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Thermoreversible Gelation in Solutions of Associative Polymers.
1. Statics

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ABSTRACT: An equilibrium mean−field theory for reversible network formation in solutions of associative polymers is presented. We study polymer solutions with many associating groups per chain and consider pairwise association of these groups. A simple analytical expression for the free energy of these systems is derived and is shown to be consistent with the classical gelation picture developed by Flory and Stockmayer. It is shown that association and formation of a reversible network is always accompanied by a tendency for phase separation which might occur even under marginal solvent conditions. The mean-field theory is also generalized to take into account the effect of local intrachain loops as well as excluded volume interactions (partial swelling of polymer chains). It is shown that phase separation might be suppressed by the excluded volume interactions.

1. Introduction

Heteropolymers which contain both soluble and insoluble monomers are sometimes called associating (amphiphilic) polymers. These amphiphilic systems include traditional associating polymers consisting of hydrophobic groups connected by longer water−soluble fragments, ionomers, and block−copolymers in selective solvents. The properties of these systems are governed by the presence of stickers—relatively small strongly interacting associating groups (ionic groups for the case of ionomers, or insoluble blocks for the case of block-copolymers) which tend to form stable aggregates (or multiplets). These aggregates can play a role of reversible junctions between different polymer chains. A reversible polymer network (infinite cluster of connected chains) might be formed at some critical concentration c_g which is not necessarily high (it typically corresponds to the semidilute regime). The reversible network structure implies remarkable static and more importantly dynamic properties of these systems.

The qualitative features of associative polymers (thermoreversible gelation and tendency for phase separation) have been understood for almost 2 decades.[1−9] The quantitative details depend on the particular model of associations and were studied analytically only for a few simple cases. One of the simplest models is a system of polymer chains containing $f \gg 1$ stickers each (which are capable of pairwise association) was studied recently by Tanaka.[6−10] Unfortunately, we found essential flaws in Tanaka's approach leading to some incorrect results. In the present paper we provide an analytical description of the equilibrium properties of solutions of associating polymers on the basis of this simple model.

In the next section we describe in detail the mean field theory of associative polymers. One of our conclusions is that thermoreversible gelation under Θ-solvent conditions is normally accompanied by a phase separation of the solution, which is driven by the association of stickers rather than by the poor quality of the solvent. This effect is completely absent in Tanaka's theory. In section 3 we study the competition between local intrachain and interchain pairing. In section 4 we consider the effect on the thermoreversible gelation due to partial swelling of polymer fragments caused by the excluded volume interactions.

The results of this paper will be utilized in the second paper of the sequence[11] in the development of the theory of associative polymer dynamics.

2. Mean Field Theory of Associative Polymers

Mean field theory is valid in the regime of strongly overlapping coils.

2.1. Model. Consider a solution of linear chains (N-mers) with associating groups (stickers). Each chain contains f stickers ($f \ll N$), separated by spacers of $l = N/f$ monomers each, with $l \gg 1$. In most cases below we also assume that $f \gg 1$. Stickers can associate in pairs with the energy of each association equal to $\epsilon k_B T$, where k_B is the Boltzmann constant and T is the absolute temperature. The monomer concentration in solution is c. The number density of polymer chains in the solution is c/N and the density of stickers if $fc/N = c/l$ (since there are l monomers between stickers). The number of stickers in volume V is

$$N_{st} = f\frac{c}{N}V = \frac{c}{l}V \tag{2.1}$$

Let p be the fraction of stickers that are associated in pairs (the degree of conversion). The number of such pairs of associated stickers is

$$N_p = \frac{1}{2}pN_{st} \tag{2.2}$$

because two associated stickers form one pair. The

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density of temporary bonds (pairs of stickers) is

$$\varrho = \frac{N_p}{V} = \frac{p}{2}\frac{fc}{N} = \frac{p}{2}\frac{c}{l} \qquad (2\ 3)$$

2.2. Free Energy. The free energy density of the system can be divided into two parts—the part F_{int} from interactions of nonsticker monomers, and the contribution F_{st} from sticker interactions

$$F = F_{int} + F_{st} \qquad (2.4)$$

The interaction part F_{int} can be written in terms of two- and three-body interactions between nonsticker monomers

$$\frac{F_{int}}{k_B T} = \frac{v}{2}c^2 + \frac{w}{6}c^3 \qquad (2.5)$$

where v is the excluded volume parameter and w is the three-body interaction parameter.

In order to calculate the free energy density due to the association of stickers, F_{st}, we introduce a reference system, which is a system of noninteracting polymers.[12] Its free energy density is purely entropic

$$\frac{F_{ref}}{k_B T} = -\frac{1}{V}\ln Z_{ref} = \frac{c}{N}\ln\left(\frac{c}{eN}\right) \qquad (2.6)$$

where Z_{ref} is the partition function of the reference state: a solution of noninteracting polymers. Next we require that $2N_p$ stickers form N_p bonds. The partition function of the system with bonds is

$$Z_{st} = Z_{ref}P_{comb}W\exp(\epsilon N_p) \qquad (2.7)$$

where P_{comb} is the number of different ways of choosing N_p pairs of stickers out of total number N_{st} stickers and W is the probability that all chosen stickers in the absence of attractive interactions can be found close enough to their partners to form bonds

$$W = \left(\frac{v_b}{V}\right)^{N_p} \qquad (2.8)$$

where v_b is the bond volume.

The number of different ways of selecting $2N_p$ stickers out of total number N_{st} stickers is a binomial coefficient

$$\frac{N_{st}!}{(N_{st} - 2N_p)!(2N_p)!} \qquad (2.9)$$

Next we need to find the number of different ways of pairing $2N_p$ stickers. If we take one of them, there are $2N_p - 1$ possible partners. By choosing one of these partners, we have selected the first pair. Next we take any of the unpaired stickers and select its partner out of remaining $2N_p - 3$ unused stickers. Thus there are $(2N_p - 1)(2N_p - 3)$ ways of selecting the first two pairs. Continuing this process, we find that there are $(2N_p - 1)!!$ different ways of selecting N_p pairs out of $2N_p$ stickers. Here $(2N_p - 1)!!$ denotes the product of all odd numbers between 1 and $2N_p - 1$. Therefore the combinatorial factor is

$$P_{comb} = \frac{N_{st}!\,(2N_p - 1)!!}{(N_{st} - 2N_p)!\,(2N_p)!} = \frac{N_{st}!}{(N_{st} - 2N_p)!N_p!2^{N_p}} \qquad (2.10)$$

Thus the part of the free energy density due to stickers is

$$\frac{F_{st}}{k_B T} = -\frac{1}{V}\ln Z_{st} = \frac{c}{N}\ln\left(\frac{c}{eN}\right) - \frac{cp}{2l}\ln\left(\frac{c}{el}v_b\right) + \frac{c}{2l}[p\ln p + 2(1 - p)\ln(1 - p)] - \epsilon\frac{cp}{2l} \qquad (2.11)$$

The same result is derived in the Appendix starting from the classical gelation theory of Flory and Stockmayer.[15]

The above result corresponds to the mean field theory. We have estimated the sticking probability W, neglecting any correlation between the sticker positions. These correlations are due to the fact that some sticker pairs might belong to the same chain. Thus the mean-field theory is valid if the coils strongly overlap,[16] i.e. in the semidilute regime

$$c \gg c^* \sim N/R^3 \qquad (2.12)$$

where c^* is the coil overlap concentration and R is the coil size.

The total free energy density $F = F_{st} + F_{int}$ should be minimized with respect to the density of temporary bonds ρ or, equivalently, with respect to the degree of conversion p. The condition for the free energy minimum is

$$\frac{p}{(1 - p)^2} = \frac{c}{l}v_b e^{\epsilon} = \frac{c}{l}\lambda \qquad (2.13)$$

where the attractive volume of a bond is

$$\lambda = v_b e^{\epsilon} \qquad (2.14)$$

A similar equation was also obtained by Tanaka.[9,10] Substituting this condition into eq 2.11 we obtain the free energy density[17]

$$\frac{F}{k_B T} = \frac{c}{N}\ln\left(\frac{c}{eN}\right) + \frac{v}{2}c^2 + \frac{w}{6}c^3 + \frac{c}{l}\left[\frac{p}{2} + \ln(1 - p)\right] \qquad (2.15)$$

where the probability p is the solution of eq 2.13

$$p = 1 - \frac{\sqrt{4\frac{c}{l}\lambda + 1} - 1}{2\frac{c}{l}\lambda} \qquad (2.16)$$

There are two limiting behaviors of this solution—for low fraction of closed (associated) stickers

$$p \approx c\lambda/l \quad \text{for} \quad c\lambda/l \ll 1 \qquad (2.17)$$

and for high fraction of closed (associated) stickers

$$p \approx 1 - 1/\sqrt{c\lambda/l} \quad \text{for} \quad c\lambda/l \gg 1 \qquad (2.18)$$

The first term on the rhs of eq 2.15 is the ideal-gas free energy of the associating chains. The next two terms correspond to the two-body and the three-body excluded volume interactions of monomers, and the last term accounts for association of stickers. Note that the free energy of association depends on the concentration of stickers c/l only. It does not explicitly depend either on the functionality f, or on the degree of polymerization N. This is a consequence of the mean-field nature of the theory that neglects the correlations of the sticker positions.

Note also that for a low fraction of bonds (for $p \ll 1$) the last term in the free energy (eq 2.15) (related to associations) takes the form of pairwise attraction between the stickers $-(\lambda/2)(c/l)^2$. This term reduces the excluded volume parameter by the attractive volume per monomer, λ/l^2

$$v_{\rm eff} = v - \frac{\lambda}{l^2} \quad \text{for} \quad p \ll 1 \tag{2.19}$$

where λ is the attractive volume of a bond (eq 2.14), and $l = N/f$ is the number of monomers between the neighboring stickers. To determine the stability of the single phase in this regime of low conversion (for $p \ll 1$) we can use the results for polymers in marginal solvents by replacing the excluded volume parameter v by $v_{\rm eff} = v - \lambda/l^2$.

