Thermoreversible Gelation Strongly Coupled to Polymer Conformational Transition

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ABSTRACT: The effect of polymer conformational transition on thermoreversible gelation with multiple cross-link junctions in natural and synthetic polymers is studied on the basis of the recent theory of associating polymers. The effective number of associative groups carried by each chain in such solutions is not a fixed number but varies with conformation change induced by the temperature and other environmental conditions. Transition from intra- to intermolecular bonding due to denaturation of some proteins on heating leads to high-temperature gelation, while coil-to-helix transition (or coil-to-globule transition), followed by aggregation of helices (globules), leads to low-temperature gelation. We calculate the sol/gel transition concentration as a function of temperature and find that, in both cases, it is not a monotonic function but takes a minimum value at an intermediate temperature. At low temperatures gelation is prevented due to the lack of active groups or due to the strict restriction in helix sequence selection. Typical phase diagrams in which sol/gel transition coexists with phase separation are derived.

I. Introduction

Most natural polymers undergo a conformational transition preceding gelation. Activation of the particular functional groups on a polymer chain accompanied by a proper three-dimensional conformation change is a necessary prerequisite for the interchain cross-linking. For instance, water-soluble natural polymers such as agarose and κ-carrageenan first change their conformation from the random coil state to a partially helical state, and then the helical parts aggregate to form network junctions.[1−6] Recently, a similar two-step mechanism of gelation through coil-to-helix transition was confirmed for synthetic polymers with stereoregularity.[7,8] It was found that, in solutions of syndiotactic poly(methyl methacrylate) in toluene, a fast intramolecular conformational change is followed by an intermolecular association leading eventually to gelation.

Other important examples are globular proteins. Proteins such as ovalbumin, or human serum albumin, are believed to form gels after some of the intramolecular bonds in a native state are broken during denaturation, with their functional groups being exposed to the outer space, followed by intermolecular recombination of the groups.[2,9,10] A certain degree of unfolding to expose functional groups is a neccessary condition for the gelation in these examples.

Gelation strongly coupled to polymer conformational change can also be found in synthetic polymers. An important example of current interest is the coil-to-rod transition of the conducting polymer 4-butoxycarbonylmethylurethane (4BCMU) preceding gelation.[11−13] Upon cooling in organic solvents, 4BCMU polymers are partially stiffened by forming hydrogen bonds between the neighboring side groups, and then the formed rodlike segments aggregate into bundles of network junctions.[13] Because the electrical conductivity becomes finite after the gel point, the sol/gel transition of 4BCMU implies important industrial applications.

A similar mechanism of gelation can also be found in polymer solutions where coil-to-globule transition of each polymer chain plays a dominant role. Upon cooling, globular nuclei are randomly formed on a random coil polymer chain due to van der Waals attraction. Some of them involve similar globular nuclei on different chains in the neighborhood and form cross-links of densely packed submolecular aggregates. Networks thus take the structure in which random coil subchain sequences are connected to each other at the junctions of compact globular aggregates.

Other important synthetic polymers whose gelation is strongly coupled to the polymer conformational change are the associating polymers. Associating polymers are water-soluble polymers partially modified by hydrophobic groups. These groups form aggregates or micelles by hydrophobic interaction. At low polymer concentrations, intramolecular association in the form of flowerlike micelles is dominant, but with increase in the concentration, more open association (intermicellar bridging) prevails, so that such bridge chains eventually form networks with multiple cross-link junctions.[14−18] Similar transition from flower micelles to bridge chains are observed in triblock copolymers in selective solvents.[19]

To study these examples systematically, let us here classify the types of gelation in the following way:

Intra-Intertransition. The functional groups hidden inside a polymer molecule are activated by the change of environmental conditions such as the temperature, polymer concentration, pH, concentration of another component, etc., and lead to gelation by forming intermolecular bonds (see Figure 1a). Since the subchain forming a loop by intramolecular association looks like a petal in a flower, as is shown in Figure 1b, and the dissociated functional groups form interchain bridges, this transition is often referred to as *loop*/*bridge* transition or *flower*/*bridge* transition.[18] In the case where functional groups are thermally activated, this type of conformational transition leads to high-temperature gels.

Coil/Helix, Coil/Rod, or Coil/Globule Transition. Polymers in random coil conformation first partially form helices (or rods, globules) as the temperature is

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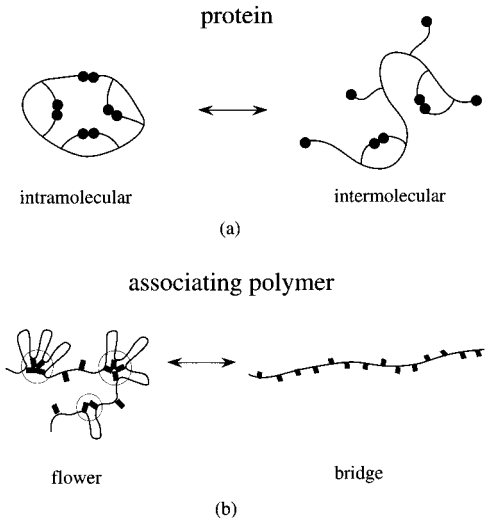

Figure 1. Breakage of intramolecular bonds (a) and dissociation of intramolecular flower micelles (b) by changing the temperature, concentration, pH, etc.

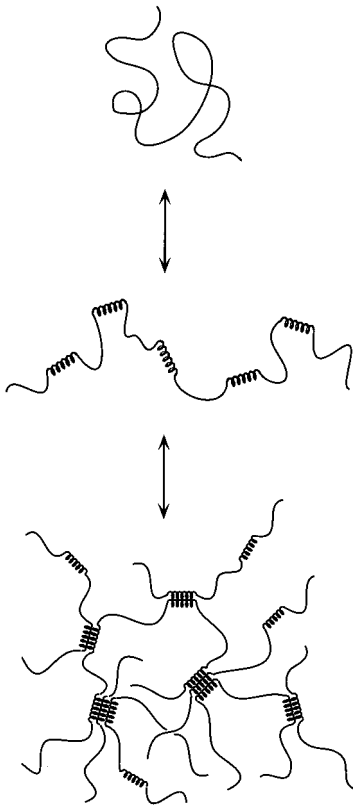

Figure 2. Coil-to-helix transition of polymer chains followed by aggregation of helices leading to gelation.

lowered, and then helices (rods, globules) aggregate into network junctions (Figure 2). This mechanism results in the low-temperature gelation as complex cross-linking regions are cohesively formed by the attractive interactions. At extremely low temperatures, however, helix sequences become longer, and as a result, the total number of helices on a chain decreases. The restriction in selecting helix sequences from the limited chain length, thus, tends to prevent gelation.

Two-State Transition. Each monomeric unit A along a polymer chain can take either an active state A* or an inert state A. The active monomeric units form cross-links of the type $(A^*)_k$ with multiplicity k ($k = 2$, 3, 4, ...) (Figure 3). This type may also lead to high-temperature gelation.

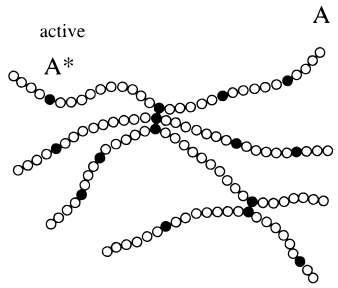

Figure 3. A model polymer carrying monomers that can take inert state (A) and active state (A*). Monomers in the active state can form junctions of variable multiplicity.

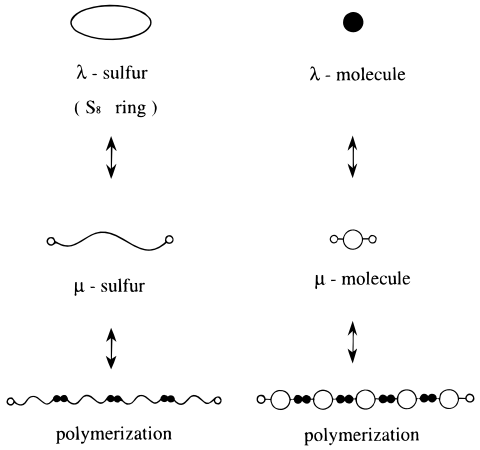

Figure 4. Equilibrium polymerization of sulfur. Ring sulfur called λ-sulfur is thermaly activated into an open chain and then polymerized.

At this stage, it should be remarked that the equilibrium polymerization of surfur[20,21] is a special case of the above intra-intertransition. A ring polymer S_8 (called λ-sulfur), which is inert at room temperature, first opens its ring into a linear chain carrying reactive groups on both its ends (called μ-sulfur) as the temperature is raised and then polymerized through interchain bonding at 160 °C (Figure 4). Since the reaction takes place pairwisely and the functionality f (number of active sites on a molecule) of μ-sulfur is two, molecules form linear chains instead of three-dimensional networks. In analogy to sulfur polymerization, we may therefore generally call a molecule staying in the inert state "*λ-molecule*" and one in the active state "*μ-molecule*" also for our gel-forming polymer solutions. The λ/μ-transition described above in an extended meaning is schematically summarized in Figure 5.

II. Stoichiometric Definitions

In order to study the equilibrium gelation that is strongly coupled to the polymer conformational change, we consider a polydisperse mixture of primary polymer chains carrying variable numbers of functional groups in a solvent. The number of statistical segments on a molecule is assumed in the present work to take a single unique value n. A molecule is distinguished by the number f of active functional groups it carries, each functional group being capable of taking part in the junctions which may bind together any number k of such groups. Hereafter we shall call k the *multiplicity* of a junction. Chemical gelation with multiple junctions was

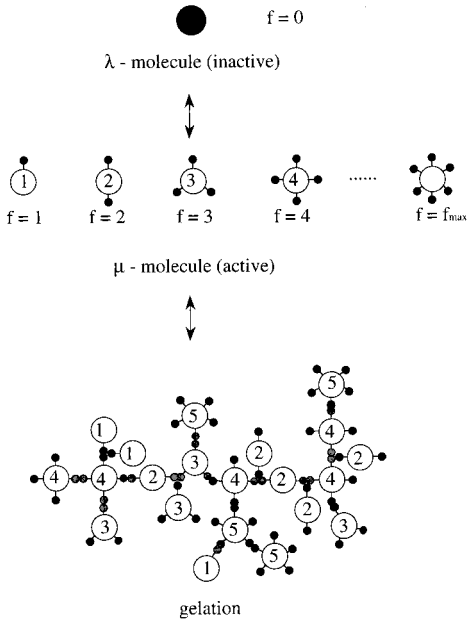

Figure 5. Inactive primary molecules called λ-molecules activated into molecules carrying variable numbers of functional groups, followed by network formation with junctions of variable multiplicity. Figures in the circles show their functionalities.

