditions: $n = 100$, $f = 10$, $\lambda_0 = 1.0$, $\gamma = 1.0$, and $\psi_1 = 1.0$.

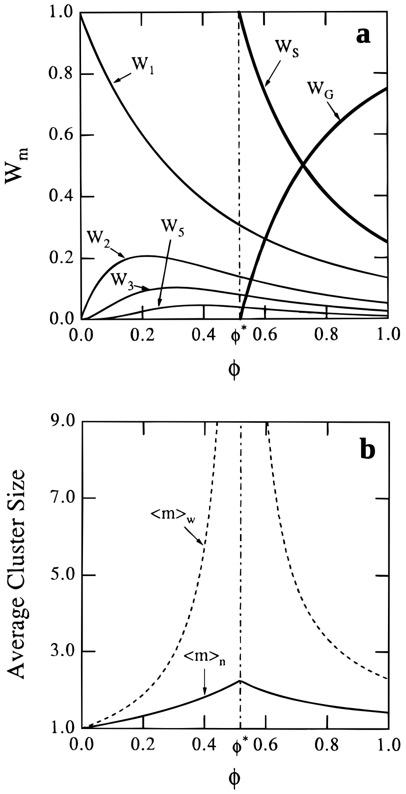

Figure 3. Flory's treatment: (a) Weight distribution of the clusters as a function of the total volume fraction ϕ of the polymer at a given temperature with the same parameters as in Figure 2. W_m, W_S, and W_G represent weight fractions of the m-clusters and the sol and gel networks, respectively. (b) Number-average (solid line) and weight-average (dashed line) cluster size are shown as a function of the total volume fraction ϕ for the same parameters as the case of a.

Figure 2 shows the free energy change δ_∞ in Flory's treatment as a function of the total volume fraction of the polymer. It is clear that the free energy change depends on the total polymer volume fraction, and hence this treatment permits cycle formation in a gel network.

Parts a and b of Figure 3 show the weight distribution of the clusters and the number- and weight-average cluster sizes calculated on the basis of Flory's treatment as functions of the total volume fraction ϕ of the polymer. Here, $W_m \equiv \phi_m/\phi$ represents the weight fraction of m-clusters relative to the total polymer weight. In Figure 3b solid and dashed lines show the number- and weight-average cluster sizes, respectively.

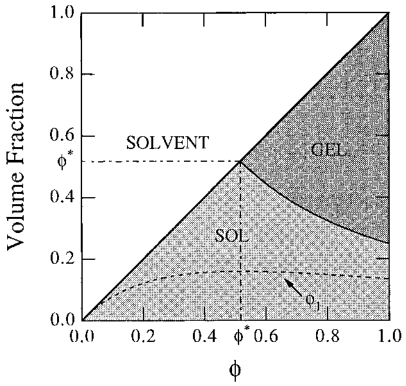

Figure 4. Relative amount of the three portions (solvent, sol, and gel) shown as a function of the total polymer concentration in Flory's treatment. The dashed line indicates the volume fraction ϕ_1 of the unreacted polymer chains. The asterisk indicates the amount at gelation ($n = 100$, $f = 10$, $\lambda_0 = 1.0$, $\gamma = 1.0$, $\psi_1 = 1.0$).

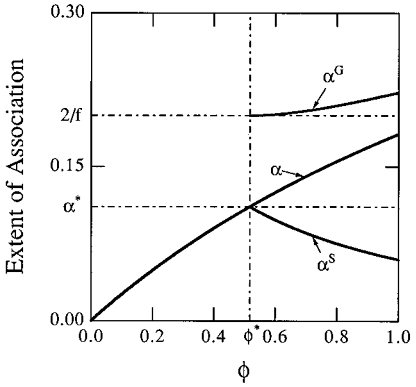

Figure 5. Extent of association α for the entire solution, α^S for the sol, and α^G for the gel in Flory's treatment shown as functions of the total polymer volume fraction ϕ at a given temperature ($n = 100$, $f = 10$, $\lambda_0 = 1.0$, $\gamma = 1.0$, $\psi_1 = 1.0$).

