Thermoreversible Gelation with Junctions of Variable Multiplicity

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ABSTRACT: This paper presents a molecular theory of the thermodynamic properties of reversible gels whose junctions are formed by the clustering of an arbitrary number of associating groups, or segments, on the constituent molecules (or primary chains for polymeric gels). Cross-linking by the microcrystalline segments on the polymer chains or by associating groups attached to the chain ends are examples. We focus our interest specifically on the interference between gelation and two-phase separation. We study how these transitions depend on the molecular weight, functionality, and the aggregation number (multiplicity) of the network junctions.

1. Introduction

The cross-links in thermoreversible gels may involve crystallization of chain segments[1–4] or other types of association.[5] A large body of experimental data now exists[6–9] but there is room for further theoretical study. In general, such reversible gel formation is essentially an equilibrium phenomenon.[10–13] In this paper, we extend previous studies(I)[14–16] of such equilibrium and of the possible interference between gelation and liquid–liquid phase separation. In the earlier work (referred to as I), standard Flory–Huggins solution theory[17,18] was combined with the standard tree statistics[19,20] by assuming cross-links exclusively due to pairwise contacts between polymer segments.

Since microcrystalline junctions must usually involve far more than two chains, it was considered useful to extend the earlier results (referred to as II)[21] on the basis of the relevant statistical treatment of Fukui and Yamabe[22] (hereafter FY). In this way it was possible to rationalize two frequent (but not necessarily universal) experimental observations: (1) the critical gel concentration may depend only weakly on molecular weight;[2] (2) the onset of association prior to gelation may be noticeable over only a small range of concentration just below the critical value (but this is not always the case[23,24]). The purpose of the present paper is to give a more detailed theoretical description of polymer solutions capable of forming gels via multichain junctions and to find the common thermodynamic characteristics derived from this multiplicity.

2. Stoichiometric Definitions

We consider a polydisperse mixture of functional molecules (or primary polymer chains) in a solvent. A molecule is distinguished by the number f of the functional groups it carries, each functional group being capable of taking part in junctions which may bind together any number k of such groups. Hereafter we shall call k the *multiplicity* of a junction. In the previous papers, the multiplicity was restricted to a single value (2 in I, or $s \geq 2$ in II) in a given system, in addition to the value $k = 1$ representing unreacted groups. We now abandon this restriction and allow junctions of all multiplicities to coexist, in proportions determined by the thermodynamic equilibrium conditions. The number of statistical segments on an f-functional molecule is denoted by r_f, and is in the present work taken to have a single unique value for each functionality. Thus, fluctuations in chemical or stereochemical composition of the primary molecules are ignored. These could be included easily, but only at the expense of a more cumbersome notation which does not seem worth while for present purposes.

In thermal equilibrium, the solution has a distribution of clusters with a population distribution fixed by the equilibrium conditions. Following the FY notation,[22] we define a cluster of type ($\mathbf{j}$; $\mathbf{n}$) to consist of n_f primary molecules of functionality f ($f = 1, 2, 3, ...$) and j_k junctions of multiplicity k ($k = 1, 2, 3, ...$) (see Figure 1). The bold letters $\mathbf{n} \equiv \{n_1, n_2, n_3, ...\}$ and $\mathbf{j} \equiv \{j_1, j_2, j_3, ...\}$ denote the sets of indices. Note that $k = 1$ indicates unreacted functional groups. An isolated molecule of functionality f, for instance, is indicated by $\mathbf{j}_{0f} \equiv \{f, 0, 0, ...\}$, and $\mathbf{n}_{0f} \equiv \{0, ..., 1, 0, ...\}$.

Let $l \equiv \sum n_f$ be the total number of primary molecules in a cluster. Then the following two independent algebraic conservation conditions hold, provided there are no cyclic structures:

$$\sum n_f = l = \sum (k-1) j_k + 1 \tag{2.1}$$

$$\sum j_k = \sum (f-1) n_f + 1 \tag{2.2}$$

One of these relations can be replaced by the useful identity

$$\sum k j_k = \sum f n_f \tag{2.3}$$

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

$$w_f = f N_f / (\sum f N_f) \tag{2.4}$$

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.

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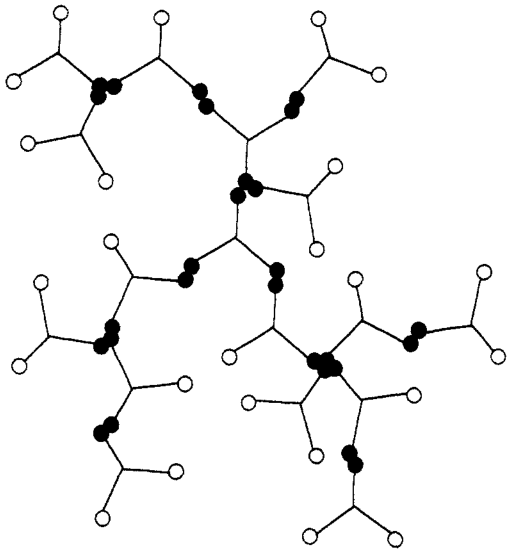

Figure 1. Tree formed by trifunctional molecules carrying reactive groups capable of forming junctions of variable multiplicity. Open circles show the unreacted groups ($k = 1$). The multiplicity index of this tree is given by $\mathbf{j} = \{24, 7, 3, 1, 0, 0, ...\}$.

Thus, if $N(\mathbf{j}; \mathbf{n})$ is the number of $(\mathbf{j}; \mathbf{n})$ clusters in the system, their number density is

$$\nu(\mathbf{j}; \mathbf{n}) = N(\mathbf{j}; \mathbf{n})/\Omega \qquad (2.5)$$

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

$$\phi(\mathbf{j}; \mathbf{n}) = (\sum r_f n_f)\nu(\mathbf{j}; \mathbf{n}) \qquad (2.6)$$

The total volume fraction of the polymer component is thus

$$\phi = \sum_{\mathbf{j},\mathbf{n}} \phi(\mathbf{j}; \mathbf{n}) \qquad (2.7)$$

or equally well

$$\phi = \sum_f r_f N_f/\Omega \qquad (2.8)$$

It will also be useful later to consider the total volume concentration of functional groups,

$$\psi = (\sum f N_f)/\Omega \qquad (2.9)$$

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

$$\phi_f = r_f N_f/\Omega \qquad (2.10)$$

From (2.4) we easily find

$$\phi/\psi = \sum r_f f^{-1} w_f \equiv R \qquad (2.11a)$$

and

$$\phi_f/\psi = r_f f^{-1} w_f \qquad (2.11b)$$

The ratio R gives the average number of statistical segments per functional group.

3. Multiple Equilibria

3.1. Free Energy of the Mixture. We now consider the free energy of the system at a temperature T and polymer volume fraction ϕ, by applying classical Flory–Huggins theory for multicomponent systems[17,18] and letting the interaction parameter χ be the same for all the species. The chosen standard states are pure solvent and separated pure unmixed amorphous primary solute species. The free energy change on passing from the standard states to the final solution, at equilibrium with respect to cluster formation, is given by the expression[14–16]

$$\frac{\beta \Delta F}{\Omega} = \nu_0 \ln \phi_0 + \sum_{\mathbf{j},\mathbf{n}} \nu(\mathbf{j}; \mathbf{n})[\Delta(\mathbf{j}; \mathbf{n}) + \log \phi(\mathbf{j}; \mathbf{n})] + \chi \phi_0 \phi + \sum_f \nu_f^{\mathrm{G}} \delta_f \qquad (3.1)$$

where the subscript zero denotes the solvent, with volume fraction $\phi_0 = 1 - \phi$ and $\beta \equiv 1/k_{\mathrm{B}}T$. The quantity $\Delta(\mathbf{j}; \mathbf{n})$ involves the free energy change accompanying the formation of a $(\mathbf{j}; \mathbf{n})$ cluster in a hypothetical undiluted amorphous state from the separate primary molecules in their standard states (superscript zero):

$$\Delta(\mathbf{j}; \mathbf{n}) \equiv \beta\{\mu^0(\mathbf{j}; \mathbf{n}) - \sum_f n_f \mu^0(\mathbf{j}_{0f}; \mathbf{n}_{0f})\} \qquad (3.2)$$

We may call it the "internal free energy" of the cluster. The mixing entropy and interaction terms in (3.1) are recognizable. The final term appears only after the gel point is passed and a macroscopic network begins to form; it contains the number density ν_f^{G} of f-functional primary molecules in the network and the free-energy change δ_f produced on bringing an isolated primary molecule into the network:

$$\delta_f = r_f \lim_{l \to \infty} \Delta(\mathbf{j}; \mathbf{n})/(\sum n_f r_f) \qquad (3.3)$$

The total volume fraction of the gel is then

$$\phi^{\mathrm{G}} = \sum_f \phi_f^{\mathrm{G}} = \sum_f r_f \nu_f^{\mathrm{G}} = \phi - \phi^{\mathrm{S}} \qquad (3.4)$$

where superscript S denotes the sol.