2.3. Gel Point. The gel point in the mean field theory corresponds to the degree of conversion[15,18]

$$p_{\rm g} = 1/(f - 1) \tag{2.20}$$

Thus the concentration at this point is (using eq 2.13)

$$c_{\rm g} = \frac{l}{\lambda}\frac{(f-1)}{(f-2)^2} \tag{2.21}$$

The critical degree of conversion defining the gelation point, eq 2.20, can be also obtained in the framework of the present theory. Note that the concentration of free chains, $\tilde{C}_1$, (with all f stickers open) is simply given by the product of the total concentration of chains, c/N, and the probability that all f stickers are open, $(1 - p)^f$: $\tilde{C}_1 = (c/N)(1 - p)^f$, where p is defined in eq 2.16. This concentration is increasing as the total polymer concentration, c, is increased in the pregel (sol) region, $c < c_{\rm g}$. However, $\tilde{C}_1$ could not possibly increase any more in the postgel regime as this would mean simultaneous increase of the concentration of all finite clusters (which are being reversibly formed by free chain units) and hence an increase of the total sol concentration above $c_{\rm g}$. Therefore the gel point should correspond to a maximum of $c(1 - p)^f$ as a function of c. Using eq 2.13 we thus get $p_{\rm g} = 1/(f - 1)$, i.e. eq 2.20.

In the pregel regime ($c < c_{\rm g}$) our theory agrees with the classical gelation theory of Flory and Stockmayer. Thermoreversible gelation in solutions of associating polymers with multichain junctions (i.e. more than two stickers per junction) was considered by Stockmayer[19] in the pregel regime. The osmotic pressure obtained in that paper when applied to the case of pairwise association agrees with our free energy expression, eq 2.15 (also see below, eq 2.32).

With regard to the postgel regime ($c > c_{\rm g}$), the situation is less obvious: two models on this regime has been proposed long ago by Flory[20] and Stockmayer.[18] The Flory model allows cycles within the gel, while assuming that finite clusters are treelike. The Stockmayer model does not allow cyclization of the gel and also assumes that the shape of molecular weight distribution of finite clusters does not change in the postgel regime. The shape of the molecular weight distribution of clusters is determined by the mean conversion degree of sol component, $p_{\rm s}$, which in turn is related to the total concentration of finite clusters, $c_{\rm s}$: $p_{\rm s}/(1-p_{\rm s})^2 = (\lambda/l)c_{\rm s}$, i.e. the same relation as in the pregel regime (see eq 2.13). Therefore the Stockmayer model, when applied to the *reversible* gels, implies that both the shape of finite cluster distribution and their concentration is independent of the total concentration c for $c > c_{\rm g}$. That means that concentration of clusters of any size (in particular, free units, i.e. free chains) is also concentration independent. This kind of behavior disagrees with our predictions: using eq 2.13 one can easily see that concentration of free chains, $C_1 = (c/l)(1 - p)^f$, is decreasing as c is increased in the postgel regime.

On the other hand it is possible to show that our results (both for the free energy and for the cluster distribution) completely agree with the Flory postgel model. Since our model does not involve any assumptions concerning the structure of either finite clusters or the reversible gel, we believe that the dispute between the Flory and Stockmayer approaches is thus resolved in favor of the Flory model, at least as far as *reversible* gelation is concerned: a reversible network structure without cycles is impossible.

Very recently (actually after the present paper has been submitted) Ishida and Tanaka[10] considered phase equilibria in thermoreversible gels using both postgel approaches (due to Flory and due to Stockmayer). One might expect that the free energy[10] obtained with the Flory approach must coincide with that derived in the present paper. This is not the case, however: the two free energy expressions are essentially different in the postgel region. Ishida and Tanaka incorrectly treated the gel contribution to the free energy, and arrived at a fundamentally inconsistent result: in their model the free chain concentration and the chain chemical potential are not properly matched.

An important question: what is the thermodynamic character of the gelation transition? There are two possible scenarios: (1) discontinuous gelation accompanied by phase separation (sol phase in equilibrium with a more concentrated gel phase) and this possibility is considered in the next sections; (2) continuous gelation. The theory of Stockmayer and Tanaka[9] implies that continuous gelation (remember that we consider reversible gels only) is a third-order phase transition.[21] Our prediction is essentially different: the reversible continuous gelation is not a thermodynamic transition at all. In fact one can easily check that the free energy, eq 2.15,[23] and all its derivatives are perfectly analytical at the gel point. This is an exact result within the framework of the basic mean-field approximation (also adopted in all relevant models by Flory, Stockmayer, and Tanaka). However we believe that this result is even more general; i.e., it should be also valid outside the mean-field regime. We believe that the opposite conclusion[9] is incorrect and is a result of the unrealistic treatment of the gel regime, which we discussed above.

Note however that gelation (being not a thermodynamic transition) plays a very important role in the dynamics of associative polymers, even when it is not accompanied by a phase separation (see the second paper of this series[11]).

2.4. Critical Point. The chemical potential can be calculated by differentiating the free energy density, eq 2.15, with respect to concentration

$$\frac{\mu}{k_BT} = \frac{1}{k_BT}\frac{\partial F}{\partial c} = \frac{1}{N}\ln\left(\frac{c}{N}\right) + vc + \frac{w}{2}c^2 + \frac{1}{l}\ln(1-p) \tag{2.22}$$

where we have used eq 2.13 and the fact that $\partial F/\partial p = 0$.

The critical point can be determined by simultaneously solving $\partial\mu/\partial c = 0$ and $\partial^2\mu/\partial c^2 = 0$. Differentiating the chemical potential with respect to concentration, we obtain

$$\frac{1}{k_BT}\frac{\partial\mu}{\partial c} = v + wc + \frac{1}{cN}\left(1 - \frac{fp}{1+p}\right) = 0 \tag{2.23}$$

$$\frac{1}{k_BT}\frac{\partial^2\mu}{\partial c^2} = w - \frac{1}{c^2N}\left[1 - \frac{fp^2(3+p)}{(1+p)^3}\right] = 0 \tag{2.24}$$

Note that for $v = w = 0$ the derivative $\partial\mu/\partial c$ is negative above the gel point (for $c > c_g$). Therefore the system with no excluded volume interactions *is unstable* in the region $c > c_g$ above the gel point and *must phase separate.*

This system of equations for the critical point (eqs 2.23 and 2.24) can be rewritten for low degree of conversion $p \ll 1$ using eq 2.18 (i.e., for $c\lambda/l \ll 1$; below we show that this condition is valid if $f \gg 1$):

$$\frac{1}{k_BT}\frac{\partial\mu}{\partial c} \approx v + wc + \frac{1}{cN} - \frac{\lambda}{l^2} + 3\frac{\lambda^2}{l^3}c = 0 \tag{2.25}$$

$$\frac{1}{k_BT}\frac{\partial^2\mu}{\partial c^2} \approx w - \frac{1}{c^2N} + 3\frac{\lambda^2}{l^3} = 0 \tag{2.26}$$

As expected, these equations can be obtained by replacing the excluded volume parameter v in the equivalent expressions for ordinary polymer solutions with $v_{\rm eff}$ (see eq 2.19), and replacing the third virial coefficient w with $w_{\rm eff} = w + 3\lambda^2/l^3$. The above equations can be easily solved in two asymptotic regimes:

(i) Close to the Θ-conditions, for $v \ll (w/l)^{1/2}$, the critical concentration is equal to that of an ordinary polymer solution

$$c_{\rm cr} \approx 1/\sqrt{Nw} \quad \text{for} \quad v \ll \sqrt{w/l},\ f \gg 1 \tag{2.27}$$

and the critical attractive volume of a bond is

$$\lambda_{\rm cr} \approx l^2\left(v + 2\sqrt{\frac{w}{N}}\right) \quad \text{for} \quad v \ll \sqrt{w/l},\ f \gg 1 \tag{2.28}$$

(ii) Further away from the Θ-point, for $v \gg (w/l)^{1/2}$, the critical parameters are

$$c_{\rm cr} \simeq \frac{1}{\sqrt{3}N^{1/2}l^{1/2}v} \quad \text{for} \quad v \gg \sqrt{w/l},\ f \gg 1 \tag{2.29}$$

$$\lambda_{\rm cr} \simeq l^2 v \quad \text{for} \quad v \gg \sqrt{w/l},\ f \gg 1 \tag{2.30}$$

Note that in all cases the critical point corresponds to the gel state: $c_{\rm cr} > c_g(\lambda_{\rm cr})$ if $v > 0$.

It is now straightforward to check that the initial assumption $p \ll 1$ is always valid near the critical point: eqs 2.27−2.30 imply that $c\lambda/l \ll 1$ in both regimes considered above if $f \gg 1$. Note that eq 2.30 can be understood by recalling that bonds between the stickers renormalize the excluded volume parameter $v_{\rm eff} = v - \lambda/l^2$.

Note also that eqs 2.29 and 2.30 are valid if v is not too high

$$\sqrt{w/l} \ll v \ll a^3/l^{1/2} \tag{2.31}$$

where a is the monomer (statistical segment) size. This condition ensures that $c_{\rm cr}$ defined by eq (2.29) is higher than the coil overlap concentration $c^* \sim 1/(N^{1/2}a^3)$. For a large third virial coefficient $w \approx a^6$ this regime disappears.

For larger values of the excluded volume parameter v the mean field theory has to be modified to include the good solvent effects and also a renormalization of λ because of local loops (see sections 3 and 4 below).[24]

2.5. Phase Diagram. If the parameter λ is small enough, $\lambda < \lambda_{\rm cr}$ (for small ϵ, or large l), the second derivative $\partial^2F/\partial c^2$ is positive, and the system does not phase separate. For stronger bonds $\lambda > \lambda_{\rm cr}$ the homogeneous state is unstable and the system phase separates into more dilute and more concentrated phases.

The phase behavior of the system can be analyzed in a standard way, using the free energy (eq 2.15), by equating the chemical potentials μ (see eq 2.22) and osmotic pressures Π in both phases. The osmotic pressure can also be calculated from the free energy

$$\frac{\Pi}{k_BT} = \frac{1}{kT}\left(c\frac{\partial F}{\partial c} - F\right) = \frac{v}{2}c^2 + \frac{w}{3}c^3 + \frac{c}{N} - \frac{p}{2}\frac{c}{l} \tag{2.32}$$

Let us consider the Θ-regime[25]: $v \ll (w/l)^{1/2}$.