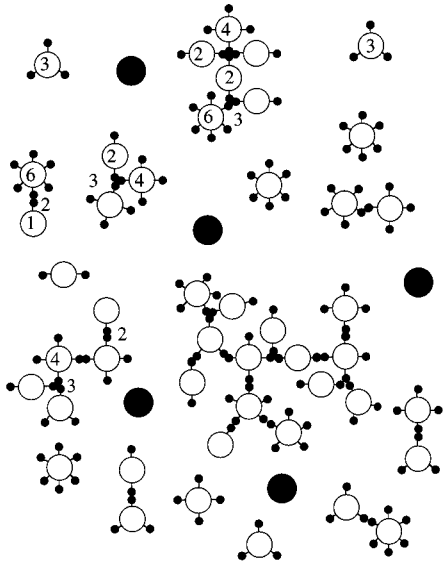

Figure 6. Equilibrium distribution of clusters in a solution. Inert λ-molecules are indicated by black circles.

first theoretically studied by Fukui and Yamabe[22] (referred to as FY) by extending the conventional Flory–Stockmayer tree statistics[23,24] to the multiple cross-linking. Recently we applied this theory to equilibrium gelation in order to study physical gels and derived phase diagrams in which gelation and phase separation interfere[25] (referred to as TS). In the study, we allowed junctions of all multiplicities to coexist, in proportions determined by the thermodynamic equilibrium conditions. In contrast to these preceding works, the functionality f in the present study is a variable depending on the temperature and polymer concentration and, in some cases, on other environmental parameters such as pH, added surfactant concentration, etc.

In thermal equilibrium, the solution has a distribution of clusters with a population distribution fixed by the equilibrium conditions. Following FY notation,[22] we define a cluster of the type (**j**;**l**) to consist of l_f primary molecules of functionality f (f = 0, 1, 2, 3, ...) and j_k junctions of multiplicity k (k = 1, 2, 3, ...) (Figure 6). The bold letters $\mathbf{l} \equiv \{l_0, l_1, l_2, l_3, ...\}$ and $\mathbf{j} \equiv \{j_1, j_2, j_3, ...\}$ are sets of numbers to characterize the cluster type. For instance, the $(f+1)$th number l_f in **l** gives the number of f-functional molecules forming the cluster, and the kth number j_k in **j** gives the number of junctions of multiplicity k included in the cluster. Note that $f = 0$ indicates λ-molecules and $k = 1$ indicates unreacted functional groups. An isolated molecule of functionality f, for instance, is indicated by $\mathbf{j}_{0f} \equiv \{f, 0, 0, ...\}$, and $\mathbf{l}_{0f} \equiv \{0, ..., 1, 0, ...\}$ (the $(f+1)$th number is unity). In what follows we assume, as in FY, that all finite clusters take tree forms to make the combinatorial counting problem as simple as possible. However, we allow the network (infinite cluster) in the post-gel regime to form internal loops as in Flory's conventional treatment of gelation.

Let us consider a typical tree cluster consisting of the μ-molecules. Let $l \equiv \sum_{f\geq 1} l_f$ be the total number of primary molecules in a cluster. Then the following two independent conservation relations hold due to the absence of internal loops:

$$l \equiv \sum_{f\geq 1} l_f = \sum (k-1) j_k + 1 \tag{2.1}$$

$$\sum_{k\geq 1} j_k = \sum_{f\geq 1} (f-1) l_f + 1 \tag{2.2}$$

One of these relations can be replaced by the useful identity

$$\sum_{k\geq 1} k j_k = \sum_{f\geq 1} f l_f \tag{2.3}$$

Further, let N_f be the total number of primary molecules with f activated functional groups in the system. The fraction of reactive groups residing on such f-functional μ-molecules is then given by

$$w_f = f N_f / (\sum_{f\geq 1} f N_f) \tag{2.4}$$

To deal with concentrations, we choose the unit of volume to be that of a unit cell, and we make the customary simplifying assumption that the solvent molecules, the functional groups, and the statistical repeat units of the primary chain molecules all occupy this same volume, a^3. This is not a serious restriction.

Thus, if N(**j**;**l**) is the number of (**j**;**l**) clusters in the system (including the λ-molecules), their number density is

$$\nu(\mathbf{j};\mathbf{l}) = N(\mathbf{j};\mathbf{l})/\Omega \tag{2.5}$$

where Ω is the total number of cells in the system and their volume fraction is

$$\phi(\mathbf{j};\mathbf{l}) = (n \sum_{f\geq 0} l_f) \nu(\mathbf{j};\mathbf{l}) \tag{2.6}$$

The total volume fraction of the polymer component is thus given by

$$\phi = \sum_{\mathbf{j},\mathbf{l}} \phi(\mathbf{j};\mathbf{l}) \tag{2.7}$$

or equally well

$$\phi = \sum_{f\geq 0} nN_f/\Omega \tag{2.8}$$

now $f = 0$ term being included in the summation (see Figure 6). Counting λ-molecules only, we also define their volume fraction $\phi_\lambda \equiv nN_\lambda/\Omega$. The subscript λ-indicates $f = 0$ throughout this paper and should not be confused with the index 0 for the solvent component. Consequently, the volume fraction of μ-molecules is given by

$$\phi_\mu = \phi - \phi_\lambda = \sum_{f\geq 1} nN_f/\Omega \tag{2.9}$$

It will also be useful later to consider the total number density of the functional groups,

$$\psi = (\sum_{f\geq 1} fN_f)/\Omega \tag{2.10}$$

and the volume fraction of polymers derived from the f-functional primary molecules,

$$\phi_f = nN_f/\Omega \tag{2.11}$$

From (2.4) we easily find

$$\phi_f/\psi = nw_f/f \tag{2.12}$$

and

$$\phi_\mu/\psi = n\sum_{f\geq 1} w_f/f \tag{2.13}$$

Since

$$\sum_{f\geq 1} w_f/f \equiv 1/f_n \tag{2.14}$$

is the reciprocal of the number average functionality f_n of μ-molecules, we find $\phi_\mu = n\psi/f_n = \tilde{n}\psi$. The ratio $\tilde{n} \equiv n/f_n$ gives the average number of statistical segments per functional group. The weight-average functionality of μ-molecules is similarly defined by

$$f_w \equiv \sum_{f\geq 1} fw_f \tag{2.15}$$

These averages concern μ-molecules only. The entire distribution function including λ-molecules must, however, be used to calculate the average molecular weight of all clusters.

III. Free Energy of the Model Solution

We now consider the free energy of the system at a given temperature T and polymer volume fraction ϕ on the basis of the classical Flory−Huggins theory for multicomponent polymer solutions.[26] The chosen standard reference states are pure solvent and separated pure unmixed amorphous primary solute polymer in the λ state. The free energy change on passing from the reference states to the final solution, at equilibrium with respect to cluster formation, consists of three parts:

$$\Delta F = \Delta F_{\text{conf}} + \Delta F_{\text{rea}} + \Delta F_{\text{mix}} \tag{3.1}$$

where ΔF_{conf} is the free energy associated with the change in molecular conformation, ΔF_{rea} the free energy of reaction required to connect μ-molecules into clusters, and ΔF_{mix} the free energy produced on mixing all clusters with the solvent.

The first term is newly introduced here in this work to study the cooperative effect between conformational change and gelation. It is written as

$$\Delta F_{\text{conf}} = A_\lambda N_\lambda + \sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 1} A_f l_f)N(\mathbf{j};\mathbf{l}) + \sum_{f\geq 1} A_f N_f^G \tag{3.2}$$

where N_λ is the number of λ-molecules, N_f^G the number of primary molecules in the gel network that carry f active functional groups, A_λ the conformational free energy of a single λ-molecule and A_f the same of a μ-molecule with f active groups. The free energy required for the activation of a molecule is therefore given by

$$\Delta A_f \equiv A_f - A_\lambda \tag{3.3}$$

In this context, the λ-state of a chain should be regarded as a reference conformation. One may choose another conformation as the reference conformation. The totally activated state, for instance, can be an equally possible candidate. The following theoretical framework may then look superficially different, but the final results are independent of the choice.

The second term ΔF_{rea} in eq 3.1 gives the free energy required to form $N(\mathbf{j};\mathbf{l})$ clusters of the type $(\mathbf{j};\mathbf{l})$ from the primary chains and also to form a gel network containing N_f^G polymer chains of functionality f. It is written as

$$\beta\Delta F_{\text{rea}} = \sum\Delta(\mathbf{j};\mathbf{l})N(\mathbf{j};\mathbf{l}) + \sum_{f\geq 1}\delta_f(\phi)N_f^G \tag{3.4}$$

where $\beta \equiv 1/k_BT$ is the reciprocal temperature and

$$\Delta(\mathbf{j};\mathbf{l}) \equiv \beta\{\mu^\circ(\mathbf{j};\mathbf{l}) - \sum_f l_f\mu^\circ(\mathbf{j}_{0f};\mathbf{l}_{0f})\} \tag{3.5}$$

is the free energy change accompanying the formation of a $(\mathbf{j};\mathbf{l})$ cluster in a hypothetical undiluted amorphous state from the separate primary molecules with partially activated states. The superscript circle refers to the undiluted state. We may call $\Delta(\mathbf{j};\mathbf{l})$ "*free energy of cluster formation*" in the unit of thermal energy. The second term on the right-hand side of eq 3.4 appears only after the gel point is passed and a macroscopic network begins to form; it contains the number N_f^G of f-functional primary molecules connected to the network. The free-energy change $\delta_f(\phi)$ assigned to each chain in the network is the free energy required on bringing an isolated primary f-molecule into the network. Since the degree of association increases with the polymer concentration, it is assumed to be a function of the total polymer concentration (and the temperature).