The classical Flory–Huggins lattice model is incompressible, but for real compressible systems the free enthalpy change ΔG should be understood for ΔF in (3.1).

Now the chemical potentials corresponding to (3.1) are given by

$$\beta \Delta \mu_0 = \ln(1 - \phi) + \left(1 - \frac{1}{D_{\mathrm{n}}(\phi)}\right)\phi + \chi \phi^2 \qquad (3.5)$$

for the solvent, and

$$\beta \Delta \mu(\mathbf{j}; \mathbf{n}) = 1 + \Delta(\mathbf{j}; \mathbf{n}) + \ln \phi(\mathbf{j}; \mathbf{n}) + (\sum r_f n_f)\left[-1 + \left(1 - \frac{1}{D_{\mathrm{n}}(\phi)}\right)\phi + \chi {\phi_0}^2\right] \qquad (3.6)$$

for a cluster of type $(\mathbf{j}; \mathbf{n})$. Here we have introduced the number-average polymerization degree of the clusters

$$D_{\mathrm{n}} = D_{\mathrm{n}}(\phi) \equiv \sum_{\mathbf{j},\mathbf{n}} (\sum n_f r_f)\nu(\mathbf{j}; \mathbf{n}) / \sum_{\mathbf{j},\mathbf{n}} \nu(\mathbf{j}; \mathbf{n})$$
$$(= \phi^{\mathrm{S}}/\nu^{\mathrm{S}} \quad \text{before the gel point}) \qquad (3.7)$$

Similarly, the weight-average polymerization degree is

$$D_{\mathrm{w}} = D_{\mathrm{w}}(\phi) \equiv \sum_{\mathbf{j},\mathbf{n}} (\sum n_f r_f)\phi(\mathbf{j}; \mathbf{n})/\phi \qquad (3.8)$$

Now the equilibrium conditions for association

$$\mu(\mathbf{j};\mathbf{n}) = \sum_f n_f \mu(\mathbf{j}_{0f};\mathbf{n}_{0f}) \tag{3.9}$$

lead to the population distribution,

$$\phi(\mathbf{j};\mathbf{n}) = K(\mathbf{j};\mathbf{n}) \prod_f \phi(\mathbf{j}_{0f};\mathbf{n}_{0f})^{n_f} \tag{3.10}$$

with

$$\ln K(\mathbf{j};\mathbf{n}) = l - 1 - \Delta(\mathbf{j};\mathbf{n}) \tag{3.11}$$

In the postgel regime, we have the excess $\phi^{\mathrm{G}} \equiv \phi - \phi^{\mathrm{S}}$, and so differentiation of the free energy leads to the chemical potential

$$\beta \Delta\mu_f^{\mathrm{G}} = \delta_f - r_f(1 - \phi + \nu^{\mathrm{S}} - \chi\phi_0^{\,2}), \tag{3.12}$$

for a chain of f-type in the network. We have an additional condition that in equilibrium this must balance with the chemical potential $\Delta\mu(\mathbf{j}_{0f};\mathbf{n}_{0f})$ of an isolated molecule:

$$\Delta\mu_f^{\mathrm{G}} = \Delta\mu(\mathbf{j}_{0f};\mathbf{n}_{0f}) \tag{3.13}$$

or explicitly

$$\phi(\mathbf{j}_{0f};\mathbf{n}_{0f}) = \mathrm{e}^{\delta_f - 1} \tag{3.14}$$

3.2. Internal Free Energy. As long ago emphasized by Flory,[18] the conformational entropy of flexible chains plays an important role in determining polymerization or association equilibria. We therefore evaluate $\Delta(\mathbf{j};\mathbf{n})$ by considering the following hypothetical four-step process:

(a) Select the primary chains which are to be bound together into a special $(\mathbf{j};\mathbf{n})$ cluster.

(b) Bring each selected primary chain separately from its amorphous flexible standard state into the hypothetical ordered state described by Flory.[18]

(c) Combine the selected ordered primary chains into the specified cluster in its hypothetical ordered "Flory state".

(d) Disorient the cluster by allowing each of its parts to assume random flexible conformations.

The first contribution can be taken from FY and reads

$$\Delta_a = -\ln[\omega(\mathbf{j};\mathbf{n}) / \prod_f n_f! \omega(\mathbf{j}_{0f};\mathbf{n}_{0f})] \tag{3.15}$$

where the combinatory factor is given by

$$\omega(\mathbf{j};\mathbf{n}) = (\sum j_k - 1)!(l-1)! \prod_f f^{n_f} / \prod_k j_k! [(k-1)!]^{j_k} \tag{3.16}$$

In the derivation[20,22] of this factor, each primary chain, each functional group, and each junction are first taken to be distinguishable, with a subsequent correction for indistinguishability, as in "corrected" Boltzmann statistics.

The second and fourth contribution can be considered together, in a direct application of Flory's procedure.[18] Their importance resides in their dependence on chain length: if they were ignored, the internal free energy would violate the well-established "principle of equal reactivity", according to which the reactivity of a functional group must be a local property independent of the size of the molecule to which it is attached. This is made clear in Flory's treatment of simple linear polymerization equilibria.

Going now to the details, we set all molecular symmetry numbers equal to unity (the exceptions being highly improbable) and replace (as did Flory) the model lattice coordination number ζ by $\zeta - 1$ for the first bond of each chain. This gives

$$\Delta_b + \Delta_d = (l-1)[1 - \ln(\zeta - 1)] + \sum n_f \ln r_f - \ln(\sum n_f r_f) \tag{3.17}$$

and surely overestimates the flexibility in the neighborhood of a junction. However, this can be remedied in principle by a factor applied to the contribution of step c. Here we must consider the actual bond formation (*e.g.*, crystallization if the junction is a microcrystallite) which in general will involve both enthalpy and entropy changes and would include changes in solvation free energy and contributions from internal molecular degrees of freedom. Recalling that the functional groups were considered as distinguishable in the derivation of eq 3.16 and that the correction must be applied only once and is already contained in Δ_a, we find

$$\Delta_c = -\sum j_k \ln[(k-1)!] + \beta \sum j_k \Delta g_k^0 \tag{3.18}$$

where Δg_k^0 is a function only of the multiplicity k.

We now add the contributions to $\Delta(\mathbf{j};\mathbf{n})$ from eqs 3.15–3.18, and with (3.11) we then obtain the cluster distribution constant as

$$K(\mathbf{j};\mathbf{n}) = (\sum j_k - 1)!(l-1)!(\zeta - 1)^{l-1} (\sum n_f r_f) \prod_f \frac{(f/r_f)^{n_f}}{n_f!} \prod_k \frac{(\mathrm{e}^{-\beta \Delta g_k^0})^{j_k}}{j_k!} \tag{3.19}$$

Now we compare this result with that of FY, which is expressed in terms of the probabilities p_k that a functional group is part of a junction of multiplicity k. Their equation can be expressed in terms of the number densities as

$$\nu(\mathbf{j};\mathbf{n}) = \psi(\sum j_k - 1)!(l-1)! \prod_f \frac{w_f^{n_f}}{n_f!} \prod_k \frac{p_k^{j_k}}{j_k!} \tag{3.20}$$

Since p_1 is the probability that a functional group is uncombined, we can write the volume fraction of free f-functional molecules as

$$\phi(\mathbf{j}_{0f};\mathbf{n}_{0f}) = (r_f w_f / f) \psi p_1^{\,f} \tag{3.21}$$

where use has been made of relations (2.4)–(2.8). Then from (3.10) and (3.19) we find complete agreement of (3.20) with (3.19), provided that

$$p_k = K_k \psi^{k-1} p_1^{\,k} \tag{3.22}$$

with

$$K_k = (\zeta - 1)^{k-1} \exp(-\beta \Delta g_k^0) \tag{3.23}$$

The equilibrium condition (3.22) was earlier presented in II without derivation.

3.3. Special Cases. For sufficiently large junction multiplicity we may expect a constant increment in the binding free energy for each functional group added to a junction. Thus, for large k we could put

$$\Delta g_k^0 = (k-1) g_0 \tag{3.24}$$

This would be a poor approximation for small multiplicity (*e.g.*, a crystallite with both surface and bulk contributions to the free energy of crystallization), and more generally, we should write

$$K_k = [\lambda(T)]^{k-1}\gamma_k \tag{3.25}$$

where

$$\lambda(T) \equiv (\zeta - 1)\exp(-\beta g_0) \tag{3.26}$$

and the factor γ_k approaches unity for large k. In many of the calculations to follow, we shall set γ_k equal to unity for all k, confident that this useful simplification will not affect our qualitative conclusions. If we make this approximation, the distribution law can be expressed in the simpler form

$$\lambda(T)\nu(\mathbf{j};\,\mathbf{n}) = \left(\sum j_k - 1\right)!(l-1)!\prod_f (x_f^{n_f}/n_f!)\prod_k (1/j_k!), \tag{3.27}$$

where renormalized concentrations of isolated molecules are defined by

$$x_f \equiv f\lambda(T)\nu(\mathbf{j}_{0f};\,\mathbf{n}_{0f}) \tag{3.28}$$

In I, the special analog of $\lambda(T)$ was called a *temperature shift factor*, since it always accompanies and rescales the concentration variables.