We begin by considering the asymptotic regime $\lambda \gg \lambda_{\rm cr}$, still assuming that the degree of conversion is low, $p \ll 1$ (that is $c\lambda/l \ll 1$). These two conditions are compatible if $f \gg 1$. The concentration in the dilute phase is exponentially low and the osmotic pressure in the coexisting phases nearly vanishes. The concentration of the dense phase c_2 can be found from $\Pi \approx 0$. Obviously c_2 must be much higher than $c_{\rm cr} \approx 1/\sqrt{Nw}$ for $\lambda \gg \lambda_{\rm cr}$, so that the third term in the rhs of eq 2.32 can be neglected in comparison with the second term. Hence the equation $\Pi = 0$ can be rewritten as

$$\frac{v}{2}c_2^2 + \frac{w}{3}c_2^3 - \frac{c_2}{2l}\frac{c_2\lambda}{l} = 0 \tag{2.33}$$

Therefore the concentration of the dense phase is

$$c_2 \simeq \frac{3}{2}\frac{1}{w}\left(\frac{\lambda}{l^2} - v\right) \quad \text{for} \quad \lambda_{\rm cr} \ll \lambda \ll \lambda_1 \quad \text{and} \quad v \ll \sqrt{w/l} \tag{2.34}$$

Recalling the condition $c\lambda/l \ll 1$, we obtain the upper boundary of the region of validity of eq 2.34:

$$\lambda_1 = l^{3/2}w^{1/2} \tag{2.35}$$

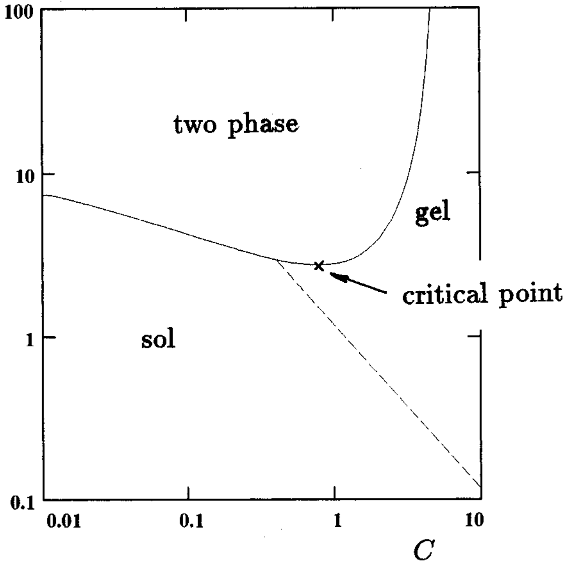

Figure 1. Phase diagram of a Θ-solution of associating polymers for $f = 20$ and $v = 0$ in the reduced variables $C = c(wN)^{1/2}$ vs $\tilde{\lambda} = \lambda f^2/(wN^3)^{1/2}$.

From the equation $\mu(c_2) = \mu(c_1)$ we get the concentration in the dilute phase (note that $\mu(c_2) \simeq (w/2)c_2^2 - c_2\lambda/l^2 + vc_2$, and $\mu(c_1) \simeq 1/N \ln(c_1/N)$)

$$c_1 \sim \exp\left[-\frac{3}{8}\frac{N}{w}\left(\frac{\lambda}{l^2} - v\right)^2\right]$$
$$\text{for} \quad \lambda_{cr} \ll \lambda \ll \lambda l \quad \text{and} \quad v \ll \sqrt{w/l} \quad (2.36)$$

which is indeed exponentially small since $\lambda/l^2 - v \gg \lambda_{cr}/l^2 - v \approx (w/N)^{1/2}$; see eq 2.28 (a pre-exponential factor is omitted in eq 2.36).

For higher bond strengths $\lambda \gg \lambda_l = w^{1/2}l^{3/2}$, the fraction of closed bonds p approaches unity, and one obtains a quadratic equation for the concentration of the dense phase

$$\frac{\Pi}{k_B T} = \frac{v}{2}c_2^2 + \frac{w}{3}c_2^3 - \frac{c_2}{2l} \approx 0$$
$$\text{for} \quad \lambda \gg \lambda_{cr},\ v \ll \sqrt{w/l},\ f \gg 1 \quad (2.37)$$

Note that in this strong attraction regime the concentration c_2 is independent of the bond strength λ. The excluded volume term can be neglected since $v \ll (w/l)^{1/2}$, and thus the concentration of the dense phase has a simple form

$$c_2 \approx \sqrt{\frac{3}{2wl}} \quad \text{for} \quad \lambda \gg \lambda_{cr},\ v \ll \sqrt{w/l},\ f \gg 1 \qquad (2.38)$$

The latter equation can be easily generalized for the case of arbitrary f. The result is

$$c_2 \simeq \sqrt{\frac{3(f-2)}{2wN}} \quad \text{for} \quad \lambda \gg \lambda_{cr} \quad \text{and} \quad v \ll \sqrt{w/l} \qquad (2.39)$$

Figure 1 shows an example of a phase diagram for $f = 20$, $v = 0$ in the reduced variables $C = c(wN)^{1/2}$ vs $\tilde{\lambda} = \lambda f^2/(wN^3)^{1/2}$. The dashed line corresponds to the sol-gel transition, $C = f(f-1)/(f-2)^2\lambda$, in accordance with eq 2.21. The region of phase separation is bounded by a solid curve. The concentration C_1 of the more dilute phase rapidly decreases with $\tilde{\lambda}$ (see eq 2.36). The concentration C_2 of the denser phase approaches $C_2 = (3(f-2)/2)^{1/2} \simeq 5.2$ as $\tilde{\lambda}$ is increased. Unfortunately the region of validity of the intermediate asymptotics, $C_2 \propto \tilde{\lambda}$ (see eq 2.34), is still narrow for $f = 20$; hence, this regime is not apparent in Figure 1. Note also the critical point $C \simeq 0.79$, $\tilde{\lambda} \simeq 2.69$ (compare with the exact result for $f \to \infty$: $C = 1$, $\tilde{\lambda} = 2$; see eqs 2.27 and 2.28), which is located inside the gel region.

2.6. Globule. The calculated phase diagram is based on the mean field theory, which is valid only in the regime of strongly overlapping chains ($c \gg c^*$). In the dilute regime ($c \ll c^*$) the system is an ideal solution of virtually isolated (noninteracting) coils. If the bond energy ϵ is large (for $\lambda > \lambda_{cr}$), the strong attraction between the stickers would promote intrachain bridging, leading to the collapse of coils into rather dense globules. The density inside the globules is defined by the balance between the entropy associated with different ways of bridging and the three-body repulsion.

The number of different ways of bridging can be calculated, using exactly the same arguments that were employed above to calculate the combinatorial term in the free energy of the system of many strongly overlapping coils (eq 2.11). The only difference is that now the total number of stickers $N_{st} = f$, since all stickers are bound to the same polymer chain. Therefore the first (ideal gas) term in eq (2.11) does not enter the free energy F in the single globule case. Hence the free energy of the globule is

$$F_{gl} = k_B T\frac{N}{c}\left\{\frac{v}{2}c^2 + \frac{w}{6}c^3 + \frac{c}{l}\left[\frac{p}{2} + \ln(1-p)\right]\right\} \qquad (2.40)$$

where p is defined in eq 2.13.[26]

The minimization of the free energy with respect to c gives the equilibrium density inside the globule

$$c_{gl} \approx c_2 \approx -\frac{3v_{eff}}{2w} \approx \frac{3\lambda}{2wl^2} \quad \text{for} \quad \lambda_{cr} \ll \lambda \ll \lambda_l \qquad (2.41)$$

$$c_{gl} \approx c_2 \approx \sqrt{\frac{3}{2wl}} \quad \text{for} \quad \lambda \gg \lambda_l \qquad (2.42)$$

Note that c_{gl} nearly coincides with the concentration in the dense phase $c_{gl} \approx c_2$ (eqs 2.34 and 2.38), as it should (since in the regime of strongly overlapping coils the intensive thermodynamic parameters nearly do not depend on the degree of polymerization). Note also that for $\lambda \gg \lambda_{cr}$ the concentration c_{gl} is much larger than the mean density inside an unperturbed chain $\sim 1/(a^3 N^{1/2})$, so the globule is well-defined. In this regime the low-density phase is a very dilute solution of globules, which must be in equilibrium with the high-density phase. The latter can be considered as a precipitate (densely packed condensate of chains). It will be interesting to compare the above mean field estimates with more careful non-mean-field calculations of the cactuslike conformations of the chain satisfying the closed bonds requirements.

3. Renormalization of the Bond Strength

Let us consider the limit of very high bond strengths $\lambda \to \infty$. In this regime all bonds must be saturated (all stickers paired) at any concentration, even in a very dilute state. The easiest way to create a bond in a dilute state is to pair stickers that are close to each other along the chain. At low concentration (when coils do not overlap) the probability of an inter-chain pairing is very

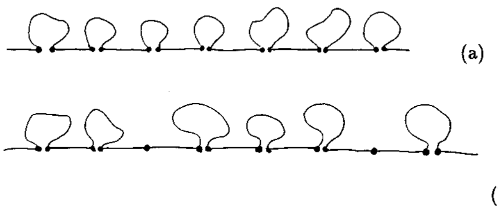

Figure 2. Polymer chain with $f = 14$ stickers: (a) all stickers are locally paired (intrachain bonds between the nearest neighbors); (b) two stickers are open and ready to form interchain bonds.

low (unless f is odd for $\lambda \to \infty$). Consider an arbitrarily chosen sticker. The probability that its nth neighbor along the chain makes a contact with it is roughly

$$P_n \approx \frac{v_b}{a^3 l^{3/2}} n^{-3/2} \tag{3.1}$$

The total probability of a contact

$$P = \sum p_n \tag{3.2}$$

and P is dominated by the small n behavior. We therefore expect that at low concentrations nearly all sticker pairs are local.[30]

The entropy associated with intra-chain pairing of all f stickers of one chain is $S_f = k_B \ln P_f \sim f k_B/2 \ln P$, where P_f is the a priori probability that all stickers are paired (a priori means that it does not include the energetic Boltzmann factor), and $f/2$ is the total number of intramolecular bonds. Note that the above estimate for S_f can be also obtained with a simplified model that allows only nearest neighbor intramolecular bonds (Figure 2a). In this case $P = P_1 \simeq v_b/a^3 l^{3/2}$ is the probability of the smallest loop (see eq 3.1). The entropy for this simplified model differs from the exact result by an additive constant of order k_B per sticker.

Obviously these local intrachain bonds do not contribute either to the interchain associations or to the effective attraction between remote segments of the polymer chains. Therefore these local pairs cannot lead to a phase separation. It is clear that only nonlocal interchain bonds are important for gelation and phase separation.

We thus have to introduce an *effective* degree of conversion, p, that is the fraction of interchain bonds among all possible bonds between the stickers. The total fraction of all bonds (both intra- and intermolecular) can be denoted as p_{tot}. Note that all equations considered in the previous sections are actually valid in the regime when $p \simeq p_{tot}$. Indeed, mean-field theory ignores intrachain bonds.