Finally, the last term ΔF_{mix} in eq 3.1 gives the free energy for mixing the above clusters and the network with the solvent. We employ the conventional Flory−Huggins lattice theoretical free energy for polydisperse polymer solutions and write it as

$$\beta\Delta F_{\text{mix}} = N_0 \ln \phi_0 + N_\lambda \ln \phi_\lambda + \sum_{\mathbf{j},\mathbf{l}} N(\mathbf{j};\mathbf{l}) \ln \phi(\mathbf{j};\mathbf{l}) + \Omega\chi\phi_0\phi \tag{3.6}$$

where χ is Flory's interaction parameter.

IV. Equilibrium Conditions

We now minimize this total free energy by changing the number $N(\mathbf{j};\mathbf{l})$ (and N_f^G in the post-gel regime) of the clusters and find their most probable distribution. This procedure can be systematically done by deriving the chemical potentials of the clusters and imposing on them the equilibrium conditions. By differentiating the total free energy with respect to the number of molecules or clusters of the specified type, we find the chemical potentials as

$$\beta\Delta\mu_0 = 1 + \ln\phi_0 - \nu^S + \chi\phi^2 - [\sum_f \delta'_f(\phi)\nu_f^G]\phi \quad (4.1)$$

for a solvent molecule,

$$\beta\Delta\mu_\lambda/n = (1 + \ln\phi_\lambda + \beta A_\lambda)/n - \nu^S + \chi\phi_0^2 + [\sum_f \delta'_f(\phi)\nu_f^G](1-\phi) \quad (4.2)$$

for a λ-molecule,

$$\beta\Delta\mu(\mathbf{j};\mathbf{l})/nl = \{1 + \ln\phi(\mathbf{j};\mathbf{l}) + \Delta(\mathbf{j};\mathbf{l}) + \beta\sum_{f\geq 1} A_f l_f\}/(nl) - \nu^S + \chi{\phi_0}^2 + [\sum_f \delta'_f(\phi)\nu_f^G](1-\phi) \quad (4.3)$$

for a cluster of the type $(\mathbf{j};\mathbf{l})$, and

$$\beta\Delta\mu_f^G/n = (\beta A_f + \delta_f)/n - \nu^S + \chi{\phi_0}^2 \quad (4.4)$$

for an f-molecule in the gel network. Here, ν^S stands for the sum of the number density of solvent molecules and the total number density of clusters in the sol:

$$\nu^S \equiv 1 - \phi + \sum_{\mathbf{j},\mathbf{l}} \nu(\mathbf{j};\mathbf{l}) \quad (4.5)$$

This indicates the total number density of particles in the system that possess translational degree of freedom. In contrast, $\nu_f^G \equiv N_f^G/\Omega$ denotes the number density of f-functional μ-molecules connected to the gel network with no translational motion.

First let us consider the activation equilibrium, i.e., the equilibrium between λ-molecules and f-molecules in the μ-state. It is given by the condition

$$\Delta\mu_\lambda = \Delta\mu(\mathbf{j}_{0f};\mathbf{l}_{0f}) \quad (4.6)$$

In what follows we call this λ/μ *equilibrium*. On substitution of the explicit forms of the chemical potentials, we find that the volume fraction of f-molecules in the solution is uniquely related to the volume fraction of the λ-molecules through the equation

$$\phi(\mathbf{j}_{0f};\mathbf{l}_{0f}) = \phi_\lambda \exp(-\beta\Delta A_f) \quad (4.7)$$

where $\Delta A_f \equiv A_f - A_\lambda$ is the conformational free energy produced when a molecule changes from the λ-state to f-functional state.

Let us next consider the equilibrium cluster formation. In order for the cluster-forming reaction to be in an equilibrium, the chemical potential $\Delta\mu(\mathbf{j};\mathbf{l})$ of an arbitrary type $(\mathbf{j};\mathbf{l})$ should satisfy the multiple-equilibrium condition

$$\Delta\mu(\mathbf{j};\mathbf{l}) = \sum_{f\geq 1} l_f \Delta\mu(\mathbf{j}_{0f};\mathbf{l}_{0f}) \quad (4.8)$$

These conditions lead to the most probable distribution of clusters for which the volume fraction of the type $(\mathbf{j};\mathbf{l})$ is connected to the power products of the isolated μ-molecules as

$$\phi(\mathbf{j};\mathbf{l}) = K(\mathbf{j};\mathbf{l}) \prod_{f\geq 1} \phi(\mathbf{j}_{0f};\mathbf{l}_{0f})^{l_f} \quad (4.9)$$

by the reaction constant

$$K(\mathbf{j};\mathbf{l}) \equiv \exp[l - 1 - \Delta(\mathbf{j};\mathbf{l})] \quad (4.10)$$

Finally, an isolated f-molecule should also be in equilibrium with an f-molecule attached to the gel network in the post-gel regime. Hence we have

$$\Delta\mu_f^G = \Delta\mu(\mathbf{j}_{0f};\mathbf{l}_{0f}) \quad (4.11)$$

which leads to the relation

$$\phi(\mathbf{j}_{0f},\mathbf{l}_{0f}) = \exp(\delta_f - 1) \quad (4.12)$$

With the help of all these relations, the volume fraction of molecules or clusters of any type can be expressed in terms of a single unknown, for which we choose the volume fraction ϕ_λ of the λ-molecules in the following sections.

V. Probability Distribution of the Clusters

In an association equilibrium, the total number ψ of associative groups (per unit cell) in the active state is given by

$$\psi = \sum_{f\geq 1} f\nu_f \quad (5.1)$$

where $\nu_f \equiv N_f/\Omega$ is the number density of f-molecules (per unit cell) in the solution. This density can be split into two parts:

$$\nu_f = \nu_f^S + \nu_f^G \quad (5.2)$$

where ν_f^S is the number density of chains in the sol part and ν_f^G that belonging to the gel part. The weight distribution w_f of the functional groups introduced in FY study (and also in TS) is then given by

$$w_f = f\nu_f/\psi \quad (5.3)$$

In the previous studies TS, this was a distribution fixed in the sample preparation stage, but here it is determined by the thermodynamic requirements. The number-average functionality f_n of the μ-molecules is then given by

$$f_n \equiv \psi/\sum\nu_f \quad (5.4)$$

and the weight-average functionality f_w by

$$f_w \equiv \sum f^2\nu_f/\psi \quad (5.5)$$

These depend on the temperature and the concentration and play the central role in the following analysis of the sol/gel transition.

Let us proceed to finding the cluster distribution as a function of the temperature T and the volume fraction ϕ of the primary molecules. These two variables are the thermodynamic variables that can be controlled in the experiments. Our final purpose is to draw phase diagrams on a plane whose axes consist of such thermodynamic variables. To do this, we introduce the probability p_k for an arbitrarily chosen functional group to be in a k-junction. As in the previous work TS, we assume the most general form

$$p_k = p_1 \gamma_k z^{k-1} \tag{5.6}$$

where

$$z \equiv \lambda(T)\psi p_1 \tag{5.7}$$

is a parameter refering to the unreacted functional groups. Here, p_1 is the probability for a functional group to remain unreacted, and

$$\lambda(T) \equiv \exp(-\beta \Delta f_0) \tag{5.8}$$

with Δf_0 being the binding free energy per associative group, is the association constant for binding a single functional group into a junction. The coefficient γ_k comes from the surface term in the free energy to form a k-junction. The probability p_1 is written as $p_1 = 1 - \alpha$ in the conventional theory of gelation, where α is the extent of reaction, or conversion, i.e., the probability for a functional group to be bound in a junction. The relation (5.6) was derived in TS by assuming the equilibrium condition

$$\psi p_k = K_k (\psi p_1)^k \tag{5.9}$$

in forming each junction with the reaction constant K_k that takes the form

$$K_k = \gamma_k \lambda^{k-1} \tag{5.10}$$

All contributions other than the binding free energy are included in the prefactor γ_k.

The normalization condition

$$\sum_{k \geq 1} p_k = 1 \tag{5.11}$$

gives

$$p_1 = 1/u(z) \tag{5.12}$$

where

$$u(z) \equiv \sum_{k \geq 1} \gamma_k z^{k-1} \tag{5.13}$$

is a function specifying the junctions.

Now eq 5.7 leads to the relation between the total concentration ψ of the associative groups and that of the unassociated groups as

$$\lambda \psi = z u(z) \tag{5.14}$$

The number density of functional groups (times the association constant) carried by the isolated μ-molecules is given by

$$x_f = \frac{f\lambda}{n} \phi(\mathbf{j}_{0f}, \mathbf{l}_{0f}) \tag{5.15}$$

Since the association constant λ always accompanies the concentration, it can be regarded as a temperature shift factor. By definition, x_f is given by

$$x_f \equiv \lambda \psi w_f {p_1}^f = w_f z / u(z)^{f'} \tag{5.16}$$

where $f' \equiv f - 1$. More detailed description of this parameter x_f is given in TS. By the use of the equilibrium condition (4.7), this parameter is expressed as

$$x_f = f x_\lambda \exp(-\beta \Delta A_f) \tag{5.17}$$

in terms of the scaled number density of the λ-molecules

$$x_\lambda \equiv \frac{\lambda(T)}{n} \phi_\lambda \tag{5.18}$$

These relations give

$$w_f = \frac{u(z)^{f'}}{z} f x_\lambda \mathrm{e}^{-\beta \Delta A_f} = \frac{f x_\lambda}{\lambda \psi} u(z)^f \mathrm{e}^{-\beta \Delta A_f} \tag{5.19}$$

for the distribution, and by the normalization condition $\sum w_f = 1$, the parameter x_λ is expressed by

$$x_\lambda = \lambda \psi / F_1(z) = z u(z) / F_1(z) \tag{5.20}$$

as a function of z, where new functions $F_m(z)$ ($m = 0, 1, 2, \ldots$) are introduced by the definitions

$$F_m(z) \equiv \sum_{f \geq 1} f^m u(z)^f \mathrm{e}^{-\beta \Delta A_f} \tag{5.21}$$

Substituting this result into eq 5.19, we find

$$w_f = f u(z)^f \mathrm{e}^{-\beta \Delta A_f} / F_1(z) \tag{5.22}$$

Thus the weight distribution w_f of the associative groups is expressed in terms of the conformational excitation free energy ΔA_f and the (scaled) number density z of the associative groups that remain unreacted in the solution.