If we specialize the case of a single primary f-functional species and allow a single multiplicity $k = s$, we have algebraic relations $j_1 = [(f's'-1)l + s]/s'$ and $j_s = (l-1)/s'$, where $f' \equiv f - 1$ and $s' \equiv s - 1$. Equation 3.27 then reduces to

$$\lambda(T)\nu(\mathbf{j};\,\mathbf{n}) = (f's'j_s + f')!(x^{s'})^{j_s}/j_s!(f's'j_s + f - j_s)! \tag{3.29}$$

In the presence of only binary ($s = 2$) junctions, this equation still further reduces to

$$\lambda(T)\nu(\mathbf{j};\,\mathbf{n}) = (fl - l)!x^l/l!(fl - 2l + 2)! \tag{3.30}$$

which is the classical[20] result that was used in earlier papers[14–16] to treat gelation and phase equilibria, although without regard to the contribution of the disorientation entropy.

The total number of clusters per unit cell is given by the sum $\nu^{\mathrm{S}}(\{x\}) = \sum_{\mathbf{j},\mathbf{n}}\nu(\mathbf{j};\,\mathbf{n})$, and also the volume fraction of the $(\mathbf{j};\,\mathbf{n})$ clusters can be found from eq 2.6. In the pregel regime the total volume fraction ϕ is given by the sum $\phi^{\mathrm{S}}(\{x\}) = \sum_{\mathbf{j},\mathbf{n}}\phi(\mathbf{j};\,\mathbf{n})$, but in the postgel regime the excess amount of eq 3.4 gives the volume fraction of the gel network. Following the strategy developed in the previous work,[16] we express the volume fractions of the primary molecules in terms of the known amount ϕ_f of f-functional molecules (which is fixed by the sample composition). In the postgel regime, this is done by solving a set of equations

$$r_f(\partial\nu^{\mathrm{S}}/\partial x_f)x_f = \phi_f \tag{3.31}$$

for all f's with respect to x_f. As soon as a network appears, however, they are fixed to be

$$x_f^*(T) = [f\lambda(T)/r_f]\exp\{\delta_f - 1\} \tag{3.32}$$

thanks to the additional balance condition (3.14), and hence ν^{S} is also fixed as $\nu^*(T) \equiv \nu^{\mathrm{S}}(\{x^*\})$. Upon finding the solution x_f as functions of the experimentally controllable composition $\{\phi_f\}$, we find the number density (and hence the volume fraction) of the $(\mathbf{j};\,\mathbf{n})$ clusters through the relation (3.27). Their chemical potentials (3.6), together with the solvent chemical potential (3.5), then provide the starting point for the study of the solution properties.

4. Sol/Gel Transition

For the general case of multifunctional junctions, FY gave the condition for gelation (appearance of macroscopic trees) as

$$(f_{\mathrm{w}} - 1)(\mu_{\mathrm{w}} - 1) = 1 \tag{4.1}$$

where

$$f_{\mathrm{w}} = \sum f w_f \tag{4.2}$$

the weight-average functionality of primary molecules, and

$$\mu_{\mathrm{w}} \equiv \sum_{k\geq 1} k p_k \tag{4.3}$$

The junction probabilities p_k are given by eq 3.22 and obey the normalization condition

$$\sum_{k\geq 1} p_k = 1 \tag{4.4}$$

Thus, from the condition (4.1) one can specify the concentration ψ^* at the gel point in terms of the association constants K_k. It may be remarked that (4.1) can be directly derived by a straightforward extension of Flory's original argument[19] about the gel point.

Upon substitution of eq 3.22 for p_k with K_k being eq 3.25 into the normalization condition (4.4), we find

$$zu(z) = \lambda(T)\psi \tag{4.5a}$$

where

$$z \equiv \lambda(T)\psi p_1 \tag{4.5b}$$

is the (scaled) number of unreacted functional groups, and a new function $u(z)$ is defined by

$$u(z) \equiv \sum_{k=1}^{\infty}\gamma_k z^{k-1} \tag{4.6}$$

The relation (4.5), when inverted, gives z as a function of the temperature and the concentration. The number density x_f of the isolated f-functional molecules is then expressed in terms of them through the relation

$$x_f = w_f z/u(z)^{f'} \tag{4.7}$$

In order to find the average cluster size, we next consider the moment μ_{w} of (4.3) which relates to the average multiplicity of the junctions. It is given by

$$\mu_{\mathrm{w}}(z) = 1 + zu'(z)/u(z) \tag{4.8}$$

in terms of the function u and its derivative u'. Similarly, the number-average μ_{n}, which is defined by $\mu_{\mathrm{n}} \equiv (\sum p_k/k)^{-1}$, is expressed as

$$\mu_{\mathrm{n}}(z) = u(z)/I(z) \tag{4.9}$$

where a new function $I(z)$ is defined by the integral of $u(z)$ as

$$I(z) \equiv \sum_{k=1}^{\infty} \frac{\gamma_k}{k} z^{k-1} = \frac{1}{z}\int_0^z u(z)\,\mathrm{d}z \tag{4.10}$$

FY expressed the average cluster size in terms of these moments. The result is

$$D_{\mathrm{w}}(z) = R/[1/\mu_{\mathrm{w}} + 1/f_{\mathrm{w}} - 1] \tag{4.11a}$$

$$D_{\mathrm{n}}(z) = R/[1/\mu_{\mathrm{n}} + 1/f_{\mathrm{n}} - 1] \tag{4.11b}$$

for the weight-average and number-average cluster size. These relations enable us to express in terms of the thermodynamic variables all important solution properties, such as the gelation concentration, chemical potentials, the osmotic pressure, and the osmotic compressibility.

At gelation where eq 4.1 is satisfied, the effective number z of the unreacted functional groups must satisfy the condition

$$\mathrm{d}\ln u(z)/\mathrm{d}\ln z = 1/(f_{\mathrm{w}} - 1) \tag{4.12}$$

Let us denote the solution of this equation as $z = z^*$. Then, the critical volume fraction ϕ^*, as a function of the temperature must satisfy

$$\lambda(T)\phi^* = Rz^*u(z^*) \tag{4.13}$$

due to the relation (4.5). This relation gives the phase boundary between the sol and the gel on the temperature–concentration plane. In the pregel regime ($z < z^*$), where the entire system consists of finite clusters, the total number ν of clusters in a unit cell is given by $\nu = \nu^{\mathrm{S}} \equiv \phi/D_n$, and hence,

$$\nu^{\mathrm{S}}(\phi,T) = z[(1/f_{\mathrm{n}} - 1)u(z) + I(z)]/\lambda(T) \tag{4.14}$$

In the postgel regime, the total solute volume fraction ϕ is larger than ϕ^*, and the excess amount $\phi - \phi^*$ is absorbed into the network, while the concentration z of the unreacted functional groups remains at a constant value z^*. The volume fraction of the unreacted molecules also remains constant. Therefore the number concentration ν of the finite clusters in the sol phase takes a value

$$\nu^*(T) = z^*[(1/f_{\mathrm{n}} - 1)u(z^*) + I(z^*)]/\lambda(T) \tag{4.15}$$

which depends only on the temperature. As already remarked in I, the above treatment of the postgel regime corresponds to the strict absence of cyclic structures even in the gel.[20] The alternative treatment of Flory,[19] which permits cycles within the gel structures but not in the finite clusters of the sol, will not be considered in this paper. Postgel point networks with junctions of arbitrary multiplicity have been considered from the Flory viewpoint by Pearson and Graessley.[25]

5. Solution Properties

5.1. Phase Equilibria. Having found the general features of the gelation transition, we now proceed to the study of the solution properties. The solvent chemical potential (3.5) is transformed into

$$\beta\Delta\mu_0 = \ln(1-\phi) + \phi - \nu(\phi, T) + \chi\phi^2 \tag{5.1}$$

over the entire (ϕ, T) plane, where $\nu(\phi, T) = \nu^{\mathrm{S}}(\phi, T)$ in the pregel regime, while $\nu(\phi, T) = \nu^*(T)$ in the postgel regime. The chemical potential (per monomeric unit) of an f-functional molecule, whether in a cluster or isolated, is given by

$$\beta\Delta\mu_f = c_f + [\ln z - f'\ln u(z)]/r_f + \phi - \nu(\phi, T) + \chi(1-\phi)^2 \tag{5.2}$$

thanks to the multiple equilibrium conditions (3.9), where $f' \equiv f - 1$, and $c_f \equiv [1 + \ln r_f w_f/f\lambda(T))]/r_f$ is the concentration-independent part. In deriving this equation, the relation

$$\phi(\mathbf{j}_{0f}, \mathbf{n}_{0f}) = (r_f w_f/f\lambda)z/u(z)^{f'} \tag{5.3}$$

which connects the volume fraction of the isolated molecules to z, has been used. The coexistence curve (or *binodal*) for a dilute phase with volume fraction ϕ' to be in an equilibrium with a concentrated phase with volume fraction ϕ'' is given by the coupled equations

$$\Delta\mu_0(\phi', T) = \Delta\mu_0(\phi'', T) \tag{5.4a}$$

$$\Delta\mu_f(\phi', T) = \Delta\mu_f(\phi'', T) \tag{5.4b}$$

If the higher-concentration phase lies in the postgel regime, the postgel form of ν must be employed in the chemical potentials. These equilibrium conditions determine, when coupled together for all existing functionalities f, the total volume fraction ϕ' and ϕ'' in each phase as well as the molecular distributions w_f' and w_f'' in them. In most of the numerical examples to follow, we do not give the binodal curve, but the more easily computed spinodals, defined by (5.15) below.