Observe that the weight average diverges at gelation, while the number-average remains finite. If the distribution and the average cluster sizes are plotted against the average extent of association α, they agree with the results obtained by Flory[7] for chemical gels as functions of the extent of reaction, but for physical gels they should be shown as functions of the polymer volume fraction ϕ and the temperature because they are thermally controlled. Figure 4 shows how the total volume is decomposed into the three portions (solvent, sol, and gel) under a certain condition. In this figure the dashed line indicates the volume fraction ϕ_1 of the free polymer chains in this solution. It is clear from Figure 4 that the amount of polymer chains in the sol and that of the free polymer chain in the solution become maximum at the sol/gel transition concentration. That is, if we add polymer chains in the solution with an arbitrary concentration, the sol portion naturally increases in the pregel regime but, in the postgel regime, the gel network absorbs not only the newly added polymer chains but also other polymer chains or clusters already existing in the sol. This result agrees with the kinetic description of Flory's model given by Ziff and Stell.[14] Their description suggests the association between unreacted functional groups in the gel network and in finite clusters. From Figure 5 it is also clear that further association between the functional groups which remain unreacted in the gel takes place with an increase of the polymer concentration, so that the extent of association α^G in the gel becomes greater

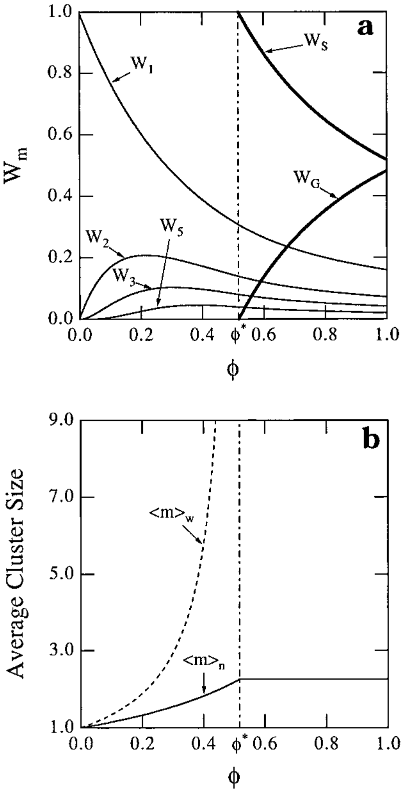

Figure 6. Stockmayer's treatment: (a) Weight distribution of the clusters as a function of the total volume fraction ϕ of the polymer. (b) Number-average (solid line) and weight-average (dashed line) cluster sizes are shown as a function of the total volume fraction ϕ ($n = 100$, $f = 10$, $\lambda_0 = 1.0$, $\gamma = 1.0$, $\psi_1 = 1.0$).

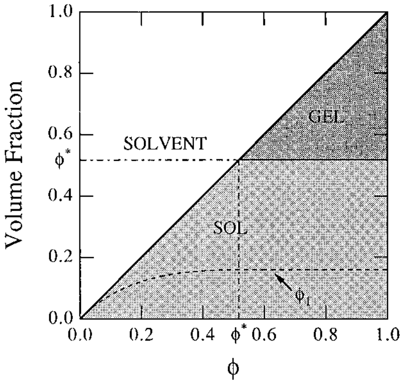

Figure 7. Relative amount of the three portions (solvent, sol, and gel) shown as a function of the total polymer concentration in Stockmayer's treatment. The dashed line indicates the volume fraction ϕ_1 of the unreacted polymer chains. The asterisk indicates the amount at gelation ($n = 100$, $f = 10$, $\lambda_0 = 1.0$, $\gamma = 1.0$, $\psi_1 = 1.0$).

than the tree value 2/*f*. That is, the increase of the polymer concentration leads to cycle formation on the gel network.

