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Phase Equilibria in Solutions of Associating Telechelic Polymers: Rings vs Reversible Network

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ABSTRACT: A mean-field theory of phase equilibria in solutions of semiflexible telechelic polymers is presented. All functional groups at the ends of telechelic chains are assumed to be associated in 2-fold and 3-fold aggregates. It is shown that with a nonzero probability of 3-fold aggregation, infinite cluster (reversible network) formation always occurs as a first-order transition, implying an equilibrium between a gas of small rings and a network of finite density, mixed with rings. The phase-separation region is narrow if the effective energy of a 3-fold cross-link is high enough, but it might be also very wide (implying a large ratio of network volume fraction to that of rings in coexisting phases) if the cross-links are favorable. In the latter case clusters of three telechelic chains (triplets) might become more favorable than rings; more complex finite clusters are never important.

1. Introduction

Polymer systems with annealed molecular weight distributions are generally interesting. As important examples we mention equilibrium polymerization,[1] reversible gels,[2–7] and living polymers.[8–12]

The equilibrium polymerization phenomenon has been extensively studied in the past.[15–18] We start with a solution of monomers which could form polymer chains. As the chemical potential, μ, conjugate to the monomer concentration increases, the average molecular weight also increases.[15–18] Only polymer rings will be present in the solution if the statistical weight associated with free ends formally tends to zero.[1,19] In this case an increase of μ results in a second-order transition accompanied by an appearance of an infinite ring (rings) at some critical μ^*. The low-concentration phase (for $\mu < \mu^*$) consists of finite rings; it is dominated by relatively small rings. This transition has been studied both for ideal solutions[17,19–21] and for a good-solvent system; in the latter case a novel critical behavior characterized by specific exponents related to those for the Ising model has been revealed.[1,22]

The aim of the present contribution is to consider the transition described above for a system where a reversible cross-linking is also allowed. In this case the "infinite ring" component is, in fact, a network. With cross-linking we predict a first-order transition which in some regimes could be described by a mean-field approach. We thus avoid complications related to a specific critical behavior in the vicinity of the original transition.[1,22] The effect of cross-links on systems of living polymers has been considered in ref 12, where the possibility of ring formation was not taken into account. The results for a system of telechelic polymers (which play the role of plain monomers for a normal polymerization) in the regime of marginal solvent quality are considered in this paper. For simplicity we focus on the case of semiflexible wormlike chains for which the mean-field approximation is valid.

The transition studied below is similar not only to a formation of an infinite ring during equilibrium polymerization but also to a sol–gel transition associated with reversible gelation which was studied theoretically in refs 2–7. These issues are discussed in the last section.

2. The Model and Free Energy

2.1. The Model. Let us consider a solution of telechelic polymers which could associate by ends and form long chains (Figure 1a). Each telechelic is assumed to be semirigid: the total length of the middle block, L, is much larger than the Kuhn segment, l: $L \gg l \gg d$, where d is the effective chain thickness. We also assume that the end blocks are very short (their length is $\ll l$).

Formally, the statistical weight of a 2-fold aggregate is defined as

$$W_2 = \int [\exp(-U_2(r)) - 1]\, \mathrm{d}^3 r$$

where $U_2(r)$ is the energy of interaction of two end functional groups separated by distance r and $k_B T$ is the energy unit. The weight can thus be estimated as $W_2 \sim v \exp(E_2)$, where $v \sim d^3$ is the effective volume of the aggregate, and $E_2 = \max(-U_2)$ is the energy of association of two end groups. We assume that the binding energy is very high, $E_2 \gg k_B T$, so that there are almost no free associating groups: they all are combined into pairs since the probability of a free end is proportional to $(1/W_2)^{1/2}$ and thus is extremely (exponentially) small.

We also allow for association of $z = 3$ groups (see Figure 1b–d). The corresponding statistical weight is

$$W_3 = \int \{ \mathrm{e}^{-U_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)} - \mathrm{e}^{-U_2(\mathbf{r}_2-\mathbf{r}_1)} - \mathrm{e}^{-U_2(\mathbf{r}_3-\mathbf{r}_2)} - \mathrm{e}^{-U_2(\mathbf{r}_1-\mathbf{r}_3)} + 2 \}\, \mathrm{d}^3 r_2\, \mathrm{d}^3 r_3$$

where $U_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ is the total energy of interaction of three functional groups. Obviously $W_3 \sim v^2 \exp(E_3)$, where $E_3 = \max(-U_3)$ is the total binding energy in a 3-fold aggregate. As there are no free ends in the system, formation of m 3-fold aggregates implies destruction of $3m/2$ of pairs. Therefore, the corresponding *relative* statistical weight is $W_3^m/W_2^{3m/2} \equiv w^m$, where

$$w = W_3/W_2^{3/2} \sim v^{1/2} \exp(E_3 - 3E_2/2) \qquad (1)$$

is the effective (relative) weight of a 3-fold aggregate; $w = 0$ corresponds to zero probability of a 3-fold junction.