5.2. Osmotic Pressure and Osmotic Compressibility. The osmotic pressure π is directly related to the solvent chemical potential through the relation $\pi a^3 = -\Delta\mu_0$. Hence we have

$$\pi a^3\beta = -\ln(1-\phi) - \phi + \nu(\phi, T) - \chi\phi^2 \tag{5.5}$$

In the dilute region, this can be expanded in powers of the concentration. To find the coefficients of this power series (*virial expansion*), let us first solve the relation (4.5) with respect to z in powers of the volume fraction ϕ and then substitute the result into the term $zI(z)$ in the right hand side of the number concentration ν^{S} given by (4.14). This is similar to the problem we encountered in the theory of condensation of a gas. If we compare our problem with the cluster expansion theory developed by Mayer,[26] we recognize that the coefficients in the power series of $zI(z)$ can be expressed in terms of the *irreducible cluster coefficients* β_k constructed from the coefficients $b_k \equiv \gamma_k/k$. The result is

$$zI(z) = \lambda\psi\left\{1 - \sum_{k=1}^{\infty}\frac{k}{k+1}\beta_k(\lambda\psi)^k\right\} \tag{5.6}$$

For instance, we have

$$\beta_1 = \gamma_2 \qquad \beta_2 = \gamma_3 - \gamma_2^{\,2}/2$$
$$\beta_3 = 2(\gamma_4 - 6\gamma_2\gamma_3 + 7\gamma_2^{\,3})/3 \tag{5.7}$$

for the first three irreducible coefficients. Upon substitution of this result into π, and using $\phi(\equiv R\psi)$ in favor of ψ, we obtain the virial series for the osmotic pressure:

$$\pi\beta a^3 = \sum_{n=1}^{\infty} A_n\phi^n \tag{5.8}$$

where

$$A_1 = 1/f_nR \qquad (5.9a)$$

$$A_2 = 1/2 - \chi - [\lambda(T)\gamma_2/2R^2] \qquad (5.9b)$$

$$A_n = \frac{1}{n}\left\{1 - \frac{(n-1)\beta_{n-1}}{\lambda}\left(\frac{\lambda(T)}{R}\right)^n\right\} \quad \text{for } n \geq 3 \qquad (5.9c)$$

As was remarked in II, the correction to the second virial coefficient is due to the existence of binary junctions ($k = 2$), and should vanish if γ_2 in (3.25) were made to vanish. Thus association does not affect the second virial coefficient if there is no binary cross-linking. The frequently observed sudden gelation in physical gels without precursor suggests the dominance of high-junction multiplicity in the case of microcrystalline cross-linking.

We next define the dimensionless isothermal osmotic compressibility K_T by the equation

$$K_T = (k_BT/a^3)(\partial\phi/\partial\pi)_T/\phi \qquad (5.10)$$

Taking the derivative of the osmotic pressure, we find

$$K_T = 1/\phi^2\sigma(\phi, T) \qquad (5.11)$$

where the function σ is given by

$$\sigma(\phi, T) \equiv \frac{1}{D(z)\phi} + \frac{1}{1-\phi} - 2\chi \qquad (5.12a)$$

Here a new function $D(z)$ without subscript, being defined by

$$D(z) \equiv R/[1/\mu_w + 1/f_n - 1] \qquad (5.12b)$$

has appeared. It agrees with the weight average $D_w(z)$ for monodisperse primary chains, and becomes infinite at gelation. For a system of polydisperse primary chains for which $f_w > f_n$ holds, however, it remains finite; in fact we have $D(z^*) = (f_w - f_n)R/f_wf_n \sim O(f_w - f_n)$. Since we have $\sigma(\phi, T) = 1/(1-\phi) - 2\chi$ in the postgel regime, the osmotic compressibility shows a finite discontinuity at gelation, the amount of which is given by

$$\Delta[K_T] \simeq -D(z^*)/\phi^* \sim O(f_w - f_n) \qquad (5.13)$$

where the symbol Δ indicates the difference between the two limiting values of the argument taken at the gelation concentration from above and from below. Since the osmotic compressibility—which is one of the second derivatives of the free energy—jumps at gelation, the reversible gelation of polydisperse primary chains is categorized as a second-order transition in Ehrenfest's sense.[27] On the contrary, K_T for monodisperse polymer chains is a continuous function of the concentration at gelation as the weight-average cluster size diverges; it approaches a finite value $K_T^* \equiv 1/[(1-\phi^*)^{-1} - 2\chi]\phi^{*2}$ with a finite slope, and then decreases with a different slope. It thus exhibits a cusp-shaped singularity at the gel point. The discontinuity in the slope at gelation is given by

$$\Delta[\partial \ln K_T/\partial\phi] = -\Delta[\partial\mu_w^{-1}/\partial\phi]/R\sigma^*\phi^* \qquad (5.14)$$

and the sol-to-gel transition becomes a *third*-order transition.

For monodisperse primary chains we have a strictly two-component system, and the thermodynamic stability limit (*spinodal*) is given by

$$\sigma(\phi, T) = 0 \qquad (5.15)$$

We observe that the singularity in K_T is enhanced near the spinodal line because of the factor σ^* in the denominator of (5.14). Further, for such strictly binary systems, the critical solution point, if it exists in the pregel regime, can be found with the aid of the additional condition $\partial^2\Delta\mu_0/\partial\phi^2 = 0$ and is given explicitly by

$$D_z(\phi_c)/D_w(\phi_c)^2 = \phi_c^2/(1-\phi_c)^2 \qquad (5.16)$$

For systems with polydisperse primary chains, the spinodal and critical conditions have to be determined from the appropriate Gibbs determinants.[28] They will not be further considered in this paper.

6. Junctions of Fixed Multiplicity

Several special models of junctions are now presented to illustrate the above results and will also be used in the phase-equilibrium calculations to follow.

The first model we consider is the one in which a single value s (≥ 2) of the junction multiplicity is allowed (*"fixed-multiplicity model"*). We have $k = 1$ (free) and $k = s$ (reacted), all other γ_k being zero. This is a rather extreme case, but the model provides an obvious advantage in clarifying the effect of multiplicity on the thermal properties of physical gels. When $s = 2$, the model reduces to the case of pairwise cross-linking, whose solution properties were already studied in I.

From the definitions we have

$$u(z) = 1 + z^{s'} \quad \text{and} \quad I(z) = 1 + s^{-1}z^{s'} \qquad (6.1)$$

where $s' \equiv s - 1$. We must now solve the equation

$$z(1 + z^{s'}) = \lambda(T)\psi \qquad (6.2)$$

with respect to z. In such a fixed-multiplicity model, one can alternatively use as an independent variable the probability p_s for a functional group to be in a junction. Let us write $p_s \equiv \alpha$. We then have $p_1 = 1 - \alpha$ by normalization. Since $z = (1-\alpha)\lambda\psi$ by definition, the relation (6.2), combined with (6.1), gives $u(z) = 1/(1-\alpha)$ or, equivalently, $z^{s'} = \alpha/(1-\alpha)$. Similarly, the integral of u is expressed as $I(z) = [1 - (s'/s)\alpha]/(1-\alpha)$. The equilibrium condition (4.5) then takes the form

$$\alpha/(1-\alpha)^s = [\lambda(T)\psi]^{s'} \qquad (6.3)$$

which was already derived in II.