On substitution into eq 2.14, we find

$$f_n = F_1(z)/F_0(z) \tag{5.23}$$

Similarly, the weight average functionality f_w is given by

$$f_w = F_2(z)/F_1(z) \tag{5.24}$$

In order to find z as a function of the total polymer concentration, let us split the volume fraction of the polymer into two terms:

$$\phi = \phi_\lambda + \phi_\mu \tag{5.25}$$

The volume fraction of the μ-molecules is given by

$$\phi_\mu \equiv n \sum_{f \geq 1} \nu_f = n\psi / f_n \tag{5.26}$$

Hence we find for the total volume fraction of the polymers

$$\frac{\lambda}{n}\phi = x_\lambda + \frac{\lambda\psi}{f_n} = [1 + F_0(z)]\, x_\lambda = \frac{1 + F_0(z)}{F_1(z)} z u(z) \quad (5.27)$$

This is a relation that connects the number density z of the unassociated functional groups to the total polymer concentration. By solving this relation with respect to z, we find z, and hence x_λ, as a function of ϕ. The solution properties, especially the chemical potentials, can then be expressed in terms of the temperature and the polymer concentration. This completes our basic procedure.

Before proceeding to the study of gelation, let us see the relation (5.27) in more detail. The numerator $1 + F_0(z)$ is transformed into a more compact form

$$1 + F_0(z) = \sum_{f\geq 0} u(z)^f \mathrm{e}^{-\beta\Delta A_f} \quad (5.28)$$

by including $f = 0$ term in the summation. We then use a new function defined by

$$\tilde{F}_0(z) \equiv 1 + F_0(z) = \sum_{f\geq 0} u(z)^f \mathrm{e}^{-\beta\Delta A_f} \quad (5.29)$$

in favor of F_0 by including $f = 0$ term. The relation (5.27) is then rewritten as

$$\frac{\lambda f_{\mathrm{av}}(z)}{n}\phi = z u(z) \quad (5.30)$$

where

$$f_{\mathrm{av}}(z) \equiv F_1(z)/\tilde{F}_0(z) \quad (5.31)$$

is the number-average functionality of polymer chains calculated by *including* λ-molecules. This relation (5.30) is formally the same as the one found for the f-functional polymer chains in our previous study TS if we replace f in it by the effective functionality f_{av}.

At this stage, it is convenient to show the explicit form of the number ν_f of the polymer chains (per a lattice cell) that carry the number f of associative groups. Since their weight distribution w_f is given by eq 5.22, ν_f is proportional to $u(z)^f \exp(-\beta\Delta A_f)$. Let us assume the form $\nu_f = Cu^f \exp(-\beta\Delta A_f)$ (including $f = 0$ term). Since the sum $\sum_{f\geq 0} \nu_f$ gives the total number density ϕ/n of the primary chains, the normalization constant C must take the value $C = (\phi/n)/\tilde{F}_0(z)$. Thus we find

$$\nu_f = \left(\frac{\phi}{n}\right)\frac{u(z)^f \mathrm{e}^{-\beta\Delta A_f}}{\tilde{F}_0(z)} \quad \text{(including } f = 0 \text{ term)} \quad (5.32)$$

The parameter z is given as a function of the polymer concentration ϕ through the relation (5.30). Especially for the λ-molecules with $f = 0$, we find $\nu_\lambda = \phi/n\tilde{F}_0(z)$, and hence $x_\lambda = zu(z)/F_1(z)$. This reduces to eq 5.20.

VI. Distribution of Clusters and Sol/Gel Transition

We now proceed to the study of cluster distribution in the solution. The general procedure developed in TS gives the number distribution $\nu(\mathbf{j};\mathbf{l})$ of the clusters consisting of μ-molecules as

$$\nu(\mathbf{j};\mathbf{l}) = \psi(\sum j_k - 1)!(\sum_{f\geq 1} l_f - 1)! \prod_{f\geq 1}\left(\frac{x_f^{l_f}}{l_f!}\right)\prod_{k\geq 1}\left(\frac{\gamma_k^{j_k}}{j_k!}\right) \quad (6.1)$$

The average number of associative groups in a cluster can then be calculated as

$$P_n^f \equiv \sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 1} f l_f)\nu(\mathbf{j};\mathbf{l})/\sum_{\mathbf{j},\mathbf{l}}\nu(\mathbf{j};\mathbf{l}) = 1/[1/\mu_n + 1/f_n - 1] \quad (6.2)$$

for the number average and

$$P_w^f \equiv \sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 1} f l_f)^2\nu(\mathbf{j};\mathbf{l})/\sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 1} f l_f)\nu(\mathbf{j};\mathbf{l}) = 1/[1/\mu_w + 1/f_w - 1] \quad (6.3)$$

for the weight average. Here, the average junction multiplicities are defined by

$$\mu_n \equiv (\sum_{k\geq 1} p_k/k)^{-1} = u(z)/I(z) \quad (6.4)$$

for the number average and

$$\mu_w \equiv \sum_{k\geq 1} k p_k = 1 + zu'(z)/u(z) \quad (6.5)$$

for the weight average. The new function $I(z)$ is defined by

$$I(z) \equiv \sum_{k\geq 1}\frac{\gamma_k}{k} z^{k-1} = \frac{1}{z}\int_0^z u(z)\, \mathrm{d}z \quad (6.6)$$

as in TS. The total number density of μ-clusters in the sol part is then given by

$$\lambda\nu_\mu^S = \lambda(\sum_{f\geq 1} f\nu_f)/P_n^f = \lambda\psi(1/\mu_n + 1/f_n - 1) = z[(1/f_n - 1)u(z) + I(z)] \quad (6.7)$$

Let us next study the average number of chains in a cluster. In contrast to the average number of associative groups, we have to include λ-molecules to calculate the average. We then have

$$P_n(z) \equiv \sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 0} l_f)\nu(\mathbf{j};\mathbf{l})/\sum_{\mathbf{j},\mathbf{l}}\nu(\mathbf{j};\mathbf{l}) = 1/f_{\mathrm{av}}[1/\mu_n + 1/f_{\mathrm{av}} - 1] \quad (6.8)$$

for the number average and

$$P_w(z) = \sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 0} l_f)^2\nu(\mathbf{j};\mathbf{l})/\sum_{\mathbf{j},\mathbf{l}}(\sum_{f\geq 0} l_f)\nu(\mathbf{j};\mathbf{l}) = 1 + f_{\mathrm{av}}(\mu_w - 1)/[1 - (f_w - 1)(\mu_w - 1)] \quad (6.9)$$

for the weight average. The average molecular weight of the clusters is then given by nP_n or nP_w. These averages are found as functions of the temperature and the polymer concentration when eq 5.30 is solved with respect to z and substituted.

The conventional definition of the gel point is the onset of the macroscopic connectivity where the weight average molecular weight becomes infinite. (The number average remains finite.) From the above calculation, we find that the sol/gel transition point is given by the condition

$$(f_w - 1)(\mu_w - 1) = 1 \quad (6.10)$$

or equivalently

$$[f_w(z) - 1]zu'(z)/u(z) = 1 \tag{6.11}$$

Here, the average functionality f_w is given by eq 5.24 as a function of z, which is related to the total polymer concentration through eq 5.30. Let z^* be the solution of eq 6.11. The gelation concentration ϕ^* is then given by the equation

$$\frac{\lambda(T)\phi^*}{n} = \frac{\tilde{F}_0(z^*)}{F_1(z^*)} z^* u(z^*) \tag{6.12}$$

This equation gives the sol/gel transition line when mapped onto the temperature−concentration plane.

VII. Solution Properties

Let us next study thermodynamic stability and phase separation of our network-forming polymer solutions. We have derived the chemical potentials for the solvent, λ-molecule, and μ-molecule. Since we have equilibrium conditions, only two of these are independent. Here we study the chemical potential of the solvent and of the λ-molecule as independent variables. The total number density ν^S of the molecules that possess translational degree of freedom in the solution is explicitly given by

$$\nu^S = 1 - \phi + \nu_\lambda + \nu_\mu^S \tag{7.1}$$

where $\nu_\lambda = zu(z)/\lambda F_1(z)$ and ν_μ^S is given in eq 6.7. Let us consider the last term in the chemical potentials that includes the free energy δ_f to bind a single f-molecule into the gel network. The equilibrium condition (4.12) gives a relation

$$\delta_f - 1 = \ln x_\lambda + \text{const}(f) \tag{7.2}$$

where $\text{const}(f) \equiv \ln(n/\lambda) - \beta\Delta A_f$ is an unimportant constant independent of the concentration. We then find

$$\sum_{f\geq 1} \delta'_f(\phi)\nu_f^G = \frac{\partial \ln x_\lambda}{\partial\phi} \sum_{f\geq 1} \nu_f^G = \frac{\phi^G}{n} \frac{\partial \ln x_\lambda}{\partial\phi} = \frac{w^G}{n} \frac{\partial \ln x_\lambda}{\partial \ln \phi} \tag{7.3}$$

where

$$w^G \equiv \phi^G/\phi \tag{7.4}$$

is the gel fraction. The chemical potentials are transformed into

$$\beta\Delta\mu_0 = \ln(1 - \phi) - \nu^S + \chi\phi^2 - w^G \frac{\phi}{n} \frac{\partial \ln x_\lambda}{\partial \ln \phi} \tag{7.5}$$

and

$$\frac{\beta\Delta\mu_\lambda}{n} = \frac{1}{n}\left[1 + w^G(1 - \phi)\frac{\partial}{\partial \ln \phi}\right] \ln x_\lambda - \nu^S + \chi(1 - \phi)^2 \tag{7.6}$$

apart from unimportant constants.