The contribution from inter-molecular associations to the free energy density, F_{st}, for a given fraction of interchain bonds, p, can be calculated in exactly the same way as in the "true" mean field regime (see section 2.2). The only difference is that now the reference system is the ideal solution of unconnected polymer chains with all stickers locally paired. Interchain bonds can then be formed if two chains come close to each other (see Figure 3). This process implies that some of the intrachain pairs break so that the *total* number of bonds (both intra- and intermolecular) is constant since $p_{tot} = 1$ as $\lambda \to \infty$. Hence the total bond energy (per unit volume), $F_\epsilon = -\epsilon k_B T c/(2l)$, is constant. However the entropy associated with local intrachain bonds does change since it is related to the number of these bonds. The corresponding entropy chainge ΔS_{intra} can be easily calculated with the simplifield model of Figure 2. For example, the appearance of two open stickers means that the number of local loops decreases by 1, so that $\Delta S_{intra} = S_{f/2} - S_{f/2-1} = -k_B \ln v_b/v_l$, where $S_{f/2}$ corresponds to the initial state (Figure 2a), $S_{f/2-1}$ corresponds to the final state (Figure 2b), and

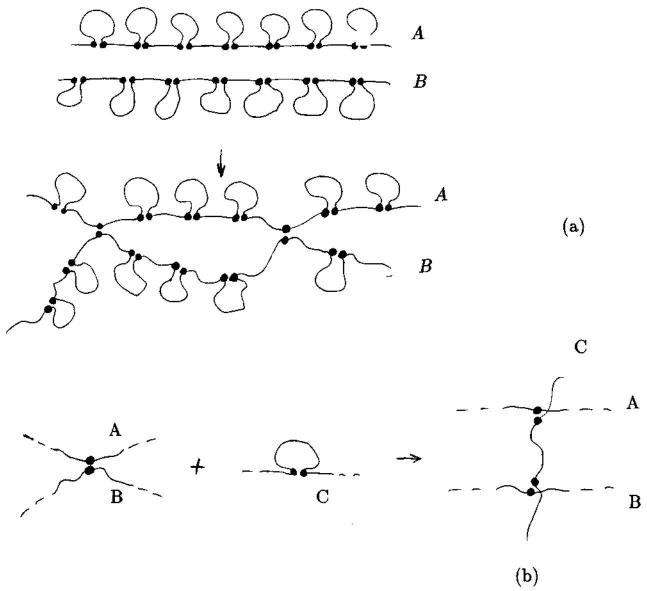

Figure 3. (a) Two chains A and B with $f = 14$ stickers per chain. Initially all stickers are locally paired, and then two interchain bonds between the chains are formed; simultaneously, the number of local loops decreases by 2. (b) One interchain bond (between the chains A and B) and one loop (local bond on chain C) transform into 2 inter-chain bonds (AC and BC).

$$v_l \approx a^3 l^{3/2} \tag{3.3}$$

Note that if we take a typical value of the three−body interaction coefficient $w \approx a^6$, then the volume occupied by a spacer v_l is equal to the crossover attraction volume of the bond λ_l (see eq 2.35)

$$v_l \approx \lambda_l \tag{3.4}$$

Formation of N_p interchain bonds implies that the number of (local) intrachain bonds must decrease by N_p; the corresponding entropy change is $\Delta S_{intra} = -N_p k_B \ln P_1 = -N_p k_B \ln(v_b/v_l)$. Hence the partition function of the system with N_p interchain bonds can be written as (compare with eq 2.7)

$$Z_{st} = Z_{ref} P_{comb} W \exp(\Delta S_{intra}/k_B) \tag{3.5}$$

where the factors P_{comb} and W are defined below eq 2.7.[31] The difference between eq 3.5 and eq 2.7 can be canceled by replacing ϵ in eq 2.7 by its effective value

$$\epsilon \to \epsilon_{eff} = \ln (v_l/v_b) \tag{3.6}$$

where ϵ_{eff} is the renormalized effective bond energy, taking into account the effect of local bonds.

The previously obtained results for the free energy are still valid if we use the renormalized bond energy.

The corresponding renormalized value of the parameter λ (see eq 2.14) is

$$\lambda_{\text{eff}} = v_1 \tag{3.7}$$

In particular the fraction of inter-chain bonds is still determined by the equation analogous to eq 2.13

$$\frac{p}{(1-p)^2} = \frac{cv_1}{l} = ca^3 l^{1/2} \tag{3.8}$$

This equation implies that the fraction of inter-chain bonds p is small (even for $\epsilon \to \infty$) in the concentration regime $c^* < c < 1/(a^3 l^{1/2})$, where the coils strongly overlap, but the strands between stickers do not.

Thus even for $\epsilon \to \infty$ the critical value of the excluded volume parameter, determined by eq 2.30, which should be solved for v, is finite

$$v_{\text{cr}} \simeq \lambda_{\text{eff}}/l^2 \approx \frac{a^3}{l^{1/2}} \tag{3.9}$$

Therefore the association of stickers does not lead to a phase separation if $v > v_{\text{cr}}(\infty) \approx a^3/l^{1/2}$. Note that the critical value of the excluded volume parameter v_{cr} is small if the spacers between stickers are long ($l \gg 1$), which is assumed in the present work. In particular, the above picture implies that there is no phase separation in a good solvent ($v \approx a^3$).

4. Scaling Picture

A direct application of the above picture to good solvents is not rigorous, as the theory is based on the essentially mean-field model, which is not valid for $v \sim v_{\text{cr}}$ when spacers are partially swollen and therefore their statistics are not exactly Gaussian (note that the Fixman parameter $Z \sim vl^{1/2}/a^3$ is on the order of 1 for $v \sim v_{\text{cr}}$). Thus we need to reconsider the effect of binary excluded volume interactions, taking into account that the chain statistics are not Gaussian on large enough scales (but are those of swollen coils). Another nontrivial effect of swollen chain statistics is an additional short-range repulsion between the links of different chains. This repulsion, which gives rise to a reduced probability of a contact between two stickers, is also taken into account below. We start the consideration with the case of a good solvent ($v \approx a^3$), and then consider the marginal regime with partially swollen chains ($(w/N)^{1/2} \ll v \ll a^3$). As with any scaling estimate, we omit all numerical prefactors in most equations below. We also do not consider variations of the three-body interaction parameter, assuming that $w \approx a^6$.

4.1. Associations in Good Solvent. As was mentioned above, we do not expect any phase separation in the good solvent regime (for $v \approx a^3$). Therefore our aim here is to locate the gelation threshold. To do that we need to calculate the fraction of interchain bonds, p, as a function of concentration. We would like to take into account both the effects of the intrachain bonds and the effects of the excluded volume statistics. Let us assume that the chains are overlapping ($c > c^*$), where the overlap concentration is

$$c^* \approx \frac{N^{1-3\nu}}{a^3} \tag{4.1}$$

with Flory exponent $\nu \approx 0.59$.[1] Let us also assume that a typical section of a chain between interchain bonds, l/p, is much larger than the correlation blob strand g, where

$$g \approx (ca^3)^{-1/(3\nu-1)} \tag{4.2}$$

is the number of monomers per standard concentration blob. Note that $g < N$ for $c > c^*$. These assumptions can be easily verified later (they are valid in all cases studied below).

Consider two stickers, that are close enough to each other (at a monomeric distance of order a) but that have not yet formed a bond. The excluded volume effects reduce the probability of a contact between two monomers along the chain (and between the stickers) by the factor

$$K(g) \approx g^{-\nu\theta_2} \tag{4.3}$$

where the exponent $\theta_2 \approx 0.78$[32−34].[35] The typical number of contacts between two overlapping blobs of g monomers each scales as $g^{2-\nu(3+\theta_2)} = g^{-z}$ where the exponent

$$z \equiv \nu(3 + \theta_2) - 2 \approx 0.225 \tag{4.4}$$

Note that for Gaussian chains these exponents are $\theta_2 = 0$ and $z = -1/2$.

The statistical weight of a bond between two stickers is now

$$\Lambda = \lambda K(g) \tag{4.5}$$

so that the fraction of bonds is now determined by the equation (c.f. eq 2.13)

$$\frac{p}{(1-p)^2} = \frac{c}{l}\Lambda \approx \frac{c\lambda}{l}(ca^3)^{\zeta-1} \tag{4.6}$$

where the exponent $\zeta - 1 \equiv \nu\theta_2/(3\nu - 1) \simeq 0.60$.

The sol−gel transition corresponds to $p_{\text{g}} = 1/(f-1)$, thus (for $f \gg 1$) we get the transition concentration

$$c_{\text{g}} \sim \frac{1}{a^3}\left(\frac{a^3 l}{\lambda f}\right)^{1/\zeta} \tag{4.7}$$

with the exponent $1/\zeta \equiv (3\nu - 1)/[\nu(3 + \theta_2) - 1] \approx 0.62$. This equation is valid if λ is small enough. For large λ (large ϵ) we need to take into account the local intrachain bonding. The probability of a local contact (i.e. the probability that two neighboring stickers along the chain get close to each other) is

$$W_0 \approx \frac{K(l)}{(al^{\nu})^3} \approx \frac{1}{a^3 l^{2+z}} \tag{4.8}$$

Using the argument of the previous section, we find

$$\lambda_{\text{eff}} \approx \frac{1}{W_0} \approx a^3 l^{2+z} \tag{4.9}$$

as $\epsilon \to \infty$. The renormalization of λ is noticeable only if it is larger than $a^3 l^{2+z}$ (in this case nearly all stickers are paired) and therefore

$$\lambda_{\text{eff}} \approx \min(v_{\text{b}}e^{\epsilon}, a^3 l^{2+z}) \tag{4.10}$$

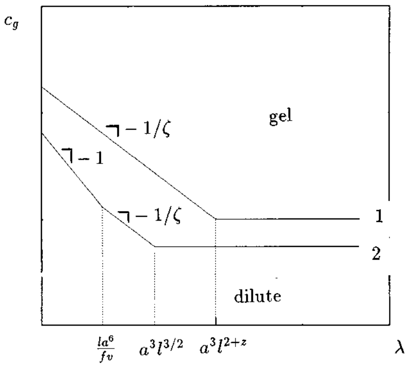

Figure 4. The log–log schematic dependence of gelation concentration c_g on λ: line 1, $v \sim a^3$, line 2, $v < a^3/l^{1/2}$.

Substituting λ_{eff} (for $\epsilon \to \infty$) from eq 4.9 into eq 4.7 for the gelation concentration, we get

$$c_g \approx a^{-3} l^{1-3\nu} f^{-1/\zeta}, \quad \lambda \gg a^3 l^{2+z} \tag{4.11}$$

A schematic plot of gelation concentration vs. attractive volume is shown in Figure 4 (see line 1). For larger attractive volume λ the gelation concentration c_g decreases to the limiting value, eq 4.11. For smaller λ the gelation concentration c_g is higher; see eq 4.7.