It is now straightforward to calculate average quantities. We find

$$\mu_w = 1 + s'\alpha \quad \text{and} \quad \mu_n = 1/(1 - s'\alpha/s) \qquad (6.4)$$

and

$$D_w = R/[1/(1 + s'\alpha) + 1/f_w - 1] \qquad (6.5a)$$

$$D_n = R/(1/f_n - s'\alpha/s) \qquad (6.5b)$$

so that we have

$$\nu^S(\phi, T) = \phi(1 - f_ns'\alpha/s)/f_nR \qquad (6.6)$$

We next find the critical values of physical quantities at gelation. Since (4.1) holds at gelation, we have $\mu_w^* = f_w/(f_w - 1)$ and hence

$$\alpha^* = 1/s'(f_w - 1) \qquad (6.7)$$

which of course reduces to Flory's classical relation for $s = 2$. The critical gel volume fraction satisfies the relation

$$\lambda(T)\phi^* = Rs'(f_w - 1)/[s'(f_w - 1) - 1]^{s/s'} \qquad (6.8)$$

or, equivalently,

$$\lambda(T)\nu^* = s'[s(f_w - 1) - f_n]/sf_n[s'(f_w - 1) - 1]^{s/s'} \qquad (6.9)$$

for the number density. This equation determines the sol/gel transition line on the temperature–concentration plane. It is a steadily increasing function of temperature.

We next proceed to the study of phase equilibria. The chemical potential of each species, written in terms of the reactivity α, takes the form

$$\beta\Delta\mu_0 = \ln(1 - \phi) + \phi + \chi\phi^2 - \nu(\phi, T) \qquad (6.10a)$$

for the solvent and

$$\beta\Delta\mu_f = c_f + [\ln\phi + f\ln(1 - \alpha)]/r_f + \phi + \chi(1 - \phi)^2 - \nu(\phi, T) \qquad (6.10b)$$

for the f-functional molecules, where $\nu(\phi, T) \equiv \nu^S(\phi, T)\theta(\phi^* - \phi) + \nu^*\theta(\phi - \phi^*)$, θ being the step function.

The function $\sigma(\phi, T)$, which is proportional to the reciprocal of the osmotic compressibility, can be written as

$$\sigma(\phi, T) = \frac{1}{R\phi}\left(\frac{1}{1 + s'\alpha} + \frac{1}{f_n} - 1\right) + \frac{1}{1 - \phi} - 2\chi \qquad (6.11a)$$

in the pregel regime, and

$$\sigma(\phi, T) = \frac{1}{1 - \phi} - 2\chi \qquad (6.11b)$$

in the postgel regime. For monodisperse system with a single f, the discontinuity in the slope of the compressibility at gelation then takes the value

$$\Delta[\partial\ln K_T/\partial\phi] = -s'^2f^3\alpha^*(1 - \alpha^*)/R\sigma^*\phi^{*2}(f')^3 \qquad (6.12)$$

In the following numerical calculation of the phase diagrams, we consider only monodisperse systems in which all solute molecules have a single number r of monomeric units and carry a single functionality f. Effects of polydispersity on the phase equilibria will be studied in a separate paper. In such a monodisperse system a cluster is specified by the number $n_f = l$ of molecules it contains. We have simply $f_w = f_n = f$ and $R = r/f$; the conversion factor R reduces in this case to the number of monomeric units per functional group on a molecule. The gelation concentration is given by

$$\lambda(T)\phi^* = rf's'/f(f's' - 1)^{s/s'} \qquad (6.13)$$

as was discussed in II.

The calculation of phase equilibria in the (T, ϕ) plane involves two different functions of temperature: the equilibrium constant $\lambda(T)$ and the interaction parameter χ. They are most compactly presented in terms of the familiar reduced temperature relative to the unperturbed Θ temperature,

$$\tau \equiv 1 - \Theta/T \qquad (6.14)$$

and we then have[17]

$$\chi = 1/2 - \psi_1\tau \qquad (6.15)$$

where ψ_1 is a number of order unity related to the entropy of solution. The temperature shift factor (3.26) is

$$\lambda(T) = (\zeta - 1)\exp(\Delta S_0/k_B)\exp(-\beta\Delta\epsilon) \qquad (6.16)$$

where ΔS_0 and $\Delta\epsilon$ are the entropy and energy contribution to Δg_0, and this may be rewritten as

$$\lambda(T) = \lambda_0\exp[\kappa(1 - \tau)] \qquad (6.17)$$

with

$$\lambda_0 \equiv (\zeta - 1)\exp(\Delta S_0/k_B) \qquad (6.18a)$$

$$\kappa = -\Delta\epsilon/k_B\Theta \qquad (6.18b)$$

Throughout the calculations to follow, we fix $\psi_1 = 1$ while varying the other parameters to see their effects.

Figure 2 shows the phase diagram for a fixed-multiplicity model with $\kappa = 4$, $r = 100$, and $\lambda_0 = 10$. The solid lines show the stability limit (*spinodals*) defined by the condition (5.15), and the broken lines, the sol/gel transition. The *critical solution points* (CP) are indicated by open circles. The multiplicity s is varied from curve to curve. The intersection between the spinodal curve and the gelation curve may be considered as a certain kind of *critical end point* (CEP) or a *tricritical point* (TCP),[29–31] depending on the relative positions of the intersection and the CP. It should, however, be emphasized that the third-order sol/gel transition is not an ordinary two-phase equilibrium, since sol and gel do not separate from each other; it might better be regarded as an order–disorder transition within a single phase. The spinodal, on the other hand, refers to a first-order liquid/liquid equilibrium. Accordingly, we use the terms "quasi-TCP" and "quasi-CEP" to denote the phenomena described above.

In Figure 2, as s is increased, the intersection on the shoulder of the spinodal approaches CP and eventually hits the CP at a certain value of s. In this figure this particular situation (hereafter called the *marginal* situation) occurs at $s = 5$. Below this critical value of s (referred to as the *submarginal regime*) the intersection of the two lines gives a quasi-CEP—the gelation concentration coexisting with a sol phase—while it gives a quasi-TCP above the critical s (referred to as the *supermarginal regime*). There are no CP's in the supermarginal regime, and the gelation line remains at finite concentration even for infinitely large s. The part of the transition line lying inside the biphasic region has physical significance only in nonequilibrium states.

7. Junctions of Variable Multiplicity

We now allow junctions to take a wide range of multiplicities. Figure 3 depicts two typical examples of polymeric gels with variable multiplicity. The top figure shows a gel network formed by crystalline segments, each having a sequence of r_c statistical units, together with the multiplicity number beside the junctions. (The length r_c of the microcrystallite agrees with the conversion factor R in this case.) The bottom figure shows a network formed by functional groups attached to the chain ends, together with the junction multiplicity.

7.1. Junctions Which Allow Multiplicity Larger Than a Fixed Value.

In order to see the effect of variable multiplicity, let us introduce a model system in which junctions of multiplicity *greater* than s_0 are allowed. When

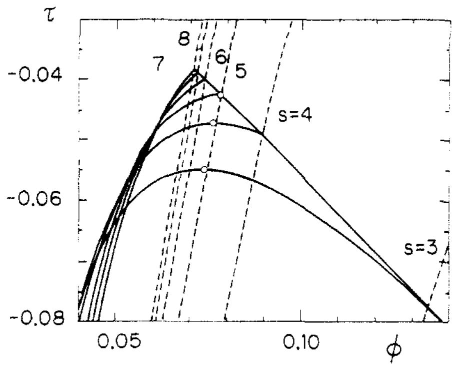

Figure 2. Phase diagram (reduced temperature τ against volume fraction ϕ) of reversible gels with a fixed junction multiplicity. Solid lines show the spinodals, and broken lines, the gelation transition. The multiplicity s is varied from curve to curve. Open circles are critical solution points. Tricritical points appear above the marginal value $s = 5$. The other parameters are fixed at $\kappa = 4$, $r = 100$, and $\lambda_0 = 10$.

$s_0 = 2$, junctions of all multiplicities can coexist at relative amounts determined by the thermodynamic balance. However, in the case of microcrystalline junctions, for instance, it is natural to assume that a minimum number s_0 (>2) of chains is required for junction formation. This is because the surface energy terms will prevent small-k units from being stable.

We have, for such a model,

$$u(z) = \sum_{k\geq s_0} z^{k-1} = 1 + z^{s'_0}/(1-z) \tag{7.1}$$

and

$$I(z) = -[\ln(1-z)]/z - z\sum_{k=1}^{s'_0-1} z^{k-1}/(k+1) \tag{7.2}$$

where the simple form (3.24) has been employed. The parameter z is a function of the volume fraction through the relation (4.13), and the critical condition is determined from (4.12) by the algebraic equation

$$[(s'_0 - 1)(f_w - 1) - 1]z^{s_0} - [s'_0(f_w - 1) - 1]z^{s'_0} + (1-z)^2 = 0 \tag{7.3}$$

The root z^* *of this equation gives the gelation concentration* when substituted into (4.13). For the unconstrained multiplicity model ($s_0 = 2$), this equation reduces to

$$\lambda(T)\phi^* = R/(f_w - 1) \tag{7.4}$$

Figure 4 shows the scaled gelation concentration $\lambda\phi^*/r$ as a function of the minimum multiplicity s_0 for the monodisperse system with a single functionality f and a single molecular weight r, so that $R = r/f$. The functionality f is varied from curve to curve. Filled circles indicate values for the unconstrained multiplicity model. The curve for $f = 3$ starts from $1/f(f-1) = 0.166\,667$ at $s_0 = 2$, takes a smaller value $2(\sqrt{5} - 2)/3 = 0.157\,38$ at $s_0 = 3$, and then steadily increases with s_0; for higher f, the curves increase monotonically.