The osmotic pressure π is then given by the general thermodynamic relation

$$\pi a^3/k_B T = -\beta\Delta\mu_0 \tag{7.7}$$

where a is the size of the fundamental cell. By taking the derivative of this pressure, we find

$$K_T \equiv \left(\frac{k_B T}{a^3}\right) \frac{1}{\phi} \left(\frac{\partial\phi}{\partial\pi}\right)_T = \frac{1}{\phi^2 \sigma(\phi, T)} \tag{7.8}$$

for the osmotic compressibility, where

$$\sigma(\phi, T) = \frac{\kappa(\phi, T)}{n\phi} + \frac{1}{1 - \phi} - 2\chi \tag{7.9}$$

Here, the new function κ is defined by

$$\kappa \equiv \frac{\partial}{\partial \ln \phi}\left(1 + w^G \frac{\partial}{\partial \ln \phi}\right) \ln x_\lambda \tag{7.10}$$

We next consider the degree of association α in the solution. This is defined by the average number of associated functional groups relative to the total number of functional groups and is often referred to as conversion in the literature. By definition, we have $\alpha = 1 - p_1$, and from $p_1 = 1/u(z)$ the conversion is given by

$$\alpha = 1 - 1/u(z) \tag{7.11}$$

as a function of z and, hence, the polymer concentration ϕ.

A. Pregel Regime. In the pregel regime, we have $w^G = 0$. The chemical potentials are given by

$$\beta\Delta\mu_0 = \ln(1 - \phi) - \nu^S + \chi\phi^2 \tag{7.12}$$

and

$$\frac{\beta\Delta\mu_\lambda}{n} = \frac{1}{n} \ln x_\lambda - \nu^S + \chi(1 - \phi)^2 \tag{7.13}$$

Here, the total number density ν^S (eq 7.1) of molecules that possess translational degree of freedom is given by

$$\nu^S = 1 - \phi + \frac{\phi}{n\tilde{F}_0(z)}\left(1 + \frac{F_1(z)}{P_n^f}\right) \tag{7.14}$$

The κ-function reduces to the reciprocal of the weight average association number P_w:

$$\kappa(z) = \frac{\partial \ln x_\lambda}{\partial \ln \phi} = 1/P_w(z) \quad \text{(pregel regime)} \tag{7.15}$$

The stability limit, or spinodal line, is found by the divergence of the osmotic compressibility

$$\frac{\kappa(\phi, T)}{n\phi} + \frac{1}{1 - \phi} 2\chi = 0 \tag{7.16}$$

The sol−sol phase equilibrium is given by the coupled conditions

$$\Delta\mu_0(\phi', T) = \Delta\mu_0(\phi'', T) \tag{7.17a}$$

$$\Delta\mu_\lambda(\phi', T) = \Delta\mu_\lambda(\phi'', T) \tag{7.17b}$$

B. Postgel Regime. In this study we extend the treatment of the postgel regime developed by Flory[26] for the case of conventional pairwise cross-linking to our present multiple cross-linking. He allowed cycle formation within the gel network while it is strictly forbidden for the finite clusters and found the conversion α' in the sol part that is different from the conversion α'' in the gel part. In the present model solution, his treatment can be applied in the following way.

The average conversion α of the solution as a whole is given by eq 5.30 with the relation

$$z = \lambda\psi(1 - \alpha) \tag{7.18}$$

For a given value of α, the concentration x_λ is calculated by the relation (5.20). Then the conversion α′ of the sol is assumed to be found by solving the condition

$$x_\lambda = z'u(z')/F_1(z') \tag{7.19}$$

with respect to z' for this given value of x_λ. This equation has a solution z by definition but has another solution z' which is smaller than z. Then, this root z' gives α′ by the relation $z' = \lambda\psi(1 - \alpha')$. For a given total concentration, the volume fraction ϕ^S of the sol is then found by the relation

$$\frac{\lambda}{n}\phi^S = \frac{\tilde{F}_0(z')}{F_1(z')}z'u(z') \tag{7.20}$$

The volume fraction ϕ^G of the gel is found by the subtraction $\phi^G = \phi - \phi^S$. This procedure gives

$$w^S = \phi^S/\phi = \tilde{F}_0(z')/\tilde{F}_0(z) \tag{7.21}$$

for the sol fraction and

$$w^G = 1 - \tilde{F}_0(z')/\tilde{F}_0(z) \tag{7.22}$$

for the gel fraction. The conversion α″ in the gel is then found by the relation

$$\alpha = \alpha' w^S + \alpha'' w^G \tag{7.23}$$

Similarly, the weight-average molecular weight of the finite clusters in the sol is given by the equation

$$\frac{\partial \ln x_\lambda(z')}{\partial \ln \phi} = \frac{1}{P_w(z')} \tag{7.24}$$

The chemical potentials in the postgel regime are given by eq 7.5 and eq 7.6, but $\nu^S(z)$ and $x_\lambda(z)$ in these equations should be replaced by $\nu^S(z')$ and $x_\lambda(z')$. Accordingly, the κ-function is changed to

$$\kappa^*(\phi) = \left[1 + w^S\left(1 - \frac{P_w(z')}{P_w(z)}\right)\right]\frac{1}{P_w(z')} + \frac{w^G}{1 - (f_w(z') - f_{av}(z') - 1)(\mu_w(z') - 1)}\frac{\mathrm{d}}{\mathrm{d}\ln z'}\left(\frac{1}{P_w(z')}\right) \tag{7.25}$$

It is different from the reciprocal of the weight-average molecular weight. This is because the average for the molecular weight is taken within the sol part, while there is a contribution from the gel part to the osmotic compressibility.

VIII. Models of the Junction

The multiplicity of junctions is in principle determined by the equilibrium requirement for a given associative interaction. In the case of hydrophobic interaction, chain length of a hydrophobe, strength of water−hydrophobe interaction, geometric form of an aggregate, and other factors determine the association constant $\lambda(T)$ and the coefficients γ_k in the junction function $u(z)$. In the present study, we avoid complexity to find the precise forms of γ_k and introduce a model junction in which multiplicities lying in a certain range from $k = s_{min}$ to s_{max} are equally allowed. We thus have

$$k = 1 \quad \text{(free)} \quad k = s_{min}, s_{min} + 1, ..., s_{max} \quad \text{(associated)} \tag{8.1}$$

The coefficient γ_k with k lying in this range is assumed to take a uniform value. We then have

$$u(z) = 1 + (z^{s_{min}-1} - z^{s_{max}})/(1 - z) \tag{8.2}$$

When only a single value is allowed, i.e., $s_{min} = s_{max} \equiv s$, we call the model *fixed multiplicity model*. In the fixed multiplicity model, all relations reduce to simple forms. We have only $k = 1$(*free*) and $k = s$(*associated*), so that $u(z) = 1 + z^{s'}$ where $s' \equiv s - 1$. In terms of the conversion, we have $p_1 = 1 - \alpha$ and $p_s = \alpha$. The relation (7.11) then gives

$$z = \left(\frac{\alpha}{1 - \alpha}\right)^{1/s'} \tag{8.3}$$

The average functionalities are

$$f_n(\alpha) = F_1(\alpha)/F_0(\alpha) \qquad f_w(\alpha) = F_2(\alpha)/F_1(\alpha) \tag{8.4}$$

with the functions F_m now written in terms of α as

$$F_m(\alpha) \equiv \sum_{f\geq 1} f^m \mathrm{e}^{-\beta\Delta A_f}(1 - \alpha)^f \tag{8.5}$$

Similarly, the average junction multiplicities are given by

$$\mu_n(\alpha) = 1/[1 - (s'/s)\alpha] \qquad \mu_w(\alpha) = 1 + s'\alpha \tag{8.6}$$

The fundamental relation connecting α with the total polymer concentration then takes the form

$$\frac{\lambda}{n}\phi = \frac{\tilde{F}_0(\alpha)}{F_0(\alpha)}S_1(\alpha) \tag{8.7}$$

where

$$S_1(\alpha) \equiv \alpha^{1/s'}/[f_n(\alpha)(1 - \alpha)^{s/s'}] \tag{8.8}$$

is the first moment of the multiple tree distribution. This function reduces to the first moment of the conventional Stockmayer distribution in the special case of the pairwise junction $s = 2$ with monodisperse functionality $f_n = f$. Similarly, we find

$$S_0(\alpha) \equiv \alpha^{1/s'}(1 - f_n s'\alpha/s)/[f_n(1 - \alpha)^{s/s'}] \tag{8.9}$$

for the zeroth moment and

$$S_2(\alpha) \equiv \alpha^{1/s'}[1 - (f_w - f_n - 1)s'\alpha]/[f_n(1 - \alpha)^{s/s'}\{1 - (f_w - 1)s'\alpha\}] \tag{8.10}$$

for the second moment. All solution properties can be expressed in terms of these three moments. For instance, we have

$$x_\lambda = S_1(\alpha)/F_0(\alpha) \tag{8.11}$$

for the concentration of the λ-molecules and

$$\lambda\nu_\mu^S = S_0(\alpha) \tag{8.12}$$

for the total number density of clusters in the sol. Similarly, the weight average molecular weight is given by

$$P_w(\alpha) = \frac{x_\lambda + S_2(\alpha)}{x_\lambda + S_1(\alpha)} = 1 + \frac{f_{av}s'\alpha}{1 - (f_w - 1)s'\alpha} \tag{8.13}$$

Therefore, the gel point is given by the solution of the equation

$$s'\alpha[f_w(\alpha) - 1] = 0 \tag{8.14}$$

In the postgel regime, Flory's treatment gives the conversion α' in the sol by solving the equation $x_\lambda(\alpha) = x_\lambda(\alpha')$ with respect to α' for a given α or explicitly,

$$(\alpha')^{1/s'}/F_1(\alpha')(1 - \alpha')^{s/s'} = \alpha^{1/s'}/F_1(\alpha)(1 - \alpha)^{s/s'} \tag{8.15}$$

IX. Models of Excitation

We now discuss specific forms of the functions $F_m(z)$. By definition it depends on the excitation free energy ΔA_f of the conformation with possible number f of active groups measured relative to the reference conformation. Throughout this paper, we take λ-state as the reference conformation. In our forthcoming paper studying the effect of loop formation on the sol/gel transition, however, a different choice of the reference conformation will be made.