Note that the gelation concentration is always higher than the overlap concentration

$$\frac{c_g}{c^*} \geq f^{(z/(z+1))(3\nu-1)} \tag{4.12}$$

The probability of interchain bonds increases with concentration according to eq 4.6, where λ should be replaced by λ_{eff}.

4.2. Marginal Solvent Regime: Gelation and Phase Separation.

4.2.1. Gelation Threshold.

Let us consider the effect of two-body interactions, assuming that the excluded volume parameter v is small enough:

$$\frac{a^3}{\sqrt{N}} < v < \frac{a^3}{\sqrt{l}} \tag{4.13}$$

The latter inequality ($v < a^3/l^{1/2}$) implies that the spacers between stickers (of l monomers) are not swollen yet. The mean field equations for the free energy, derived in section 2 above (eqs 2.11–2.15), are valid if the mean-field concentration blobs are not swollen

$$v g^{1/2}/a^3 < 1 \tag{4.14}$$

where the number of monomers per blob is

$$g \approx (ca^3)^{-2} \tag{4.15}$$

Thus mean field theory is valid of $c > c^{**}$ where the crossover concentration

$$c^{**} = v/a^6 \tag{4.16}$$

Below this crossover concentration (for $c < c^{**}$) the scaling arguments should apply. The length G of the sub-section of the chain that begins to swell (thermal blob[1]) is defined by condition $v\sqrt{G}/a^3 \sim 1$ (eq 4.14), so that

$$G = a^6/v^2 \tag{4.17}$$

Note that in the regime $c < c^{**}$, the concentration blobs are clearly swollen: $g > G$.

Let us consider the scaling regime, $c < c^{**}$. As $v < a^3/l^{1/2}$, the spacers between stickers are not swollen ($G > l$) and obey Gaussian statistics, so that $\nu = 1/2$, $\theta_2 = 0$, and $z = -1/2$. Therefore the renormalization of a bond attraction volume can be rewritten as (see eqs 3.3, 3.7, and 4.10)

$$\lambda_{eff} = \min(v_b e^{\epsilon}, a^3 l^{3/2}) \equiv \min(\lambda, v_l) \tag{4.18}$$

A reduction of an interchain contact probability due to excluded volume interactions comes from scales between G and g, so that the reduction factor is (see eq 4.3)

$$K(g) = \left(\frac{g}{G}\right)^{-\nu\theta_2} \tag{4.19}$$

where g is the number of monomers per blob in the partially swollen regime (same as eq 4.2):

$$g \approx G\left(\frac{c^{**}}{c}\right)^{1/(3\nu-1)} \tag{4.20}$$

Therefore the statistical weight (attraction volume) of a bond is

$$\lambda_{eff} K(g) = \lambda_{eff}\left(\frac{c}{c^{**}}\right)^{\nu\theta_2/(3\nu-1)} \tag{4.21}$$

with the exponent $\nu\theta_2/(3\nu - 1) = \zeta - 1 \approx 0.60$ (same as in eq 4.6; note that $\zeta = (z + 1)/(3\nu - 1) \simeq 1.60$). Thus the effective degree of conversion (the fraction of interchain bonds) implied by the classical gelation theory (which is still valid since the coils strongly overlap, $c > c^*$) is defined as

$$\frac{p}{(1-p)^2} = \frac{c}{l}\lambda_{eff}\left(\frac{c}{c^{**}}\right)^{\zeta-1} \quad \text{for} \quad c < c^{**} \tag{4.22}$$

$$\frac{p}{(1-p)^2} = \frac{c}{l}\lambda_{eff} \quad \text{for} \quad c > c^{**} \tag{4.23}$$

where λ_{eff} is given by eq. 4.18.

The concentration at the sol–gel transition ($p_g \simeq 1/f$, $f \gg 1$) is (see line 2 in Figure 4)

$$c_g \approx c^{**}\left(\frac{l}{f\lambda_{eff}c^{**}}\right)^{1/\zeta} \quad \text{for} \quad \lambda_{eff} > l/(c^{**}f) \tag{4.24}$$

$$c_g \approx \frac{l}{f\lambda_{eff}} \quad \text{for} \quad \lambda_{eff} < l/(c^{**}f) \tag{4.25}$$

where $1/\zeta = (3\nu - 1)/[\nu(3 + \theta_2) - 1] \approx 0.62$ (same as in eq 4.7). These equations are applicable only if $c_g > c^*$, where c^* is the overlap concentration (for $v > a^3/N^{1/2}$)

$$c^* = \frac{N}{(N/G)^{3\nu} G^{3/2} a^3} = a^{-3} N^{1-3\nu} (v/a^3)^{3-6\nu} \tag{4.26}$$

If eq 4.26 formally gives $c_g < c^*$, it means that gelation must occur as soon as coils overlap: $c_g \to c^*$. However in this case the point $c_g \simeq c^*$ is always located within the phase separation region.

4.2.2. Free Energy. Let us consider the problem of phase stability in the region $a^3/N^{1/2} < v < a^3/l^{1/2}$, and $c < c^{**}$ (scaling regime). The free energy density of the system can be divided into two parts

$$F = F_{\rm st} + F_{\rm int} \tag{4.27}$$

where $F_{\rm st}$ is the sticker part corresponding to the entropy and energy due to pairing of stickers and $F_{\rm int}$ is the energy density of excluded volume interactions. The latter is

$$\frac{F_{\rm int}}{k_{\rm B}T} \approx \frac{c}{g} \simeq vc^2 \left(\frac{c}{c^{**}}\right)^{(2-3\nu)/(3\nu-1)} \tag{4.28}$$

where g is defined in eq 4.20.

The sticker part of the free energy density can be calculated in exactly the same way as was done earlier in the mean-field theory (within the framework of the classical gelation model valid for $c \gg c^*$). The result is

$$\frac{F_{\rm st}}{k_{\rm B}T} = \frac{c}{N}\ln\left(\frac{c}{eN}\right) + \frac{c}{l}\left[\frac{p}{2} + \ln(1-p)\right] \tag{4.29}$$

where p is defined in eq 4.22.

The phase diagram can now be constructed in a standard way: we need to calculate the chemical potentials μ and the osmotic pressures Π and to balance them between the two phases. For $c < c^{**}$ we obtain the chemical potential (using eqs 4.27, 4.28, 4.29, and 4.22)

$$\frac{\mu}{k_{\rm B}T} = \frac{1}{k_{\rm B}T}\frac{\partial F}{\partial c} = \frac{1}{N}\ln\frac{c}{N} + \frac{1}{l}\ln(1-p) - (\zeta - 1)\frac{p}{2l} + \frac{3\nu}{3\nu-1}\frac{1}{G}\left(\frac{c}{c^{**}}\right)^{1/(3\nu-1)} \tag{4.30}$$

and the osmotic pressure

$$\frac{\Pi}{k_{\rm B}T} = \frac{1}{kT}(c\mu - F) = \frac{c}{N} - \zeta\frac{cp}{2l} + \frac{1}{3\nu-1}\frac{c}{G}\left(\frac{c}{c^{**}}\right)^{1/(3\nu-1)} \tag{4.31}$$

where c^{**} and G are given by eqs 4.16 and 4.17. If $c > c^{**}$ we can use the mean-field expressions (eqs 2.22 and 2.32).

4.2.3. Phase Diagrams. Let us consider phase diagrams in variables v (the excluded volume parameter), c (concentration) for fixed values of bond strength λ. We start from low λ and then follow the changes of the phase diagram with increasing bond length, λ.

The Mean-Field Regime, $\lambda \lesssim \lambda_{\rm mf}$. For small values of $\lambda < \lambda_{{\rm m}f}$, where

$$\lambda_{{\rm m}f} \sim a^3\frac{l^{3/2}}{f^{1/2}} \tag{4.32}$$

there is no phase separation even for $v = 0$. In this case the phase separation region moves to the poor solvent regime, $v < 0$, so that the mean field theory is fully applicable. Note that $\lambda_{\rm mf}$ is defined in eq 2.28 with $v = 0$ and $w \sim a^6$.

One can sketch the gelation line in the v, c diagram for $\lambda < \lambda_{\rm mf}$, $\lambda/\lambda_{\rm mf} = 0.2$, and $f = 25$ (Figure 5a). For low values of the excluded volume parameter $v < \tilde{v} = la^6/(\lambda f)$ the gelation concentration does not depend on the excluded volume parameter v

$$c_{\rm g} \approx \frac{l}{\lambda f} \quad \text{for} \quad \lambda < \lambda_{\rm mf} \quad \text{and} \quad v < \tilde{v} \tag{4.33}$$

(see eq 4.25; also see eq 2.21 for $f \gg 1$). For large values of the excluded volume parameter $v > \tilde{v} \equiv la^6/(\lambda f)$, the gelation concentration $c_{\rm g}$ increases

$$c_{\rm g} \approx \frac{l}{\lambda f}\left(\frac{v\lambda f}{la^6}\right)^{1-1/\zeta} \quad \text{for} \quad \lambda < \lambda_{\rm mf} \quad \text{and} \quad v > \tilde{v} \tag{4.34}$$

as can be obtained from eq 4.24 (see Figure 5a).

For $\lambda \lesssim \lambda_{\rm mf}$ the critical point corresponds to the true Θ-regime, $|v_{\rm cr}| \sim a^3/N^{1/2}$ and $c_{\rm cr} \sim c^*_{\rm mf} \sim 1/(a^3N^{1/2})$.