Figure 5 shows typical phase diagrams for gels with a minimum multiplicity. The relevant parameters are fixed as $\kappa = 3$, $r = 500$, $f = 50$, and $\lambda_0 = 1$, so that the average monomer sequence length in a junction is given by $r_c = 10$. The value of minimum multiplicity s_0 is varied from 2 to 6. As s_0 increases, the spinodal and the gelation line both shift toward the low-temperature and high-concentration region. Parts a–c of Figure 6 show the effects of changing the parameter λ_0 on both binodals and spinodals, in this case for a system with $s_0 = 2$ and low primary molecular weight ($r = 3$) and functionality ($f = 3$). The relative binding energy is fixed at $\kappa = 2$. For this one example, the asymptotic expressions (section 8) were used, to simplify calculations.

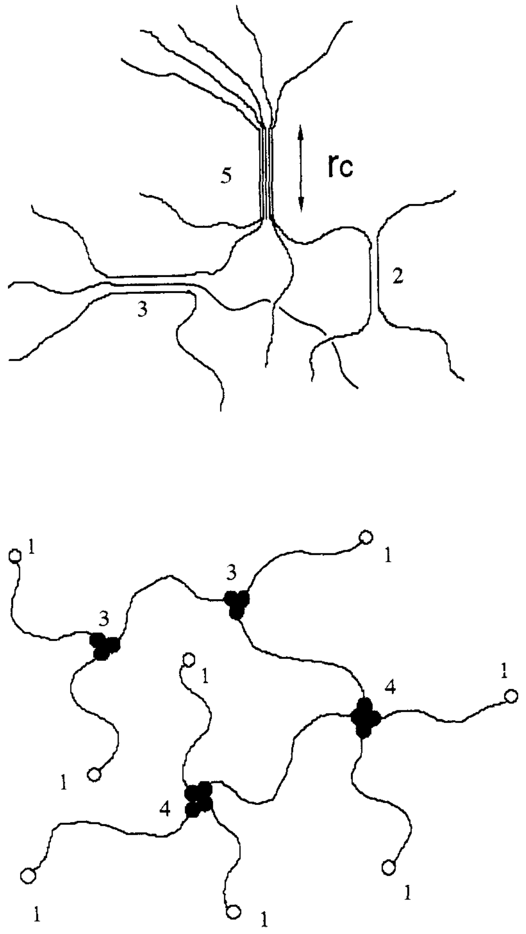

Figure 3. Two typical physical gels with junctions of variable multiplicity. A network with junction zones formed by the crystalline segments (top figure) and a network formed by the end-functional groups (bottom figure) are schematically drawn. The figures beside the junctions show their multiplicity.

7.2. Saturating Junctions. When the association force has a saturating nature, the number of functional groups in a junction is limited *below* a certain maximum value s_m. Junctions formed by dipole aggregation and micellization of hydrophobic polymer segments, for instance, belong to this important category.

The function u for a saturating junction takes the form

$$u(z) = (1 - z^{s_m})/(1-z) \tag{7.5}$$

The critical value of z at gelation is now found from the equation

$$[s'_m(f_w - 1) - 1]z^{s_m+1} - [s_m(f_w - 1) - 1]z^{s_m} + f_w z - 1 = 0 \tag{7.6}$$

All other solution properties are derived by the general method developed above.

Figure 7 shows the scaled gelation concentration as a function of the maximum multiplicity s_m for a monodisperse system. The functionality f is varied from curve to curve. Filled circles indicate the values of the pairwise-

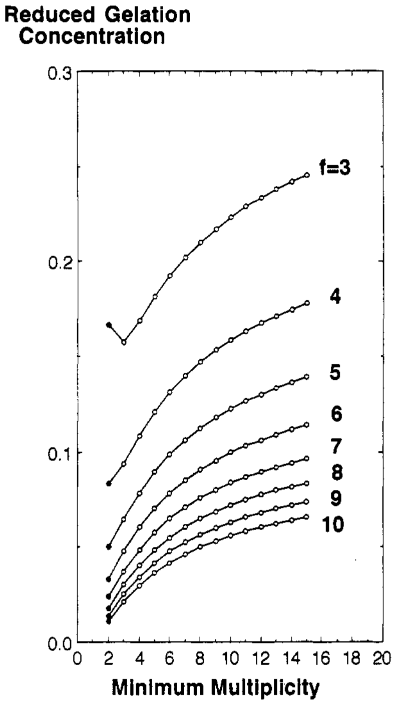

Figure 4. Reduced gelation concentrations $\lambda(T)\phi^*/r$ as functions of the minimum junction multiplicity s_0. The functionality f is changed from curve to curve. The filled circles show gelation concentrations for the unconstrainedly-variable multiplicity model.

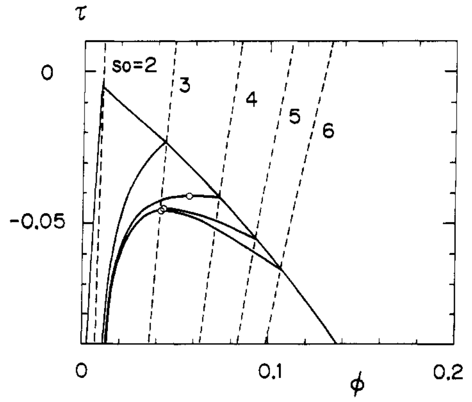

Figure 5. Phase diagrams of physical gels with a minimum junction multiplicity. Spinodals and gelation lines are shown for crystalline polymers with minimum length $r_c = 10$ of crystallization ($f = 50$, $r = 500$, $\kappa = 3$, $\lambda_0 = 1$).

junction models. The concentration for large s_m approaches the limiting value of the unconstrained multiplicity model which was shown by the filled circles in Figure 4.

Figure 8 shows the phase diagram of a physical gel formed by the association of functional groups attached to the chain ends ($f = 2$ and $r = 100$). In this case it is difficult for a functional group to join in a large junction around which the chain segments are densely packed, thus revealing the saturating nature. The entropy parameter is fixed as $\lambda_0 = 10$. The topological structure of the phase diagram is the same as that in Figure 5.

Figure 9 shows the cusp-shaped singularities in the osmotic compressibility of the same system. The compressibility for $s_m = 5$ is plotted on a logarithmic scale against the concentration. The temperature is varied from curve to curve near the TCP to see how the singularlity grows as the system approaches the TCP (which itself lies on the spinodal).

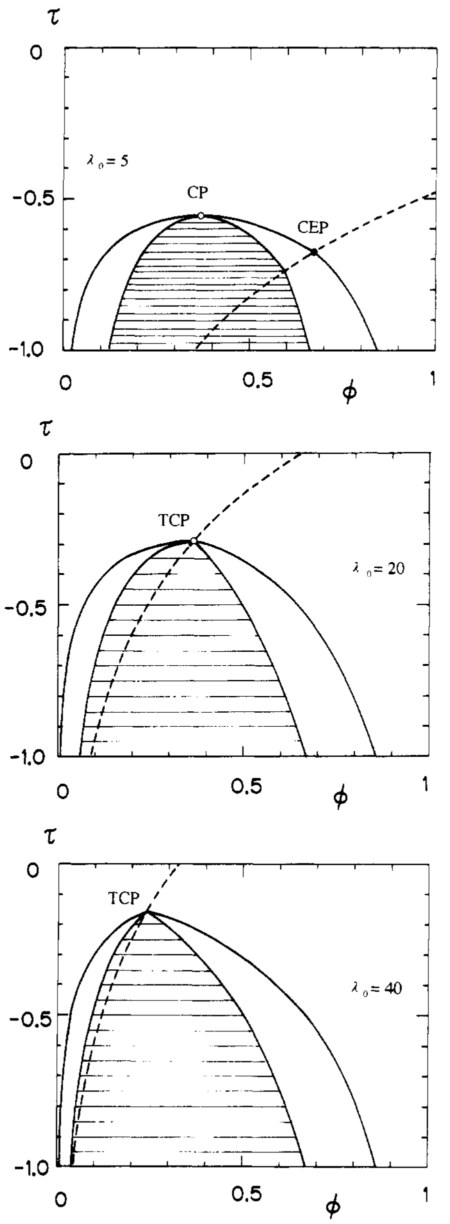

Figure 6. Phase diagrams (approximate) for low-molecular-weight gels with junctions of unrestricted multiplicity. The fixed parameters are $r = 3$, $f = 3$, and $\kappa = 2$. Key: binodals (outer solid curves), spinodals (inner solid curves), unstable regions (shaded area), and the gelation transition (dashed curve). (a, top) Submarginal regime, $\lambda_0 = 5$: (open circle) critical solution point; (filled circle) critical end point. (b, middle) At marginality, $\lambda_0 = 20$, showing a tricritical point. (c, bottom) Supermarginal regime, $\lambda_0 = 40$.