Figures 6–8 show the results obtained by Stockmayer's treatment. As Figure 7 shows, the sol fraction and the volume fraction of free polymer chains always stay constant in the postgel regime. Similarly, the fraction of the finite clusters remains constant because it depends only on the amount of the free polymer chains. Similarly, various types of average cluster sizes remain also constant in the postgel regime, especially the weight-average cluster size being always infinite. Thus, if we add polymer chains in the solution in the postgel regime, all added polymer chains are absorbed into the gel. In contrast to Flory's treatment, we have no association between any finite cluster and the gel network. The average extent of association α in the solution asymptotically approaches the tree value 2/*f* as the polymer volume fraction ϕ increases. This behavior distinguishes Stockmayer's tree model from that proposed by Ziff and Stell.[14]

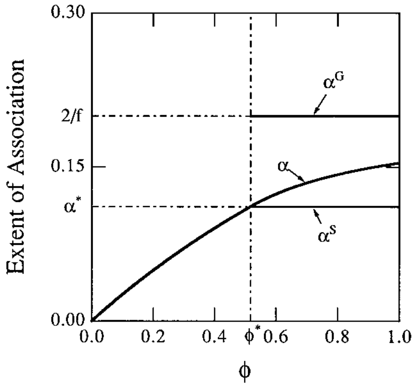

Figure 8. Extent of association α for the entire solution, α^S for the sol, and α^G for the gel in Stockmayer's treatment shown as functions of the total polymer volume fraction ϕ at a given temperature ($n = 100$, $f = 10$, $\lambda_0 = 1.0$, $\gamma = 1.0$, $\psi_1 = 1.0$).

Parts a–c of Figure 9 show the calculated phase diagrams in Flory's treatment. The parameter λ_0 is varied from figure to figure. The sol/gel transition curve, binodal, spinodal, and critical solution point are drawn by dashed line, thick line, thin line, and open circle, respectively. U indicates the unstable region. For smaller values of λ_0, and/or γ, a critical point lies in the sol region (Figure 9a). As λ_0 increases, we find two critical points, one lying in the sol region and the other in the gel region (Figure 9b). The existence of a critical point in the gel region suggests the possibility of gel/gel phase equilibrium. [This phenomenon corresponds to the volume transition of chemical gels. In chemical gels analogous phase diagrams have been derived (*e.g.*, ref 22).] As λ_0 further increases, the critical point in the sol region and the critical end point approach and unite with each other, so that this critical point disappears and sol/sol phase separation becomes impossible (Figure 9c).

Parts a and b of Figure 10 magnify the critical region in the phase diagrams for two different values of intermediate association strength. Although one of the two critical points always lies on the stable binodal, the other does not always lie on it; the critical point in the gel region lies at the inner position, *i.e.*, on the metastable binodal, away from the stable binodal in the case of Figure 10a. In the case where both of the critical points lie on the stable binodal, we can generally find a three-phase equilibrium temperature, τ_{TP}, at which we will probably observe either sol/gel or gel/gel phase equilibrium (Figure 10b) depending on the overall concentration ϕ.

Parts a–c of Figure 11 show the same as parts a–c of Figure 9 but with calculated phase diagrams in Stockmayer's treatment. A filled circle in Figure 11c indicates the tricritical point (TCP) at which the sol/gel transition curve (continuous phase transition) merges into the coexistence curve (first-order phase transition). If either λ_0 or γ exceeds a certain critical value, the solution can always have a tricritical point instead of a critical point in this treatment. This is in contrast to Flory's treatment in which we always find a critical