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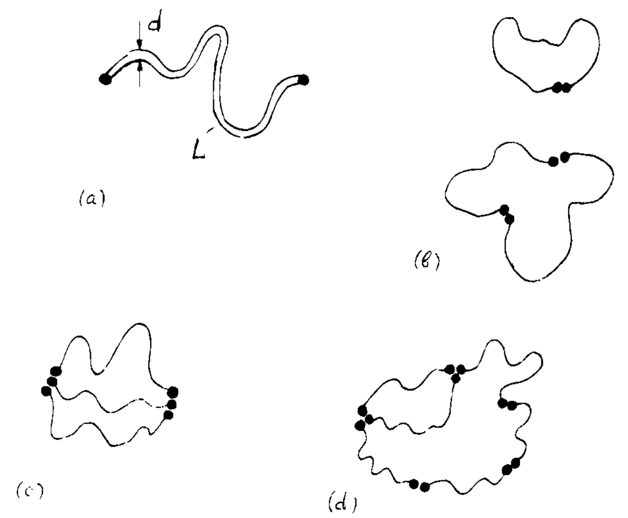

Figure 1. (a) Telechelic chain with L, the total contour length, l, the Kuhn segment, and d, the effective thickness. (b) Small rings. (c) A triplet. (d) A cross-linked ring.

Larger multiplets (with $z > 3$) are assumed to be very unfavorable and thus are *forbidden*.

Thus, in the general case the system consists not only of telechelic rings and a network component but also of more complex finite clusters such as are shown in Figure 1c,d. We shall see that these finite clusters do not normally give a noticeable contribution to the free energy of the system: they are dominated by rings (the only special case where finite clusters other than rings are important is considered at the end of the next section). It is only the infinite cluster (a network with functionality $z = 3$) that is important.

The solution is assumed to be athermal: interaction between polymer chains is exclusively due to excluded volume, with a virial coefficient equal to $B_2(\lambda) = (\pi/2)\lambda^2 d$ [23] for two short parts of chains of length λ (it is assumed that $d \ll \lambda \ll l$). In a very dilute solution telechelics must form primarily the smallest possible rings, with one telechelic per ring; their spatial size is $R_0 \sim (Ll)^{0.5}$. As we are going to develop a mean-field theory, we assumed that even in the dilute limit a telechelic chain is not swollen, that is, the Fixman parameter of excluded-volume interactions, $Z \sim B_2(l)(L/l)^2/R_0^3 \sim L^{0.5}d/l^{1.5}$, is small, i.e.,[24]

$$L \ll l^3/d^2 \tag{2}$$

The last condition ensures that the system is in the marginal solvent regime, and thus a simple virial expansion for the free energy of interaction, F_{int}, is valid if the concentration is low enough. In the second virial approximation we write[23]

$$F_{\text{int}} = (4/\pi)\phi^2 \tag{3}$$

per unit volume. Here ϕ is the polymer volume fraction ($\phi = cV_0$, where c is the concentration of telechelic chains and $V_0 = (\pi/4)Ld^2$ is the volume per chain) which is assumed to be small throughout the paper, $\phi \ll 1$. The diameter d is taken as a unit length here and below. Equation 3 is valid provided that the solution is isotropic, i.e., for $\phi \lesssim 10d/l$.[23]

The total free energy is $F = F_{\text{int}} + F_{\text{conf}}$, where F_{conf} is the conformational part, which is considered below for the system of rings and for the network.