8. Asymptotic Solution and Universal Nature of the Gelation Transition

For several purposes it is useful to display the asymptotic form of the distribution for very large clusters, as developed by FY with the method of steepest descents. The result is that eq 3.27 can be written for large l as

$$\lambda(T) \sum_{\Sigma n_f = 1} \nu(\mathbf{j};\, \mathbf{n}) \simeq A(\{x\}) l^{-5/2} [h(z_0)/z_0]^l \qquad (8.1)$$

where a polynomial $h(z)$ is defined by

$$h(z) \equiv \sum_f x_f \mu(z)^f \qquad (8.2)$$

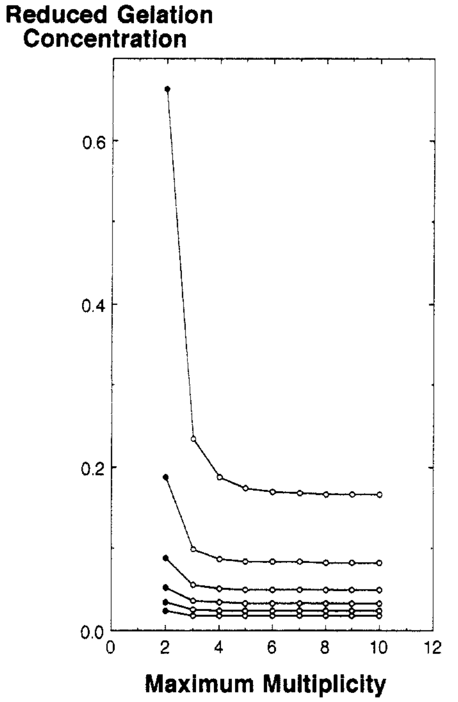

Figure 7. Reduced gelation concentrations as functions of the maximum junction multiplicity s_m. The functionality f is changed from curve to curve. The filled circles show gelation concentrations for pairwise association.

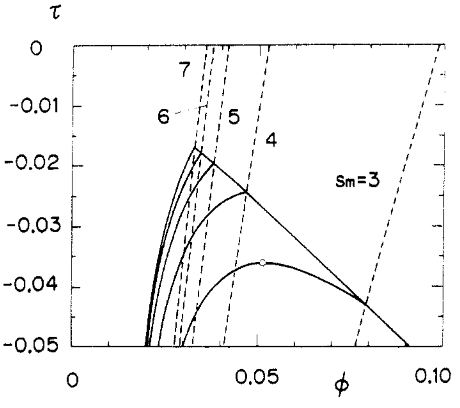

Figure 8. Phase diagrams of end-functional polymeric gels formed by junctions with a maximum multiplicity s_m. The maximum multiplicity is varied from curve to curve. The other parameters are fixed at $f = 2$, $r = 100$, $\kappa = 5$, and $\lambda_0 = 10$.

with

$$u(z) \equiv \sum_{k=1}^{\infty} \gamma_k z^{k-1} \tag{8.3}$$

This function $u(z)$ has already appeared in our rigorous treatment given in section 3. The prefactor A in this asymptotic form comes from Gaussian integration along the path of steepest descent and is given by

$$A(\{x\}) \equiv z_0 u'(z_0)/[2\pi h''(z_0)/h(z_0)]^{1/2} \tag{8.4}$$

The special value z_0 is the root of the saddle-point condition

$$h(z) - zh'(z) = 0, \tag{8.5}$$

and is a function of the concentrations $\{x\}$. For a monodisperse system for which only a single f is allowed, this equation reduces to the gelation condition (4.12) (with f_w replaced by f), and hence we have $z_0 = z^*$. In the reminder of this section, we limit our arguments to the case of monodisperse chains. For a single f, we have $h(z) = xu(z)^{f'}$, and z_0 is given by the unique root of the equation

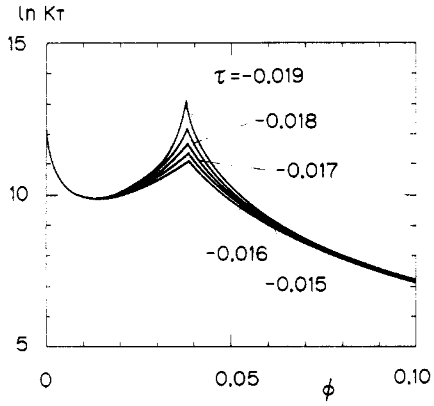

Figure 9. Osmotic compressibility of end-functional polymeric gels as a function of concentration. The temperature is varied from curve to curve near the tricritical point. At gelation, the compressibility exhibits a cusp-shaped singularity. It is enhanced as the temperature approaches the tricritical temperature. The other parameters are the same as in Figure 8.

$$\sum_k [1 - f'(k-1)]\gamma_k {z_0}^{k-1} = 0 \tag{8.6}$$

which is the same as the result of (4.1)–(4.3). This is to be expected, since the asymptotic form must give the correct description of the largest clusters.

We then find $h(z_0)/z_0 = \xi x$, where

$$\xi \equiv u(z_0)^{f'-1}/z_0 \tag{8.7}$$

The prefactor can be rewritten as

$$A = \frac{1}{\sqrt{2\pi f'}} \frac{z_0 u(z_0) u'(z_0)}{[(f'-1)u'(z_0)^2 + u(z_0)u''(z_0)]^{1/2}} \tag{8.8}$$

and is now a constant which depends only on f and the junction multiplicity.

At this point we may remind the reader that the exponent of l^{-1} in eq (8.1), $\tau = {}^5/_2$, is characteristic of all classical Bethe-lattice gelation theories. According to percolation theory[32] we should expect $\tau = 2.20$, while two recent careful experimental studies on polyesters[33,34] have yielded $\tau = 2.29 \pm 0.03$ and $\tau = 2.35 \pm 0.03$. Our remarks below on the nature of the transition are not altered by these differences.

Now from eq 2.6 we have $\phi_l = rl\nu_l$, and so the total volume fraction ϕ^S of clusters in the sol phase is then given by

$$\lambda(T)\phi^S(x) \simeq rA\Phi({}^3/_2;\ \xi x) \tag{8.9}$$

where new functions $\Phi(p;\ y)$ are defined by

$$\Phi(p;\ y) = \sum_{l=1}^{\infty} \frac{y^l}{l^p} \tag{8.10}$$

These functions, with a radius of convergence $y = 1$, are well-known, for $p = {}^3/_2$ and ${}^5/_2$, in the expressions for the density and pressure of an ideal Bose–Einstein gas. They also appear in the theory of ring–chain equilibria of linear polycondensates, and in this context are sometimes called Truesdell functions after a special study[35] of their properties.

Similarly, the total number concentration of clusters ν^S is given by

$$\lambda(T)\nu^S(x) \simeq A\Phi(^5/_2;\, \xi x) \tag{8.11}$$

and hence the number-average molecular weight of the clusters (3.7) takes the form

$$D_n(\phi) \simeq \frac{\Phi(^3/_2;\, \xi x)}{\Phi(^5/_2;\, \xi x)} r \tag{8.12}$$

In a similar way, the weight-average molecular weight of the clusters (3.8) can be evaluated as

$$D_w(\phi) \simeq \frac{\Phi(^1/_2;\, \xi x)}{\Phi(^3/_2;\, \xi x)} r \tag{8.13}$$

As ξx approaches unity, $\Phi(^3/_2;\, \xi x)$ and $\Phi(^5/_2;\, \xi x)$ converge to the finite values $\zeta(^3/_2) = 2.612$ and $\zeta(^5/_2) = 1.341$, respectively, but $\Phi(^1/_2;\, \xi x)$ diverges. This fact indicates that the condition $\xi x = 1$ defines the gelation point. The volume concentration of the clusters at this point takes the value

$$\lambda(T)\phi^* \simeq \zeta(^3/_2) r A(x^*) \tag{8.14}$$

where $x^* \equiv 1/\xi$. Because $A(x^*)$ depends only on f (in fact, it is independent of x^* for the monodisperse case), this relation gives the phase boundary between the sol and the gel on the temperature–concentration plane. For concentrations larger than ϕ, the excess amount $\phi - \phi^*$ is absorbed into the network, while the concentration of the isolated molecules stays at a constant value x^*. The number concentration of the clusters in the sol phase stays at a constant value $\nu^* = \zeta(^5/_2)A/\lambda(T)$. As already remarked in I, the above treatment of the postgel regime corresponds to the strict absence of cyclic structures even in the gel.[20] The alternative treatment of Flory,[19] which permits cycles within the gel structures but not in the finite molecules of the sol, will not be considered in this paper.