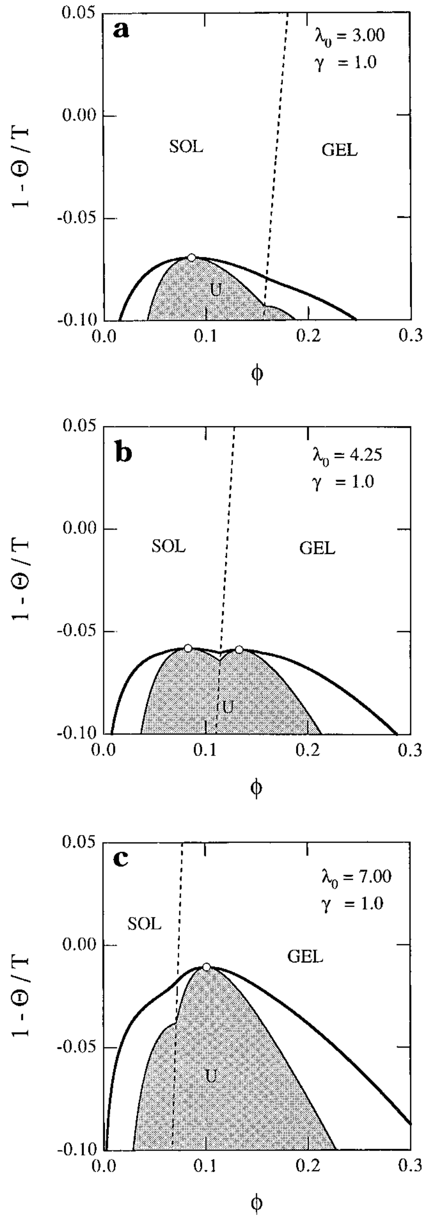

Figure 9. Phase diagrams of thermoreversible gels for various association constants, (a) $\lambda_0 = 3.00$, (b) $\lambda_0 = 4.25$, and (c) $\lambda_0 = 7.00$, in Flory's treatment. Lines in the figure show sol/gel transition (dashed line), binodal (thick line), and spinodal (thin line). U indicates the unstable region. The open circle denotes the critical point ($n = 100$, $f = 10$, $\gamma = 1.0$, $\psi_1 = 1.0$).

point either in the sol region or in the gel region or in both of them.

VII. Conclusions and Discussion

We have studied the phase diagrams of thermoreversible gels with special attention to the postgel regime. In particular, two conventional models in the postgel regime developed for chemical gels are reinterpreted for the study of physical gels. It turns out that these two different models can be successfully applied to the physical gels without violating the thermodynamic requirements. Flory's postgel treatment produces critical points in both sol and gel concentration regions. The existence of a critical point in the gel region suggests the possibility of gel/gel phase separation. Another remarkable point of Flory's treatment is the possibility of a critical point lying off the stable binodal. In this case there are two sets of conjugate concentrations which can satisfy the conditions (6.1a) and (6.1b), and a metastable two-phase equilibrium, *i.e.*, the metastable binodal, appears in a nucleation process. We can find similar phase behavior in polydisperse polymer solutions with a concentration-dependent interaction parameter[23] and also in a polymer mixture which consists of two different species of polymer chains capable of reversibly forming dimers.[24]

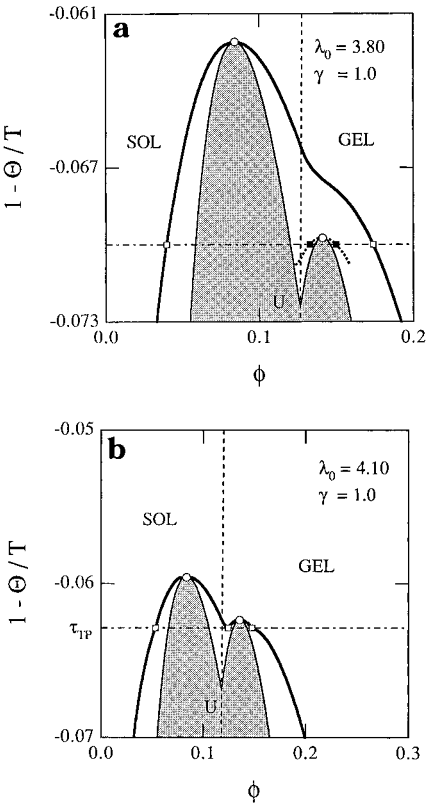

Figure 10. Magnification of the critical region in phase diagrams of thermoreversible gels with intermediate association strengths, (a) $\lambda_0 = 3.80$ and (b) $\lambda_0 = 4.10$, in Flory's treatment. Lines in the figure show sol/gel transition (dashed line), binodal (thick line and hollow square), and spinodal (thin line). The metastable two-phase coexistence condition (filled square) is indicated by a dotted line. The temperature τ_{TP} is the three-phase coexistence temperature ($n = 100$, $f = 10$, $\gamma = 1.0$, $\psi_1 = 1.0$).

On the other hand, Stockmayer's treatment will never lead to a gel/gel phase separation, because the coexistence of phases with the same specified tree structure at different concentrations seems physically impossible. It, instead, leads to the appearance of a tricritical point at the intersection of the sol/gel transition line and the binodal.