Scaling Regime, $\lambda_{\rm mf} < \lambda < v_l$. This regime should be treated using the free energy defined by eqs 4.28 and 4.29. The critical point is defined by the system of equations $\partial\mu/\partial c = 0$ and $\partial^2\mu/\partial c^2 = 0$. Using eq 4.30 we get

$$\frac{1}{k_{\rm B}T}\frac{\partial\mu}{\partial c} = \frac{1}{Nc} - \frac{\zeta}{lc}\frac{p}{1+p} - \frac{\zeta(\zeta-1)}{2cl}\frac{{\rm p}(1-p)}{1+p} + \frac{3\nu}{(3\nu-1)^2}v\left(\frac{c}{c^{**}}\right)^{(2-3\nu)/(3\nu-1)} \tag{4.35}$$

assuming that near the critical point $p \ll 1$, and using eq (4.22), we obtain

$$\frac{1}{k_{\rm B}T}\frac{\partial\mu}{\partial c} = \frac{1}{Nc} - \frac{\zeta(\zeta+1)}{2l^2}\lambda_{\rm eff}\left(\frac{ca^6}{v}\right)^{\zeta-1} + \frac{3\nu}{(3\nu-1)^2}v\left(\frac{ca^6}{v}\right)^{(2-3\nu)/(3\nu-1)} \tag{4.36}$$

From eq 4.36 we can see that the system of equations $\partial\mu/\partial c = 0$ and $\partial^2\mu/\partial c^2 = 0$ has no physical solution in the region $c > 0$ and $v > 0$ since $\zeta - 1 > (2 - 3\nu)/(3\nu - 1)$: one can easily prove that $\partial\mu/\partial c$ must be positive if $\partial^2\mu/\partial c^2 = 0$. Therefore the critical point can be located either in the mean field zone or at the crossover between scaling and mean field domains ($c_{\rm cr} \approx c^{**}$). An analysis shows that the former possibility is not true if $\lambda > \lambda_{\rm mf}$. In fact, using the mean-field equations (2.27) and (2.28) with $w \sim a^6$ we get $c_{\rm cr} \sim 1/(a^3N^{1/2})$, $v_{\rm cr} \simeq \lambda/l^2 - 2a^3/N^{1/2} \simeq \lambda/l^2$ if $\lambda \gg \lambda_{\rm mf} = a^3l^2/N^{1/2}$, so that $c_{\rm cr} \ll v_{\rm cr}/a^6$; i.e., the critical point is not located inside the mean-field domain. Therefore the critical point must be located in the crossover region; i.e. $c_{\rm cr}a^6/v_{\rm cr} \sim 1$. Substituting this relation into eq 4.36, we get from the condition $\partial\mu/\partial c = 0$ (the same results can be obtained using the analogous mean-field eq 2.25)[36]

$$v_{\rm cr} \approx \frac{\lambda}{l^2}; \quad c_{\rm cr} \approx \frac{\lambda}{l^2a^6}; \quad \lambda \gg \lambda_{\rm mf} \tag{4.37}$$

A typical phase diagram for the regime $\lambda_{\rm mf} < \lambda < v_l$ (where $v_{\rm l} \approx a^3l^{3/2}$ as defined in eq 3.3) is sketched in Figure 5b for $\lambda = 2\lambda_{\rm mf}$ and $f = 25$. Note the two-phase region with the critical point estimated from eq 4.37 to be at $v_{\rm cr} \approx \lambda/l^2$ and $c_{\rm cr} \approx \lambda/(l^2a^6)$. Note that the phase separation region increases with increasing λ. For $v < v_{\rm cr}$ the system separates into two phases with concentrations c_1 and c_2. The more concentrated phase (c_2) always corresponds to the mean-field domain, whereas the low-density phase (c_1) corresponds to the scaling

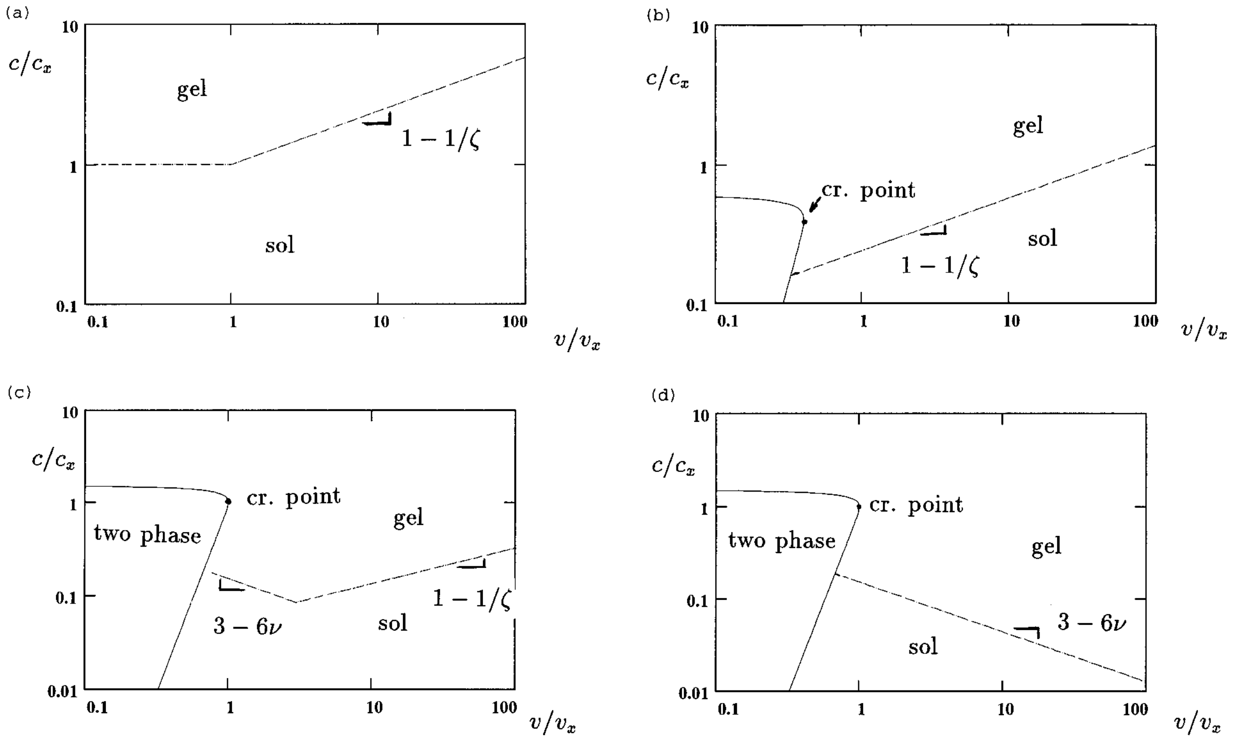

Figure 5. Schematic phase diagrams of an associating polymer solution: monomer concentration c vs. the excluded volume parameter v for $f = 25$ stickers per chain. Dashed lines correspond to gelation transition (c_g); solid lines limit the phase separation region. The reference concentration is $c_x = 1/(a^3 l^{1/2})$; the reference excluded-volume parameter is $v_x = a^3/l^{1/2}$. (a) Attraction volume $\lambda = 0.2\lambda_{mf} < \lambda_{mf} = a^3 l^{3/2}/f^{1/2}$: no phase separation. The gelation transition occurs at $c_g \sim c_x\, \lambda_{mf}/\lambda f^{1/2}$ for $v < v_x\, \lambda_{mf}/f^{1/2}\lambda$ and $c_g \sim c_x\, (\lambda_{mf}/\lambda f^{1/2})^{1/\zeta}\, (v/v_x)^{1-1/\zeta}$ for $v > v_x\, \lambda_{mf}/f^{1/2}\lambda$. (b) $\lambda_{mf} < \lambda = 2\lambda_{mf} < v_l = a^3 l^{3/2}$: a region of phase separation appears. The critical point: $c_{cr} \simeq c_x\, \lambda/f^{1/2}\lambda_{mf} = 0.4c_x$; $v_{cr} \simeq v_x\, \lambda/f^{1/2}\lambda_{mf} = 0.4v_x$. The gelation line: $c_g \sim c_x\, (\lambda_{mf}/\lambda f^{1/2})^{1/\zeta}\, (v/v_x)^{1-1/\zeta}$. (c) $v_l = a^3 l^{3/2} < \lambda = 5v_l < a^3 l^{2+z}$: the phase separation region is larger. The critical point: $c_{cr} \simeq c_x$, $v_{cr} \simeq v_x$. The gelation line: $c_g \sim c_x f^{-1/\zeta}\, (v_x/v)^{6\nu-3}$ for $v < v_x(\lambda/v_l)^{1/(1+2z)}$ and $c_g \sim c_x\, (v_l/\lambda f)^{1/\zeta}\, (v/v_x)^{1-1/\zeta}$ for $v > v_x(\lambda/v_l)^{1/(1+2z)}$. (d) $\lambda \gg a^3 l^{2+z}$: same as the previous diagram, but $c_g \sim c_x f^{-1/\zeta}\, (v_x/v)^{6\nu-3}$ everywhere (except the phase separation region). In the last case the phase transition lines are nearly independent of λ.

regime. For $v = 0$ and $\lambda \gg \lambda_{mf}$, the low-density phase is exponentially dilute: $c_1 \ll c^*$. The concentration of the higher density phase in this case was predicted in section 2.5 (eq 2.34):

$$c_2 \approx \frac{3\lambda}{2a^6 l^2} \tag{4.38}$$

The gelation transition is still expressed by eq (4.34): $c_g \propto v^{1-1/\zeta}$, where the exponent $1 - 1/\zeta = \nu\theta_2/[\nu(3 + \theta_2) - 1] \approx 0.38$. For $v \approx v_{cr}$ and $\lambda \gg \lambda_{mf}$, the gelation always takes place before the phase separation (using eqs 4.24, 4.32, and 4.37)

$$\frac{c_g}{c_{cr}} \sim \left(\frac{\lambda_{mf}}{\lambda}\right)^{2/\zeta} \ll 1 \tag{4.39}$$

but still in the regime of strongly overlapping coils:

$$\frac{c_g}{c^*} \sim \left(\frac{\lambda}{\lambda_{mf}}\right)^{2(3\nu-1)z/(1+z)} \gg 1 \tag{4.40}$$

Scaling Regime with Renormalization of the Bond Strength, $\lambda > v_l$. At higher values of parameter λ (for $\lambda > v_l$) the bond strength is renormalized (see eq 4.18). Note that v_{cr} is finite if $\epsilon \to \infty$: $v_{cr}(\infty) \simeq v_l/l^2 \simeq a^3/l^{1/2}$ (see eqs 3.9 and 4.37). The phase separation is totally suppressed if $v > v_{cr}(\infty) \sim v_l/l^2 = a^3/l^{1/2}$. Thus the scaling treatment of this section confirms the basic conclusion, which was drawn earlier within the mean-field theory, that the excluded volume interactions suppress phase separation.