In order to study the behavior of physical quantities near the gelation threshold, let us employ the following asymptotic forms of the relevant Truesdell functions near the radius of convergence $y = 1$:

$$\Phi(^1/_2;\, y) \simeq \sqrt{\pi}/(1 - y)^{1/2} \tag{8.15a}$$

$$\Phi(^3/_2;\, y) \simeq \zeta(^3/_2) - 2\sqrt{\pi}(1 - y)^{1/2} \tag{8.15b}$$

$$\Phi(^5/_2;\, y) \simeq \zeta(^5/_2) - \zeta(^3/_2)(1 - y) \tag{8.15c}$$

Note that $\Phi(^1/_2;\, y)$ diverges at $y = 1$, while the other two remain finite. Inversion of the relation (8.9) then yields the equation $1 - \xi x \simeq [\zeta(^3/_2) - \lambda\phi/rA]^2/4\pi$ for the concentration of the isolated chains. Hence we find that the weight-average mean cluster size takes the form

$$D_w \simeq \left[\frac{2\pi r^2 A}{\zeta(^3/_2)\lambda}\right]\frac{1}{\phi^* - \phi} \tag{8.16}$$

near the gelation concentration, thus giving the classic scaling exponent. Similarly, we can easily find that the ratio D_z/D_w^2 takes the finite value $\zeta(^3/_2)^2/2\pi r$, where D_z is the z-average cluster size.

We may remark that if the exponent of $(\phi^* - \phi)$ in (8.16) is changed from −1 to the percolation value[32] of −1.7, the discontinuity of slope at the gel point on the spinodal line (as for example in Figures 2, 5, 6, and 8) is removed, although the curvature remains large.

We next consider the osmotic compressibility. As was pointed out in the preceding section, the derivative of the function $\sigma(T, \phi)$ is discontinuous at gelation. Employment of the form (8.15) for the function $\Phi(^1/_2;\, y)$, which characterizes the divergence of the weight average, gives a positive amount of discontinuity $\Delta(\partial\sigma/\partial\phi) \equiv (\partial\sigma/\partial\phi)_+ - (\partial\sigma/\partial\phi)_- = \zeta(^3/_2)^2/2\pi r\phi^{*2}$ and hence leads to the relation

$$\Delta(\partial \ln K_T/\partial\phi) = -[\zeta(^3/_2)^2/2\pi r]K_T^* \tag{8.17}$$

for the logarithmic derivative of the compressibility. This discontinuity is tiny for long polymer chains at almost all concentrations, but it is drastically enhanced near the spinodal line on which K_T^* diverges.

We can also examine the accuracy of the asymptotic evaluation, for which the reduced value of the gelation concentration $\lambda(T)\phi^*/r$ is given by

$$\frac{\lambda(T)\phi^*}{r} \simeq \frac{\zeta(^3/_2) z_0 u(z_0) u'(z_0)}{[2\pi f'\{(f' - 1)u'(z_0)^2 + u(z_0)u''(z_0)\}]^{1/2}} \tag{8.18}$$

Since $z_0 = z^*$ for a monodisperse system, the ratio of this approximate value to the true one $z^*u(z^*)/f$ becomes

$$\frac{(\phi)_{\mathrm{asym}}}{(\phi)_{\mathrm{exact}}} = 1.042\,\frac{fu'(z^*)}{[f'\{(f' - 1)u'(z^*)^2 + u(z^*)u''(z^*)\}]^{1/2}} \tag{8.19}$$

For large f, therefore, the ratio is very close to unity, independent of the junction multiplicity, provided that the second term in the denominator can be neglected.

8.1. Junctions with a Fixed Multiplicity. In this model (cf. section 6), we have $h(z) = x(1 + z^{s'})^{f'}$. The saddle point is given by $z_0 = (f's' - 1)^{-1/s'}$. Straightforward calculation leads to

$$\xi = (f's')^{f'}/(f's' - 1)^{f' - 1/s'} \tag{8.20}$$

and

$$A = s'(f')^{1/2}/(2\pi)^{1/2}(f's' - 1)^{3/2 + 1/s'} \tag{8.21}$$

for the relevant parameters. Hence, with the help of eq 8.14, we have

$$\lambda(T)\phi^* \simeq 1.042 r s'(f')^{1/2}/(f's' - 1)^{3/2 + 1/s'} \tag{8.22}$$

For a very large aggregation number $s' \gg 1$, the critical concentration is proportional to $r/f'\sqrt{s'}$. In the physical gelation of primary polymer chains via cross-linking by segment crystallization, the functionality f is expected to be proportional to the molecular weight r, and therefore, the gelation concentration ϕ^* in this limit is *independent* of the molecular weight. This limit is actually seen in some of the experimental results of Domszy *et al.*[2] In the case of the gelation by the association of the end-functional groups, the functionality is fixed to be $f = 2$, and hence $\phi^* \sim r/(s - 1)^{(s+1)/2(s-1)}$.

We now compare this approximate result with the exact value (6.8) of the gelation criterion. The latter reduces to

$$\lambda(T)\phi^* = rf's'/f(f's' - 1)^{1 + 1/s'} \tag{8.23}$$

for a monodisperse system, and we find

$$(\phi^*)_{\mathrm{asym}}/(\phi^*)_{\mathrm{exact}} = 1.042f/[f'(f's'-1)]^{1/2} \quad (8.24)$$

whichi is close to $1/\sqrt{s'}$ for a large f. This relatively large discrepancy is mathematically due to the fact that the second term in the denominator of (8.19) is not negligible in this case. Physically, we rationalize it by remarking that junctions of higher multiplicity reach the asymptotic range of sizes more quickly, at a given concentration.

8.2. Junctions with Variable Multiplicity. We consider, for instance, $s_0 = 2$ in the minimum multiplicity model, for which we have $z_0 = 1/f$, and hence $\xi = f^f/f'^{f'}$ and $A = 1/(2\pi f f'^3)^{1/2}$. The critical concentration is given by

$$\lambda(T)\phi^* \simeq 1.042r/(f f'^3)^{1/2} \quad (8.25)$$

which is very close to the exact value $r/f f'$.

The asymptotic solution of our problem has thus an obvious advantage in establishing the analogy between physical gelation and the Bose condensation of an ideal gas mixture. In fact, the phase diagrams explored in this study and those observed in the mixture of He^3 and He^4 show many common features.[30]

9. Conclusion

We have attempted to develop a general theory to find the phase behavior of the reversibly gelling polymer solutions in which network junctions have variable multiplicity.

The model proposed in this study has obvious advantages in describing self-associating liquid mixtures in which the polydispersity is thermally controlled; it covers the interference phenomena between the two competing transitions—that is, gelation and macroscopic phase separation. From the theoretical and numerical results obtained in the present paper, the following conclusions can be drawn.

(1) Physical gelation is a thermodynamic transition which reveals a singularity in the derivatives of the free energy. This can be most easily seen in the singular behavior of the osmotic compressibility.

(2) Multicritical phenomena arise as a result of the competition between gelation and phase separation irrespective of the details of the junction multiplicity. This conclusion is drawn on the basis of the universal form in the asymptotic population distribution of the clusters near the gelation transition.

(3) The phase diagram varies qualitatively as the junction multiplicity is changed; the quasi-critical end point turns into the quasi-tricritical point by a small increase in the junction multiplicity.

(4) The osmotic pressure in the dilute regime is also sensitive to the junction multiplicity; its second virial coefficient reflects the population of the binary junctions only and hence exhibits no effect of association if only multiple junctions are allowed.

Our results may be directly applicable to some real thermoreversible gels, such as those of polyethylene,[2] or of poly(vinyl chloride) where microcrystalline junctions presumably are formed by stereoregular sequences. In the latter case, the formula for the equilibrium constant will involve a theory of copolymer crystallization.[36] Another familiar system, which however will require a further embellishment of our results, is atactic polystyrene in carbon disulfide in which the junctions are made of polymer/solvent complexes.[37-39] (In the special case of very long chains, where the gel-point polymer concentration is low and not much solvent will be found in the junctions, only a trivial modification is needed.)

Further modifications in the present theory would involve (1) some allowance for cyclic structures, possibly by the "spanning tree" approximation of Gordon and Scantlebury,[40] and (2) calculations of structure factors, possibly by an extension of the methods of Dobson and Gordon,[41] and aided by a random phase approximation. It is hoped to pursue these topics in later publications. We intend also to investigate the effects of using Flory's approximation for postgel relationships, as well as to attempt a more detailed comparison with experimental data.

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