2.2. Free Energy of the Gas of Rings.

Let us consider first the system of rings; let $c(n)$ be the concentration of rings consisting of n telechelic polymers. The (conformational) free energy of the system, F_R, is primarily due to the translational entropy of rings:

$$F_R = \sum_n c(n) \ln\left(\frac{2nc(n)}{eB(n)}\right) \tag{4}$$

where $B(n) = (3/2\pi)^{1.5}((nlL)^{-1.5}$ is the *a priori* probability that two ends of an n chain (a chain consisting of n telechelics) meet each other; the additional factor $2n$ under the logarithm accounts for the intrinsic symmetry of a ring (enumeration of telechelics in a ring can go in two directions and can start from any of n entities). The total concentration of telechelics in the ring phase is $c_R = \sum_n nc(n)$. Minimization of F_R for a given c_R results in

$$c(n) = \frac{B(n)}{2n}\exp(\mu n) \tag{5}$$

where $\mu \leq 0$ is the corresponding chemical potential. The free energy is

$$F_R = \mu c_R - \sum_n c(n) \tag{6}$$

The largest permissible concentration of rings is finite,

$$c_0 = \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1.5}\zeta(1.5)\frac{1}{L^{1.5}l^{1.5}} \tag{7}$$

and corresponds to $\mu = 0$. For $c_R \ll c_0$ we approximately write $c_R \simeq c(1) = [B(1)/2]\exp(\mu)$, and thus

$$F_R \simeq c_R \ln\left(\frac{2c_R}{eB(1)}\right), \quad c_R \ll c_0 \tag{8}$$

In the following we are mostly interested in the region $c_R \simeq c_0$; assuming that $\Delta c \equiv c_R - c_0$ is small and negative, we write (after some transformations and elimination of μ):

$$F_R = F_0 - \frac{1}{3}K(\Delta c)^3 + \mathcal{O}((\Delta c)^4) \tag{9}$$

where $F_0 = -1/2(3/2\pi lL)^{1.5}\zeta(2.5)$ and $K = (8\pi^2/27)(lL)^3$.

Equation 9 can also be justified as follows. Note that the distribution (eq 5) implies that $\mu = -\text{const}\ (\Delta c)^2$, where $-\Delta c > 0$ is assumed to be small (to see this, one needs to calculate $c \equiv c_0 + \Delta c = \sum nc(n)$ using eq 5). Therefore, the general relation

$$\mathrm{d}F_R/\mathrm{d}c = \mu \tag{10}$$

immediately gives rise to $F_R = F(c_0) - \text{const}(\Delta c)^3$, in agreement with eq 9.

2.3. Free Energy of the Network.

Now let us turn to the free energy, F_N, of a reversible network formed by telechelic chains.

In order to calculate F_N, we use the method proposed in ref 12 for living networks. We start with a system of *free* linear subchains consisting of telechelic molecules. Let $c(n)$ be the number of n subchains per unit volume. The system is then converted into a network of functionality z by cross-linking the end functional groups (the arguments here are generally valid for any z; we will set $z = 3$ at the end of the derivation). We first consider the cross-linking points as an independent ideal gas. The average concentration of the points is $\varrho_l = \varrho/z$, where $\varrho = 2\sum_n c(n)$ is the concentration of free ends of the subchains.

We assume that the network is "unsaturated" (weakly cross-linked), in other words, that the average spatial size of a subchain, R, is much larger than the typical spatial distance between neighboring cross-linking points: $\varrho R^3 \gg 1$. This condition is verified below.

The ideal-gas free energy of the reference system of free subchains and free cross-linking points (not connected with each other) is

$$F_{\text{ref}} = \sum_n c(n) \ln \frac{c(n)}{\text{e}} + \varrho_l \ln \frac{\varrho_l}{\text{e}} \tag{11}$$

In order to convert the reference system into a network, we need to impose an additional condition that there are exactly z free end functional groups near each cross-linking point. The probability that this condition is satisfied is thus $P_l = \Pi_m p_m$, where $m = 1, 2, ..., N$ runs over all cross-linking points.

For an unsaturated network (assumed above) the number of neighbors (other free ends) in the region R^3 accessible for a free end of a given subchain (which is about to be cross-linked) is large (on the order of $\varrho R^3 \gg 1$) so that the fluctuations of this number are relatively small and hence the probability p_m of the mth cross-linking nearly does not depend on how the chains were connected during the previous stage (does not depend on the current network topology). The probability p_m is determined only by the current density of free chain ends: $p_m = \varrho(m)^z$, where $\varrho(m) = p(1 - mz/N)$. Thus, we obtain the partition function of the network $Z_N = Z_{\text{ref}} P_l w^N$, where w^N is the effective statistical weight due to all N cross-links. The free energy $F_{\text{N}} = -\ln(Z_{\text{N}})/V$ is

$$F_{\text{N}} = F_{\text{ref}} - \varrho \ln \frac{\varrho}{e} - \frac{\varrho \ln(w)}{z} \tag{12}$$

where the second term on the right-hand side accounts for the combinatorial factor corresponding to network formation (note that this term effectively includes both topological and thermal fluctuations of the network structure!). In the last term $-\ln(w)$ is the effective free energy of a z-fold junction.