The theory can be easily generalized to treat the case $v_l/l^2 < v < a^3$. In this regime the excluded volume interactions affect the renormalization of the attractive volume. Hence a generalized definition of λ_{eff} that crosses over between eqs 4.18 and 4.10 is

$$\lambda_{eff} = \min(v_b e^{\epsilon}, \tilde{v}_l) \tag{4.41}$$

where

$$\tilde{v}_l = \begin{cases} a^3 l^{3/2}, & v < a^3/l^{1/2} \\ a^3 l^{3/2}\, (v l^{1/2}/a^3)^{1+2z}, & v > a^3/l^{1/2} \end{cases} \tag{4.41}$$

Note that the maximum value of λ_{eff} is increasing with v: it is equal to $a^3 l^{3/2}$ for $v = 0$, and to $a^3 l^{2+z}$ for $v = a^3$. The phase diagrams for $\lambda = 5v_l$ (this value of λ is assumed to be in the range $v_l < \lambda < a^3 l^{2+z}$) and $f = 25$ is shown in Figure 5c. Here the parameters of the critical point are defined by eqs 4.37 and 4.41: $v_{cr} \simeq a^3/l^{1/2}$ and $c_{cr} \simeq 1/a^3 l^{1/2}$. The gel point as defined by eqs 4.24 and 4.41 is

$$c_g \simeq \begin{cases} c_{cr} f^{-1/\zeta} \left(\dfrac{v_{cr}}{v}\right)^{6\nu-3}, & v/v_{cr} \ll \left(\dfrac{\lambda}{v_l}\right)^{1/(1+2z)} \\ c_{cr} f^{-1/\zeta} \left(\dfrac{v_l}{\lambda}\right)^{1/\zeta} \left(\dfrac{v}{v_{cr}}\right)^{1-1/\zeta}, & v/v_{cr} \gg \left(\dfrac{\lambda}{v_l}\right)^{1/(1+2z)} \end{cases} \tag{4.42}$$

Note that there is a range of concentrations above $(c_g)_{min} = c_{cr} f^{-1/\zeta}\, (v_l/\lambda)^{(6\nu-3)/(1+2z)}$ at which one may observe a reentrant gelation transition with changing temperature (the excluded volume parameter v).

A typical phase diagram for even higher attractive volumes, $\lambda \gg a^3 l^{2+z}$, is shown in Figure 5d. The phase transition lines nearly do not depend on λ in this regime. The gelation concentration here is determined by the first expression of eq 4.42 for all values of v (apart from the phase-separation region).

5. Discussion

The paper consists of two parts. In the first part (section 2) we present an exact formulation of the mean-field theory of associative polymers. A simple explicit analytical expression for the free energy is derived for the first time. It allows a quantitative consideration of the phase behavior of the system. The phase diagram obtained in the theta-regime ($v = 0$) is shown in Figure 1 (note that we defined the Θ-conditions with respect to the polymer solution with no associative groups (stickers), i.e. $v = 0$ that the second virial coefficient of monomers vanishes). The reduced concentration $C = c(wN)^{1/2}$ and reduced interaction parameter $\tilde{\lambda} = \lambda f^2/w^{1/2}N^{3/2}$ are used in Figure 1. Here c is the monomer concentration, w is the three-body monomer interaction parameter, N is the number of monomers per chain, $f = 20$ is the number of stickers per chain, and $\lambda = v_b e^{\epsilon}$ is the attractive volume of a bond between two stickers ($\epsilon k_B T$ is the association energy of stickers). If the attraction between stickers is weak (i.e. λ is small), then the system is homogeneous at all concentrations similar to an ordinary Θ-solution. A reversible (physical) gel is formed at some concentration c_g, which is decreasing as λ is increased (continuous gelation). On the contrary, the gelation transition is discontinuous in the regime of large λ (which can be achieved, e.g., by decreasing the temperature). Here the system separates into two phases (sol and gel) in a wide concentration region. The phase transition is characterized by the critical point $c_{cr} \simeq 1/(Nw)^{1/2}$ and $\lambda_{cr} \simeq 2w^{1/2}N^{3/2}/f^2$. In a narrow range of λ the gelation transition precedes the phase separation between two (less concentrated and more concentrated) gel phases.

Thus we can distinguish the following regions in the mean-field phase diagram (see Figure 1): single-phase solution (sol), single-phase reversible gel, two-phase region with coexisting sol and gel,[37] and a region with two coexisting gel phases (two-phase sol region is impossible under the Θ-conditions, but is possible when the solvent is poor, $v < 0$).

One of the important results obtained in this part is that gelation in solutions of associating (amphiphilic) polymers might be accompanied by a phase separation even under Θ-solvent or marginal solvent conditions for monomers without stickers. This result is related to the fact that an *ideal* system of associating polymers always phase separates. In fact eq 2.23 implies that the derivative of the chemical potential of the ideal system, $\partial\mu/\partial c$, is always negative if c is larger than the gelation concentration c_g ($p > p_g = 1/(f - 1)$). Therefore a reversible network phase is intrinsically unstable and would tend to collapse into a vanishing volume (in practice this collapse is prevented by the excluded volume interactions).[38] Essentially the same model of associating polymer was considered by Tanaka.[6-10] Qualitatively the phase diagrams obtained by Tanaka are similar to those considered in this paper (Figure 5); in particular, a possibility of two coexisting gel phases was also predicted there. However a phase separation above the Θ-temperature was never considered in Tanaka's work.

We are now in a position to identify the origin of the difference between our approach and the earlier Tanaka's theory.[6-8] The relevant quantity is the entropic part of the free energy (eq A2) which was obtained in the Appendix using the approach of the Flory gelation theory which was also used in Tanaka's works.[6-8] When the excluded volume interactions are switched off, the basic equations for the free energy derived by Tanaka can be represented in the same form as eq A2. The main difference, however is that in Tanaka's expression logarithm of volume fraction of clusters containing m primary N-mers, $\phi_m = \tilde{C}_m N m$, was used instead of logarithm of the number concentration of those clusters, $\tilde{C}_m$. We stress that it is the $\tilde{C}_m \ln \tilde{C}_m$ term (see eq A2) that comes from the fundamental ideal-gas partition function, eq A1, rather than the $\tilde{C}_m \ln \phi_m$ term, which incorrectly enters Tanaka's free energy. This difference would be unimportant for a one-component system (for example for a homopolymer solution); however, it is important for the present case of the system of clusters, when the concentrations $\tilde{C}_m$ are obtained by minimization of the free energy. The additional m factor under the logarithm in Tanaka's theory leads to the incorrect a posteriori statistical weights of clusters and thus to the incorrect concentration dependence of the free energy.

This mistake was eliminated in a more recent paper.[9] However we believe that the relevant phase diagrams obtained in that paper are still incorrect due to unphysical treatment (following Stockmayer) of the postgel regime (see also comments in section 2.3). In the most recent paper[10] Ishida and Tanaka calculated phase diagrams using both Stockmayer and Flory post-gel pictures. However we believe that all phase diagrams obtained in ref 10 are unphysical, even those obtained with a physically plausible Flory approach. The reason is that implementation of the Flory's approach and the resultant free energy obtained in ref 10 are incorrect (see section 2.3). No conclusion as to which model is actually valid has been drawn in ref 10.

In the second part of the paper (sections 3 and 4) the theory is extended beyond the mean-field domain in order to account for (1) the local intra-chain to inter-chain bond exchange and (2) the effects of the excluded volume interactions.

The first effect gives rise to a finite driving force for the reversible network formation (finite λ_{eff}) even in the limit of infinite association energy, $\epsilon \rightarrow \infty$. In particular, we find that both the critical concentration and the critical excluded volume parameter are finite in this limit.

The second effect can suppress the phase separation driven by the reversible network formation if the excluded volume parameter is high enough: $v > v_{cr} \sim \lambda_{eff}/l^2$, where $\lambda_{eff} = \min(v_b e^{\epsilon}, a^3 l^{3/2})$ is the effective attraction volume of a bond (here we assume that $\lambda_{eff} > a^3 l^2/N^{1/2}$). Qualitatively the phase separation is suppressed if the energy of excluded volume interactions per effective spacer (i.e. a part of a chain between two neighboring stickers associated with stickers on other chains) is larger than $k_B T$. In particular it is predicted that the system never phase separates if $v > v_{cr}(\infty) \sim a^3/l^{1/2}$, so that, for example, a phase separation is not expected under the good solvent conditions, $v \sim a^3$ (this conclusion is in agreement with the computer simulation[39]). Note however that the last statement is only tentative and is not rigorous since the critical point $c_{cr}(\infty)$, $v_{cr}(\infty)$ corresponds to the crossover regime between mean-field and good solvent domains, where the theory is not quantitative.

The predicted phase diagrams are shown in Figure 5 in concentration c vs monomeric second virial coefficient v variables (the latter is usually temperature dependent).

In the case of weak sticking energy (i.e. $\lambda < a^3N^{3/2}/f^2$) a continuous gelation transition is predicted (see figure 5a). The gelation concentration increases with increasing excluded-volume parameter v. For stronger association (larger λ: $a^3l^{3/2}/f^{1/2} < \lambda < a^3l^{3/2}$) the phase diagram includes a phase separation region which is becoming wide as λ is increased (see Figure 5b). The phase separation region stabilizes (stops increasing) when the attraction between stickers becomes very strong ($\lambda > a^3l^{3/2}$): here the phase separation lines virtually do not depend on λ. However the gelation concentration c_g does depend on λ in this regime (see Figure 5c,d). For large λ ($\lambda \gg a^3l^{2+z}$, $z \simeq 0.225$) the gelation concentration c_g always decreases as v is increased (compare parts b and d of Figure 5). The reason for this behavior of c_g is connected with the fact that nearly all stickers are paired in this regime since their association energy is very high. Therefore a gelation implies that intrachain pairs are replaced by interchain pairs of stickers. With stronger *repulsion* between nonsticking monomers the balance of intrachain/interchain pairs is shifted toward interchain pairing,[40] thus promoting gelation.

6. Conclusions

(1) We show that within the classical gelation approach the structure of the system of reversibly associating polymers is correctly described by the Flory model on the postgel regime rather than that of Stockmayer.

(2) We also show that continuous reversible gelation is not a thermodynamic transition as all thermodynamic quantities are continuous at the gel point.

(3) With no excluded-volume interactions between monomers, solutions of associative polymers are unstable above the gelation concentration and must phase separate.

(4) Phase separation accompanies gelation even if the excluded volume of nonassociative monomers is positive (but not large).

(5) Strong excluded-volume monomer–monomer repulsion totally suppresses the phase separation.

(6) The effect of local (intrachain) pairing of stickers results in a significant renormalization of the reversible gel properties when the attraction between stickers is strong enough.