A. Independent Excitation Model. In this model a polymer chain is assumed to carry a fixed number f of associative groups, each of which may independently take either an active or inert state. The energy difference between the two states is assumed to be given by ΔA_1. Then the functions $F_m(z)$ are given by

$$F_m(z) = \sum_{g=0}^{f} g^m u(z)^g \frac{f!}{g!(f-g)!}(e^{-\beta\Delta A_1})^g = \left(x\frac{d}{dx}\right)^m (1+x)^f \tag{9.1}$$

where $x \equiv \eta u(z)$ with $\eta \equiv \exp(-\beta\Delta A_1)$. The average functionalities are given by $f_{av} = fx/(1 + x)$, $f_w = (1 + fx)/(1 + x)$, and $f_n = fx(1 + x)^{f-1}/[(1 + x)^f - 1]$. The fundamental relation 5.30 now takes the form

$$\frac{f\lambda}{n}\phi = zu(z)\left[1 + \frac{1}{\eta u(z)}\right] \tag{9.2}$$

and the sol/gel transition point is given by

$$f'\eta zu'(z)/[1 + \eta u(z)] = 1 \tag{9.3}$$

The reduced concentration of λ-molecules is given by

$$x_\lambda = z/\{f\eta[1 + \eta u(z)]^{f'}\} \tag{9.4}$$

The number density of clusters is then given by

$$\lambda\nu^S = \lambda(1 - \phi) - z[f'u(z)/f + I(z)] \tag{9.5}$$

and the weight average molecular weight is

$$P_w(z) = \frac{1 + \eta[u(z) + zu'(z)]}{1 + \eta[u(z) - f'zu'(z)]} \tag{9.6}$$

in the pregel regime. In the postgel regime, the variable z in these equations must be replaced by z', which is the solution of Flory's condition $x_\lambda(z) = x_\lambda(z')$; i.e.,

$$z/[1 + \eta u(z)]^{f'} = z'/[1 + \eta u(z')]^{f'} \tag{9.7}$$

for a given z. The parameter z refers to the conversion of the entire system, while z' refers to that of the sol part only. The weight fraction of the sol is given by the ratio

$$w^S = z'[1 + \eta u(z')]/\{z[1 + \eta u(z)]\} \tag{9.8}$$

and that of the gel is given by $w^G = 1 - w^S$.

B. All-or-None Model. This model assumes that all associative groups are either active or inactive simultaneously. We then have functionality f for the excited state and 0 for the ground state, so that $f_{av} = f\eta u^f/(1 + \eta u^f)$ and $f_n = f_w = f$, where $\eta \equiv \exp(-\beta\Delta A_f)$. When $f = 2$ and association is restricted to pairwise connection, this model reduces to Scott's theory[21] developed for the study of sulfur. The fundamental relation in this model takes the form

$$\frac{f\lambda}{n}\phi = zu(z)[1 + 1/\eta u(z)^f] \tag{9.9}$$

and the sol/gel transition point is found by the condition

$$f'zu'(z)/u(z) = 1 \tag{9.10}$$

The concentration of λ-molecules is given by $x_\lambda = z/f\eta u(z)^{f'}$. The number density of clusters is then given by

$$\lambda\nu^S = \lambda(1 - \phi) + z\left[\frac{1 - f'\eta u(z)^f}{f\eta u(z)^{f'}} + I(z)\right] \tag{9.11}$$

The weight-average molecular weight is given by

$$P_w(z) = 1 + f\eta zu(z)^f u'(z)/\{[1 + \eta u(z)^f]\,[u(z) - f'zu'(z)]\} \tag{9.12}$$

In the postgel regime, z' must be found by the condition

$$z/u(z)^{f'} = z'/u(z')^{f'} \tag{9.13}$$

The sol fraction is then given by

$$w^S = [1 + \eta u(z')^f]/[1 + \eta u(z)^f] \tag{9.14}$$

In the special case of the fixed multiplicity s for this all-or-none excitation model, all relations reduce to simpler ones. For instance, the average functionality is given by

$$f_{av} = f/[1 + (1 - \alpha)^f/\eta] \tag{9.15}$$

with $f_n = f_w = f$. Since each cluster has $j_1 = [(f's' - 1)l + s]/s'$ unassociated groups and $j_s = (l - 1)/s'$ junctions, the cluster distribution (6.1) now takes a simple form

$$\lambda\nu(\mathbf{j};\mathbf{l}) = \omega_l x_f^l \tag{9.16}$$

where the combinatorial coefficient ω_l is defined by

$$\omega_l \equiv (j_1 + j_s - 1)!/(lj_1!j_s!) \tag{9.17}$$

This coefficient reduces to Stockmayer's factor $\omega_l = (fl$

$- l)!/[l!(fl - 2l + 2)!]$ studied in the classical theory of gelation for $s = 2$.

The mth moment of this distribution is then defined by

$$S_m \equiv \sum_{l\geq 1} l^m \omega_l x^l \tag{9.18}$$

For instance, the first three moments take simple forms when expressed in terms of the conversion α as

$$S_0(\alpha) = \alpha^{1/s'}(1 - fs'\alpha/s)/[f(1-\alpha)^{s/s'}] \tag{9.19a}$$

$$S_1(\alpha) = \alpha^{1/s'}/[f(1-\alpha)^{s/s'}] \tag{9.19b}$$

$$S_2(\alpha) = \alpha^{1/s'}(1 + s'\alpha)/[f(1-\alpha)^{s/s'}(1 - f's'\alpha)] \tag{9.19c}$$

The sol/gel transition point is then found from the divergence of the second moment:

$$\alpha^* = 1/(f's') \tag{9.20}$$

The fundamental relation eq 5.30 connecting α to the concentration can be written as

$$\frac{\lambda}{n}\phi = \left[1 + \frac{(1-\alpha)^f}{\eta}\right] S_1(\alpha) \tag{9.21}$$

The average junction multiplicities are given by $\mu_n = 1/(1 - s'\alpha/s)$ and $\mu_w = 1 + s'\alpha$, and the average molecular weight is given by

$$P_w(\alpha) = 1 + f_{av}s'\alpha/(1 - f's'\alpha) \tag{9.22}$$

The number densities of λ-molecules and of μ-clusters are given by

$$\lambda\nu_\lambda = (1-\alpha)^f S_1(\alpha)/\eta \tag{9.23}$$

$$\lambda\nu_\mu^S = S_0(\alpha) \tag{9.23b}$$

All of these equations reduce to those derived for the study of sulfur[21] in the special case of $f = 2$ and $s = 2$.

X. Numerical Calculation of the Phase Diagrams

In the following numerical calculation, we focus our interest mainly in high-temperature gelation, because low-temperature gelation has already been studied in the literature.[25,28] First, we introduce the dimensionless temperature τ by the equation

$$\tau \equiv 1 - \Theta/T \tag{10.1}$$

where Θ is Flory's theta temperature of our polymer solution. The segment interaction parameter χ can then be expressed by Schultz−Flory formula $\chi = {}^1/_2 - \psi_1\tau$, where ψ_1 is a material parameter of order unity.[26] We fix $\psi_1 = 1$ in the calculation of the phase diagrams. The association constant and the excitation constant take the form

$$\lambda(T) = \lambda_0 \exp[\lambda_1(1 - \tau)] \tag{10.2}$$

and

$$\eta(T) = \eta_0 \exp[\eta_1(\tau - 1)] \tag{10.3}$$

where λ_0 et al. are dimensionless positive constants.

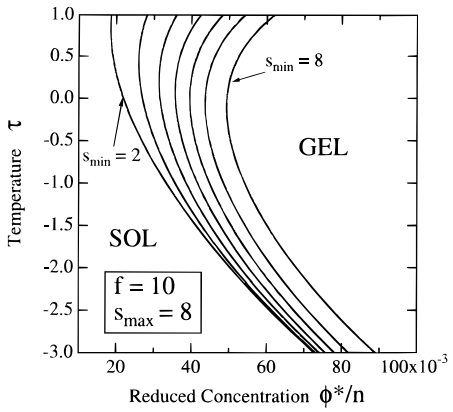

Figure 7. Sol/gel transition line of an independent excitation model with multiple junctions. The concentration is shown by using the volume fraction divided by the number of statistical units on a primary chain: functionality $f = 10$; maximum allowed multiplicity $s_{max} = 8$; minimum multiplicity varied; $\lambda_0 = 2.0$, $\lambda_1 = 1.2$; $\eta_0 = 1.0$, $\eta_1 = 1.3$.

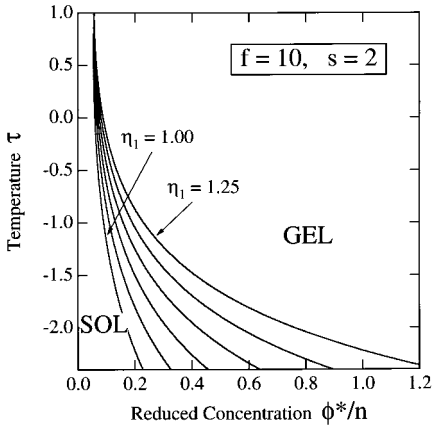

Figure 8. Same as Figure 7 for pairwise association: $f = 10$; $\lambda_0 = 1.0$, $\lambda_1 = 1.2$; $\eta_0 = 1.0$, η_1 varied from 1.00 to 1.25.

Let us consider the independent excitation model. Figure 7 shows the effect of junction multiplicity on the sol/gel transition. The functionality is fixed at $f = 10$. The association constants are fixed at $\lambda_0 = 2.0$ and $\lambda_1 = 1.2$. The excitation parameters are fixed at $\eta_0 = 1.0$ and $\eta_1 = 1.3$. The junction multiplicity between s_{min} and s_{max} is allowed. The maximum multiplicity is fixed at $s_{max} = 8$ while the minimum multiplicity is varied from curve to curve over the range from 2 to 8. The gel region shrinks as s_{min} approaches s_{max} because the range of allowed multiplicity becomes smaller. Most of the curves have the temperature at which the gelation concentration becomes minimal. This is the optimal temperature of gelation. Therefore, under a fixed concentration, the solution gels on heating, but it goes back to sol on further heating. Such a nonmonotonic behavior was already theoretically pointed out by Higgs and Ball[5] and experimentally reported in several pieces of literature.[4] Figure 8 shows the same but for different excitation parameters. The functionality is fixed at $f = 10$ again but for the pairwise association $s_{min} = s_{max} = 2$. Association constants are $\lambda_0 = 1.0$ and $\lambda_1 = 1.2$. The excitation parameter η_0 is fixed at 1.0 while η_1 is varied from curve to curve over the range from 1.00 to 1.25. Gelation becomes easier with temperature for these material parameters. There is no optimal temperature.