From a kinetic point of view, Ziff and Stell[14] proposed a new model which takes reaction between sol clusters and the gel network into account, while cycle formation in the gel is forbidden as in Stockmayer's model. If we apply this model to our theory, we must use the relation (5.25) as in Flory's treatment. The relation between α and α^S must be given by

$$\alpha = \left(\alpha^S - \frac{2}{f}\right)W_S + \frac{2}{f} \tag{7.1}$$

from eq 5.24 and the tree assumption $\alpha^G = 2/f$, while the relation between the overall polymer concentration

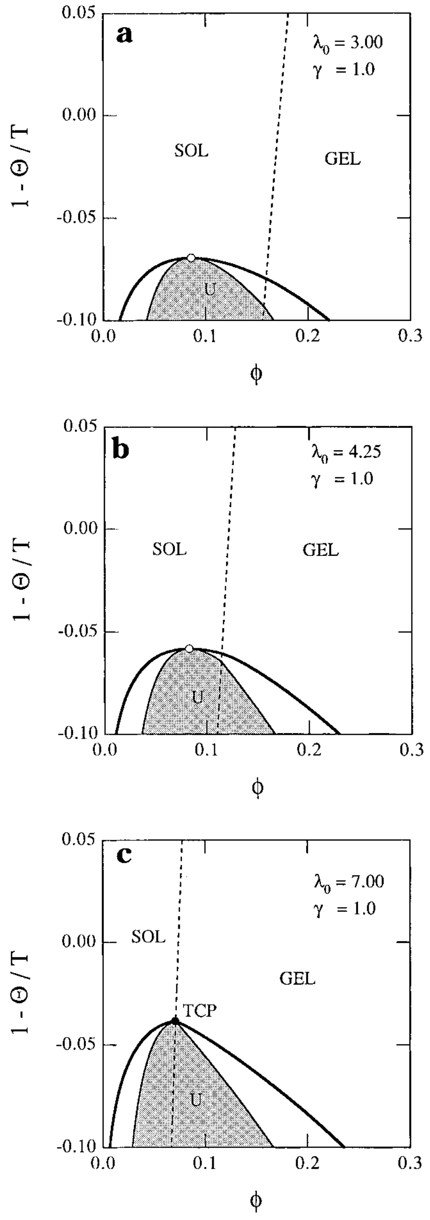

Figure 11. Phase diagrams of thermoreversible gels for various association constants, (a) $\lambda_0 = 3.00$, (b) $\lambda_0 = 4.25$, and (c) $\lambda_0 = 7.00$, in Stockmayer's treatment. Lines in the figure show sol/gel transition (dashed line), binodal (thick line), and spinodal (thin line). Open and filled circles denote the critical point and the tricritical point (TCP), respectively ($n = 100$, $f = 10$, $\gamma = 1.0$, $\psi_1 = 1.0$).

ϕ and the extent of association $\alpha > \alpha^*$ is expressed as

$$W_s = \frac{\left(1 - \frac{f\alpha}{2}\right)\left(\frac{f}{2} - (f-1)\alpha\right)}{\left(\frac{f}{2} - 1\right)^2 \alpha} \tag{7.2}$$

as derived by Yan.[20] In contrast to Stockmayer's tree treatment, we find, however, that chemical potentials do not fulfill the Gibbs–Duhem relation:

$$(1 - \phi)\, d\Delta\mu_0 + \frac{\phi}{n}\, d\Delta\mu_1 = \left[\frac{\alpha}{(1-\alpha)^2} - \frac{\alpha^S}{(1-\alpha^S)^2}\right]\frac{1 - (f-1)\alpha^S}{\alpha^S(1-\alpha^S)}\, d\alpha^S \neq 0 \tag{7.3}$$

So we must conclude either that the Ziff–Stell treatment is applicable only to the case of irreversible gelation or that we must modify our chemical potentials to cope with the situation where the extent of association decreases in the sol under the tree assumption. To ensure the equilibrium distribution, additional terms describing reversible reaction (fragmentation) were later introduced to the kinetic equation by van Dongen and Ernst.[3] Since their arguments on the postgel treatment were limited to only Flory's and Stockmayer's models, the possibility of a new treatment must further be examined together with closer experimental observation of the binodal (cloud-point curve) in the postgel regime.

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