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Appendix A. Free Energy of an Ideal System of Associating Molecules: the Flory–Stockmayer Approach

Here we calculate the free energy of an ideal system of f-functional molecules using an alternative approach based on the Flory-Stockmayer statistics[15,18] of tree-like structures. Let N_m be the number of clusters consisting of m units (only tree-like clusters are allowed). The total partition function Z of the system is

$$Z = \prod_m \frac{1}{N_m!} v^{N_m} \, [Z_m \lambda^{\mathrm{m}-1}]^{N_m} \tag{A1}$$

where Z_{m} is the combinatorial weight of one cluster (the number of different treelike structures that can be formed by m molecules, and $\lambda = v_{\mathrm{b}}e^{\epsilon}$ is the statistical weight of one bond, so that $Z_m\lambda^{m-1}$ is the total partition function of a single m-cluster. The free energy of the system (per unit volume), $F = -(k_BT/V) \ln Z$, can be written as

$$F = k_BT \sum_{m=1}^{\infty} \tilde{C}_m (\ln \tilde{C}_m - 1 - \ln Z_m - (m - 1) \ln \lambda) \tag{A2}$$

where $\tilde{C}_m = N_m/V$ is the number concentration of m-clusters. The first two terms in brackets, $\ln \tilde{C}_m - 1$ corresponds to the ideal-gas (translational) free energy of m-clusters. The free energy, eq A2, should be minimized under the condition that the total concentration of molecules

$$\tilde{C} = \sum\nolimits_m m\tilde{C}_m \tag{A3}$$

is fixed (note that $\tilde{C} = c/N$, where c is the monomer concentration. Using the method of Lagrange multipliers (i.e. minimizing $F -$ const $\tilde{C}$) we get

$$\tilde{C}_m = \lambda^{-1} Z_m e^{\mu m} \tag{A4}$$

$$F = k_BT(\mu - \ln \lambda)\tilde{C} - \Pi \tag{A5}$$

where $\mu - \ln \lambda$ is the multiplier, and $\Pi = k_BT\sum_{m=1}^{\infty}\tilde{C}_m$ is the ideal-gas pressure of clusters. The combinatorial factor is[15,18]

$$Z_m = \frac{f^m(mf - m)!}{m!(mf - 2m + 2)!} \tag{A6}$$

provided that f functional groups on a molecule are distinguishable. Using eqs A3 and A4, we get the total concentration $\tilde{C} = \lambda^{-1} Z(\mu)$, where

$$Z(\mu) \equiv \sum_m m Z_m e^{\mu m}$$

Let us note the following useful equations:

$$Z(\mu) = e^{\mu}[\Gamma(\mu)]^f \tag{A7}$$

$$\Gamma(\mu) = 1 \; fe^{\mu}[\Gamma(\mu)]^{f-1} \tag{A8}$$

One can consider the first equation, (A7), as the definition of the function $\Gamma(\mu)$. Actually $\Gamma(\mu)$ is the generating function for the number of different trees with a marked root group

$$\Gamma(\mu) = \sum_{m=0}^{\infty} (mf - 2m + 2)Z_m e^{\mu m} \tag{A9}$$

and both eqs A7 and A8 can be easily obtained with the Gordon approach[41,1] to the classical gelation problem. Noting also $1/(k_BT)\partial\Pi/\partial\mu = \tilde{C}$, so that $\Pi = k_BT\lambda^{-1}$

$\int_{-\infty}^{\mu} Z(\mu)\, d\mu$, and using eqs A5, A7, and A8 we get the free energy

$$F = k_B T\tilde{C}\left\{\ln \tilde{C} - 1 + \frac{f}{2}\frac{\Gamma - 1}{\Gamma} - f \ln \Gamma\right\} \quad \text{(A10)}$$

and the relation between $\tilde{C}$ and $\Gamma(\mu)$

$$\Gamma(\Gamma - 1) = F\tilde{C}\lambda \quad \text{(A11)}$$

Comparing eqs A11 and 2.13 we find that $\Gamma(\Gamma - 1) = p/(1 - p)^2$, so that $\Gamma = 1/(1 - p)$. Hence eq A10 can be rewritten in the form

$$F = k_B T\tilde{C}\ \{\ln \tilde{C} - 1 + f \ln(1 - p) + fp/2\} \quad \text{(A12)}$$

which is identical to eq 2.15 provided that both interaction parameters are set to zero: $v = w = 0$.

References and Notes

(1) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell Univ. Press: Ithaca, NY, 1979.
(2) Coniglio, A.; Stanley, H. E.; Klein, W. *Phys. Rev. Lett.* **1979**, *42*, 518.
(3) Joanny, J. F. *Polymer* **1980**, *21*, 71.
(4) Panyukov, S. V. *Sov. Phys. JETP* **1985**, *61*, 1065.
(5) Leibler, L.; Pezron, E.; Pincus, P. *Polymer* **1988**, *29*, 1105.
(6) Tanaka, F. *Macromolecules* **1989**, *22*, 1988.
(7) Tanaka, F. *Macromolecules* **1988**, *21*, 2189.
(8) Tanaka, F.; Matsuyama, A. *Phys. Rev. Lett.* **1989**, *62*, 2759. Tanaka, F. *Macromolecules* **1990**, *23*, 3784; 3790.
(9) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943.
(10) Ishida, M.; Tanaka, F. *Macromolecules* **1997**, *30*, 3900. Note, however, that this paper had been published after the present paper had been submitted for publication.
(11) Rubinstein, M.; Semenov, A. N. *Macromolecules* **1998**, *31*, 1386−1397.
(12) The idea of the approach considered below is somewhat similar to the ideas proposed for living networks and for networks formed by telechelic polymers.[13,14]
(13) Drye, T. J.; Cates, M. E. *J. Chem. Phys.* **1992**, *96*, 1367.
(14) Semenov, A. N.; Nyrkova, I. A.; Cates, M. E. *Macromolecules* **1995**, *28*, 7879.
(15) Flory, P. J. *Principles of Polymer Chemistry*; Cornell Univ. Press: Ithaca, NY, 1953.
(16) This is the standard criterion of validity of the classical gelation picture.[1,15]
(17) The free energy, eq 2.15, is essentially different from the one obtained by Tanaka[6−8] due to an error in his treatment which is discussed in section 5. However later Tanaka[9] modified the treatment by introducing an additional "disorientation entry" term. Yet he never commented on the difference between the theories developed in refs 6−8 and ref 9. The free energy derived in refs 9 and 10 agrees with eq 2.15 in the pregel regime ($c < c_g$) (see eq 4.14 of ref 10). However the two expressions disagree in the postgel regime, as discussed in section 2.3.
(18) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45; **1944**, *12*, 125.
(19) Stockmayer, W. H. *Macromolecules* **1991**, *24*, 6367.
(20) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(21) A different theoretical treatment of the sol−gel transition in thermoreversible systems has been recently proposed by Erukhimovich:[22] a second-order phase transition is predicted at a the gel point.
(22) Erukhimovich, I. Ya. *Sov. Phys. JETP* **1995**, *81*, 553.
(23) It is important that this equation is applicable both below and above the gel point.
(24) Actually the condition of validity of the mean-field theory is even stronger than condition 2.31 (see section 4.2).
(25) Note that the opposite limit, $v \gg (w/l)^{1/2}$, is less important, as eq 2.31 restricts this regime to a very narrow range of v. (This regime does not exist at all if $w \sim a^6$.)
(26) This type of globule with saturated bonds was considered in refs 37 and 28 using different approaches. The results presented in this section are in agreement with the earlier results. The same problem was also considered in ref 29 using an incorrect assumption that the gel structure inside the globule is compressed. This is not true since the *reversible* gel structure automatically adjusts itself to any degree of compression of the globule, so that there is no reason for the gel to be strained at equilibrium.
(27) Lifshitz, I. M.; Grosberg, A. Yu.; Khokhlov, A. R. *Rev. Mod. Phys.* **1978**, *50*, 683.
(28) Panyukov, S. V. *Sov. Phys. JETP* **1986**, *63*, 96.
(29) Tanaka, F.; Ushiki, H. *J. Chem. Phys.* **1986**, *84*, 5925.
(30) Note that nonlocal intrachain bonds must still exist and are important in the formation of the globule. Indeed, a chain with only local bonds does not collapse into a globule.
(31) Strictly speaking the combinatorial factor P_{comb} for the case $\epsilon \to \infty$ differs from the one obtained with the unrenormalized theory of section 2.2; see eq 2.10. The reason is that in the case $\epsilon \to \infty$ the number N of interchain bonds per chain can only vary in steps of 2. For example is f is even, then N must also be even. On the other hand the theory of section 2.2 assumes that N can be arbitrary. This difference however is not important if the typical value of N is large ($N \gg 1$): in this case P_{comb} in eq (3.5) is given by the rhs of eq 2.10 times a constant factor $2^{-cV/N}$, where cV/N is the total number of polymer chains.
(32) des Cloizeaux, J.; Jannink, G. *Polymers in Solution*; Section 13.1.6; Clarendon Press: Oxford, England, 1990.
(33) Des Cloizeaux, J. *J. Phys. Fr.* **1980**, *41*, 223.
(34) Schaefer, L.; Kappeler, Ch. *J. Phys. Fr.* **1985**, *46*, 1853. Kosmas, M. *J. Phys. Lett.* **1984**, *5*, L889. Broseta, D.; Leibler, L.; Joanny, J. F. *Macromolecules* **1987**, *20*, 1935.
(35) Note that eq 4.3 is equally applicable to both intra- and interchain contacts provided that the chemical distances (contour lengths) between the monomers in question and the end monomers of the corresponding chain(s) are all long enough, i.e. longer than g.
(36) Note that the first term in the rhs of eq 4.36 is negligible in the regime $\lambda \gg \lambda_{\mathrm{mf}}$.
(37) The sol and gel phases are often not completely separated due to kinetic restrictions. In this case a microgel structure appears and may persist for very long time.
(38) The fact that $\partial\mu/\partial c$ is negative for $c > c_g$ is quite general and can be proven as follows. Note that concentration c_M of clusters consisting of M chains is governed by the chemical potential: $c_M = K_M e^{\mu NM}$, where K_M is the combinatorial statistical weight of an M-cluster, which asymptotically behaves as $K_M \propto M^{-x} e^{-\mu_0 NM}$ for $M \gg 1$, with some constants x and μ_0. The terminal cluster size, $M_{\mathrm{term}} = (1/N)(1/(\mu_0 - \mu))$, is increasing with increasing μ and tends to infinity as $\mu \to \mu_0$. Therefore $\mu = \mu_0$ corresponds to the gelation point, $p = p_g$. It is well-know[15] that above the gelation point M_{term} is finite and decreases with increasing degree of conversion p (i.e. with increasing c). Therefore μ must be smaller than μ_0 in the region $c > c_g$, and must decrease as c is increased: $\partial\mu/\partial c < 0$ for $c > c_g$.
(39) Baljon, A. R. C. *Macromolecules* **1993**, *26*, 4339.
(40) This effect is connected with the fact that the static screening length ξ in a marginal polymer solution decreases with increasing v. A shorter screening length means that the effective repulsion between two stickers on different chains becomes more screened in comparison with the repulsion between two neighboring stickers creating an intrachain bond. The latter interaction is not screened at all since the typical distance between neighboring stickers is much smaller than ξ.
(41) Gordon, M. *Proc. R. Soc. London* **1962**, *268A*, 240.

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