Figure 9 shows the same but for the all-or-none excitation model with varied multiplicity for the func-

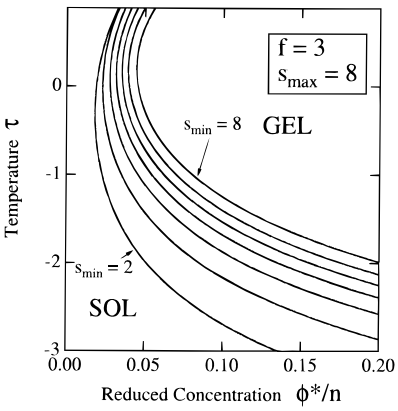

Figure 9. Sol/gel transition line of an all-or-none excitation model: $f = 3$; $s_{max} = 8$; s_{min} varied from 2 to 8; $\lambda_0 = 5.0$, $\lambda_1 = 1.0$; $\eta_0 = 4.0$, $\eta_1 = 2.0$.

tionality 3. Though the detailed shape of the curves is different, the overall behavior is the same as that of the independent excitation model. The special case of $f = 2$ and $s_{max} = s_{min} = 2$ was studied by Scott[21] with regard to equilibrium polymerization of sulfur.

Figure 10a−d shows how the phase behavior changes depending upon the relative strength of the association constant and the excitation constant. All phase diagrams are calculated for trifunctional ($f = 3$) low molecular weight molecules ($n = 1$) with triple junctions ($s = 3$). Independent excitation of the functional groups is assumed. In these diagrams, solid lines show binodal, broken lines sol/gel transition, and shaded areas unstable regions. When the association constant is large as in Figure 10a, the solution exhibits UCST type phase separation intersecting with the low-temperature sol/gel transition line at the top of the phase separation region. With decrease in the strength of association (Figure 10b), or increase in the excitation constant (Figure 10c), association in the low-temperature region becomes less favorable, and as a result, the lower part of a sol/gel line tends to shift to higher concentration region. The unstable region around the sol/gel transition line move upward following the shift of the sol/gel transition line. In Figure 10c, the two-phase region splits into two pieces. In the case of extremely large excitation constant as in Figure 10d, the gel region completely separates from the UCST miscibility dome, because strong thermal excitation is required to activate functional groups. Extra LCST and UCST appear at the top and bottom of the high-temperature isolated two-phase region. This diagram resembles that of the equilibrium polymerization of sulfur in a solution,[21] but the polymerization line is replaced by the gelation line. Tobitani and Ross-Murphy[10] confirmed a similar gelation line in the study of heat-induced gelation in aqueous solution of globular protein (bovine serum albumin). Figure 11 shows the same but for polymeric primary molecules with $n = 100$, and $f = 10$ in the case of triple junction. A new unstable region just splits from the miscibility gap with UCST in this figure.

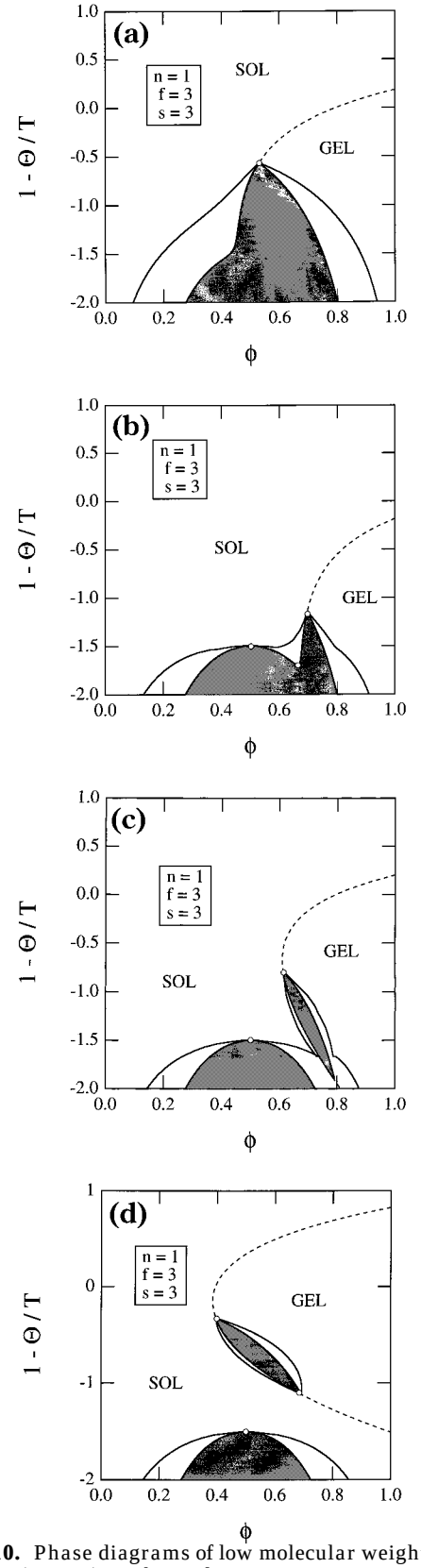

Figure 10. Phase diagrams of low molecular weight primary molecules ($n = 1$) with triple associative groups ($f = 3$). Independent excitation followed by triple association ($s = 3$) is assumed. Association constant and excitation constant are fixed at the following: (a) $\lambda_0 = 0.73$, $\lambda_1 = 2.50$, $\eta_0 = 1.00$, $\eta_1 = 2.50$; (b) $\lambda_0 = 0.49$, $\lambda_1 = 2.50$, $\eta_0 = 1.00$, $\eta_1 = 2.50$; (c) $\lambda_0 = 0.73$, $\lambda_1 = 2.50$, $\eta_0 = 1.00$, $\eta_1 = 2.80$; (d) $\lambda_0 = 1.48$, $\lambda_1 = 2.00$, $\eta_0 = 1.00$, $\eta_1 = 3.00$.

XI. Gelation by Helix/Coil Transition: Sequence Selection Problem

A large body of experimental and theoretical study on the problem of single-chain helix/coil transition now exists, but there is room for the theoretical study of gelation induced by helix/coil transition. In this section, we apply our theoretical model specifically to polymer solutions in which polymers form partial helices along

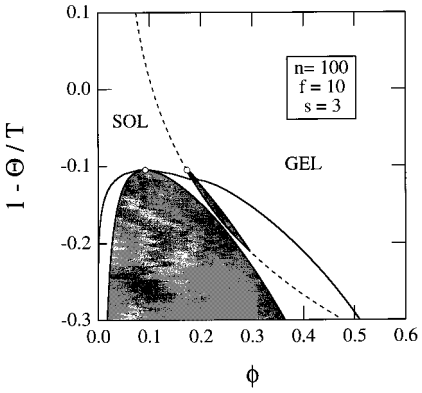

Figure 11. Phase diagram of high molecular weight primary molecules ($n = 100$) with many associative groups ($f = 10$). Independent excitation followed by triple association ($s = 3$) is assumed. $\lambda_0 = 160.7$, $\lambda_1 = 3.0$, $\eta_0 = 1.0$, and $\eta_1 = 8.5$.

their chain backbone preceding gelation. In order to focus on the many-chain problem concerning the connectivity over entire solution, we here employ the simplest model of the helix/coil transition. We consider a single polymer chain with total number n of statistical units as above from which j sequences of ζ contiguous chain segments have been selected for helix formation. We neglect possible polydispersity of the helix length and simply assume that all helix segments have the same length ζ under a given temperature and polymer concentration. The total number $W(n, j, \zeta)$ of possible arrangement of j nonoverlapping sequences of length ζ is then given by

$$W(n, j, \zeta) = (n - j\zeta + j)!/\{j!(n - j\zeta)!\} \quad (11.1)$$

Obviously, the maximum possible number f of the helices on a chain is given by

$$f = [n/\zeta] \quad (11.2)$$

where symbol $[x]$ indicates the maximum integer not exceeding the value x. A similar sequence selection problem was considered by Gornick and Jackson[30] to study the effect of segment crystallization on the rubber elasticity.

Characteristic feature of gelation by sequence selection lies in that, for the pairwise association, f must be equal to or larger than 3 in order for the solution to gel, and for multiple association, it must be equal to or larger than 2. Therefore, as the sequence ζ becomes longer with decrease in the temperature, the effective functionality becomes smaller, and at a certain critical value of ζ, the solution goes back to a nongelling system. This simple consideration suggests that gelation becomes easiest at a certain intermediate temperature. To show this nonmonotonic behavior, we now calculate the sol/gel transtion line on the temperature−concentration plane.

The excitation free energy, or partition function, of a chain with j sequences is given by

$$\exp(-\beta\Delta A_j) = W(n, j, \zeta)[\exp(-\beta\Delta A_\zeta)]^j/\sigma \quad (11.3)$$

where ΔA_ζ is the free energy produced when a single sequence changes into a helix from a random coil conformation and, to avoid overcounting, the total number is divided by the symmetric number $\sigma = 2$ of the original polymer chain in a random coil conformation. The functions $F_m(z)$ therefore take the form

$$F_m(z) = \frac{1}{\sigma}\sum_{j=0}^{n} j^m \frac{(n - j\zeta + j)!}{j!(n - j\zeta)!}(\eta_\zeta u(z))^j \quad (11.4)$$

where

$$\eta_\zeta \equiv \exp(-\beta\Delta A_\zeta) \quad (11.5)$$

is the parameter related to polymer conformational change. It is expected to take the form $\eta_\zeta = \eta(T)^\zeta$ by using the excitation free energy $\eta(T) \equiv \exp(-\beta\Delta A_1)$ per monomer along the helix sequence. The average functionalities are then given by

$$f_w(z) = F_2/F_1 = g_2(x)/g_1(x) \quad (11.6)$$

and

$$f_{av}(z) = F_1/(1 + F_0) = g_1(x)/g_0(x) \quad (11.7)$$

where functions $g_m(x)$ are defined by

$$g_m(x) \equiv \sum_{j=0}^{f} j^m \frac{(n - j\zeta + j)!}{j!(n - j\zeta)!}x^j \quad (11.8)$$

and the variable x is defined by $x \equiv \eta_\zeta u(z)$.

Now, the fundamental equation connecting the parameter z to the polymer concentration ϕ is transformed to

$$\frac{\lambda_\zeta g_1(x)}{n\, g_0(x)}\phi = zu(z) \quad (11.9)$$

The gel point is given by the condition

$$\left\{\frac{g_2(x)}{g_1(x)} - 1\right\}\frac{zu'(z)}{u(z)} = 1 \quad (11.10)$$

When $\zeta = 1$, the function $g_0(x)$ becomes $g_0(x) = (1 + x)^n$, and the model reduces to the independent excitation model with functionality n.

As a characteristic feature of the sequence selection problem, we easily see that gelation becomes impossible as soon as ζ becomes larger than $n/2$, because the average functionality is less than 2. Similarly, if ζ takes a value in between $n/3$ and $n/2$, gelation by pairwise association is impossible, but gelation by multiple association is still possible. As a typical example, we show in Figure 12a,b gelation concentration against sequence length at a given temperature, hence a given association constant λ and an excitation constant η for the fixed multiplicity model. We assume that these parameters take the form $\lambda_\zeta = \lambda(T)^\zeta$ and $\eta_\zeta = \eta(T)^\zeta$ because each statistical unit in the selected sequence length equally participates both in association and excitation. The number of statistical units on a chain is fixed at $n = 50$. Figure 12a shows that the gel concentration monotonically increases with the sequence length for $\lambda(T) = 1.10$ and $\eta(T) = 0.90$. It diverges at $\zeta = 17$ for pairwise association $s = 2$ and at $\zeta = 26$ for multiple association $s \geq 3$. Although the association free energy increases with the sequence length, the effect of decrease in the functionality (the number of selected sequences on a chain) dominates for this value of λ. As is shown in Figure 12b, however, a larger value of λ

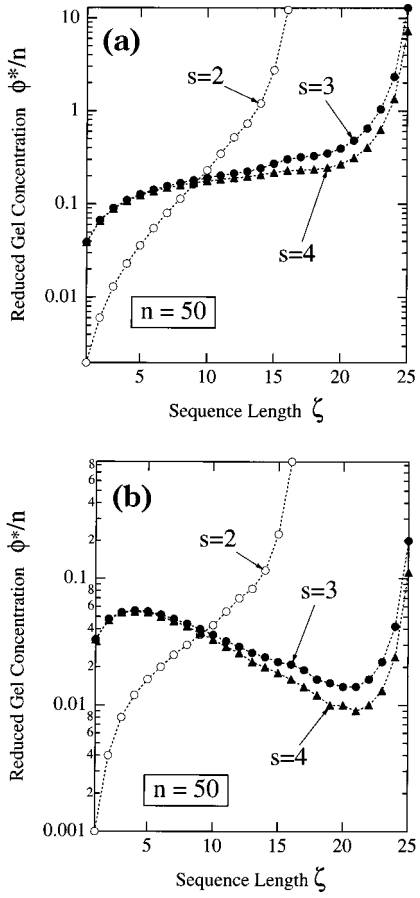

Figure 12. Sol/gel transition curve for the model helix/coil transition. The gel concentration is plotted against sequence length ζ of the helix part. The total number of statistical units on a chain is fixed at $n = 50$. For pairwise association ($s = 2$, white circles), the solution becomes nongelling for $\zeta \geq 17$. For multiple association ($s = 3, 4, ...$, black circles), it becomes nongelling for $\zeta \geq 26$. The association constant is fixed at (a) $\lambda = 1.10$ and (b) $\lambda = 1.30$, while the excitation constant is fixed at $\eta = 0.90$ in both parts.

leads to nonmonotonic behavior of the gel concentration in the case of multiple association. There is an optimal value of the sequence length at which gelation becomes easiest as a result of the competition of the two opposite tendencies described above. We therefore expect that triple association of helices, for instance, exhibits more interesting gelation than pairwise association. For a complete description of the phenomena, however, we have to study the temperature dependence of the sequence length. The results will be reported in a separate paper.

XII. Conclusions and Discussion

We have attempted to develop a general theory to find phase behavior of gelling polymer solutions in which there are strong couplings between polymer conformational change and intermolecular cross-linking. From the theoretical and numerical results obtained in the present paper, the following conclusions can be drawn:

(1) Both high-temperature gelation and low-temperature gelation are possible depending upon the type of conformational change for activating associative groups. (2) Sol/gel transition concentration can vary nonmonotonically as a function of the temperature where activation of associative groups competes with intermolecular cross-linking. A large gel region often appears at intermediate temperatures in the phase diagrams. (3) The multiplicity of cross-link junctions strongly affects the phase diagrams; the gel region shrinks as the range of allowed multiplicity is restricted. (4) In the case of gelation due to helix-to-coil transition followed by the aggregation of helices, constraints in selecting helix sequences out of the limited total number of statistical units on a chain lead to the appearance of an optimal sequence length for gelation. The effect becomes stronger with increase in the junction multiplicity.

Our results may be directly applicable to some real thermoreversible gels of natural polymers such as proteins (albumin, hemoglobin, etc.) and polysaccharides (carrageenan, agarose, gellan, etc.) and of synthetic polymers such as hydrophobically modified associating polymers under careful treatment of the excitation parameter and the association constant.

Throughout this paper, we have treated the problem on the basis of classical tree statistics. The validity of such a treatment has long been investigated in the literature for gelation by chemical reaction. But, for physical gelation, especially with complex multiple cross-links, study has just started. In hydrophobically modified associating polymers, for instance, formation of intramolecular loops has been reported to drive the solutions into micellization of loops competing with intermolecular cross-linking.[18] It is possible to incorporate such small loops as correction to the tree approximation. In fact, we have recently studied theoretically and computationally the appearance of flower micelles in telechelic associating polymers carrying two hydrophobes at both chain ends.[31] In the case of telechelic polymers, the excited state is unique, namely, a single loop. We can then map the problem onto a mixture of difunctional ($f = 2$) molecules and nomofunctional ($f = 1$) pseudomolecules. The excitation parameter η corresponds to the probability to form a loop discussed by Jacobson and Stockmayer.[32] Appearance of flower micelles and flower/bridge transition was successfully described within the present theoretical scheme. The inclusion of large-scale loops or cycles in a cluster is, however, difficult. The systematic strategy developed by Gordon and Scantlebury[33,34] may possibly be extended to multiple cross-linking.

Regarding thermoreversible gelation strongly coupled to polymer conformation change, further refinement of the present theory would involve (1) determination of the junction multiplicity and the average sequence length by thermodynamic requirements including their possible polydispersity and (2) study of possible inhomogeneous structure in gels caused by phase separation. It is hoped to pursue these topics in later publications.

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References and Notes

(1) Burchard, W. *Br. Polym. J.* **1985**, *17*, 154.
(2) Clark, A. H.; Ross-Murphy, S. B. *Adv. Polym. Sci.* **1985**, *83*, 57.
(3) Guenet, J. M. *Thermoreversible Gelation of Polymers and Biopolymers;* Academic Press, Harcourt Brace Jovanovich Publishers: San Diego, CA, 1992.
(4) Te Nijenhuis, K. *Adv. Polym. Sci.* **1997**, *130*, 1.
(5) Higgs, P. G.; Ball, R. C. *J. Phys. (Paris)* **1989**, *50*, 3285.
(6) Viebke, C.; Piculell, L.; Nilsson, S. *Macromolecules* **1994**, *27*, 4160.

(7) Berghmans, M.; Thijs, S.; Cornette, M.; Berghmans, H.; Schryver, F. C. D. *Macromolecules* **1994**, *27*, 7669.
(8) Buyse, K.; Berghmans, H.; Bosco, M.; Paoletti, S. *Macromolecules* **1998**, *31*, 9224.
(9) Biagio, P. L.; Palma, M. U. *Biophys. J.* **1991**, *60*, 508.
(10) Tobitani, A.; Ross-Murphy, S. B. *Macromolecules* **1997**, *30*, 4845, 4855.
(11) Sinclair, M.; Lim, K. C.; Heeger, A. J. *Phys. Rev. Lett.* **1983**, *51*, 1768.
(12) Peiffer, D. G.; Chung, T. C.; Schulz, D. N.; Agarwal, P. K.; Garner, R. T.; Kim, M. W. *J. Chem. Phys.* **1986**, *85*, 4712.
(13) Chen, P.; Adachi, K.; Kotaka, T. *Polymer* **1992**, *33*, 1363, 1813.
(14) Annable, T.; Buscall, R.; Ettelaie, R.; Whittlestone, D. *J. Rheol.* **1993**, *37*, 695.
(15) Annable, T.; Buscall, R.; Ettelaie, R.; Shepherd, P.; Whittlestone, D. *Langmuir* **1994**, *10*, 1060.
(16) Rao, B.; Uemura, Y.; Dyke, L.; Macdonald, P. M. *Macromolecules* **1995**, *28*, 531.
(17) Alami, E.; Almgren, M.; Brown, W.; Francois, J. *Macromolecules* **1996**, *29*, 2229.
(18) Xu, B.; Yekta, A.; Winnik, M. A. *Langmuir* **1997**, *13*, 6903.
(19) Lairez, D.; Adam, M.; Carton, J.-P.; Raspaud, E. *Macromolecules* **1997**, *30*, 6798.
(20) Tobolsky, A. V.; Eisenberg, A. *J. Am. Chem. Soc.* **1959**, *81*, 780.
(21) Scott, R. L. *J. Phys. Chem.* **1965**, *69*, 261; **1967**, *71*, 352.
(22) Fukui, K.; Yamabe, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2052.
(23) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(24) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45; **1944**, *12*, 125.
(25) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943.
(26) Flory, P. J. *J. Chem. Phys.* **1944**, *12*, 425. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(27) Tanaka, F.; Matsuyama, A. *Phys. Rev. Lett.* **1989**, *62*, 2759.
(28) Tanaka, F. *Macromolecules* **1990**, *23*, 3784, 3790.
(29) Poland, D.; Scheraga, H. A. *Theory of Helix-Coil Transitions in Biopolymers*; Academic Press: New York and London, 1970.
(30) Gornick, F.; Jackson, J. L. *J. Chem. Phys.* **1963**, *38*, 1150.
(31) Tanaka, F.; Koga, T. *Comp. Theor. Polym. Sci.*, in press.
(32) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1960**, *18*, 1600.
(33) Gordon, M.; Scantlebury, G. R. *Proc. R. Soc. (London), Ser. A* **1962**, *268*, 240.
(34) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1964**, *41*, 2389.

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