Note that w can be smaller than 1 (junctions suppressed) or larger than 1 (junctions promoted). In the latter case one can still have an unsaturated network due to the entropic penalty of junction formation, which is large since the characteristic size of one telechelic is much larger than the junction size.

Minimization of F_{N} for a given total concentration of telechelics in the network phase, $c_{\text{N}} = \sum nc(n)$, yields

$$c(n) = (zw)^{2/z} \exp(\mu n) \varrho^{2(1-1/z)}$$

where $\mu < 0$ is the chemical potential conjugated with c_{N}. The free energy is $F_{\text{N}} = \varrho(1/2 - 1/z) + \mu c_{\text{N}}$.

Assuming that $|\mu| \ll 1$, we get[12]

$$F_{\text{N}} = -(2/z)\varkappa c_{\text{N}}^{z/2} \tag{13a}$$

where $\varkappa = z2^{z-1}w$ (see eq 1). Equation 13a is valid if $c_{\text{N}} \ll \varkappa^{2/(2-z)}$. In the opposite limit (which corresponds to $|\mu| \gg 1$) the result is

$$F_{\text{N}} \simeq -c_{\text{N}}\left(\frac{2}{z} \ln \varkappa + \left(1 - \frac{2}{z}\right) \ln \frac{c_{\text{N}}}{\text{e}}\right) \tag{13b}$$

The average number of telechelics in a subchain (network strand) is on the order of $\bar{n} \sim \varkappa^{-1} c_{\text{N}}^{1-z/2} \gg 1$, in the regime corresponding to eq 13a, and on the order of 1 for the regime, eq 13b.

Now let us put $z = 3$. Note that the concentration dependence of the conformational free energy of the networks (eq 13a), $F_{\text{N}} \propto c^{3/2}$, is quite different from the standard behavior of the free energy of ideal *permanently* cross-linked networks:[13,14] for the latter systems the free energy is basically proportional to concentration. The main origin for this difference is that the structure of *reversible* networks considered here is not fixed, by rather is determined by equilibrium conditions. In particular, the equilibrium dictates that the average length, $\bar{n}L$, of a strand of the reversible network does depend on concentration, $\bar{n} \propto c^{-1/2}$, leading to a different behavior of all thermodynamic properties.

The network is unsaturated if $\varrho R^3 \gg 1$, where $\varrho \sim c_{\text{N}}/\bar{n}$ is the density of junction points and $R \sim (\bar{n}Ll)^{1/2}$ is the size of a subchain; thus, we get the condition

$$c_{\text{N}}^{3/2} \gg \varkappa(lL)^{-3} \tag{14}$$

in the regime of eq 13a or simply $c_{\text{N}} \gg c_0 \sim (lL)^{-3/2}$ in the regime of eq 13b. Note that an unsaturated network is always characterized by *three* different scales: the subchain size, R, the typical distance between neighboring junction points, $\lambda \sim \varrho^{-1/3}$, and the size of the concentration blob, ξ (the latter is determined by the relation $c_{\text{N}} \sim n(\xi)/\xi^3$, where $Ln(\xi) \sim \xi^2/l$ is the contour length of a subchain part of spatial size ξ), so that $R \gg \lambda \gg \xi$. More precisely, $R/\lambda \sim (\varrho R^3)^{1/3}$ and $\lambda/\xi \sim (\varrho R^3)^{2/3}$. For a saturated network ($\varrho R^3 \sim 1$) all these scales are of the same order.

So far we assumed that the polymer subchains obey the ideal (Gaussian) statistics. This assumption is valid in the regime of marginal solvent, that is, if the concentration of the network phase is not too low: the contour length of the concentration blob must be smaller than l^3/d^2 (see eq 2), so that

$$\phi_{\text{N}} \equiv V_0 c_{\text{N}} \gg 1/l^3 \tag{15}$$

3. Reversible Network Formation in the Telechelic System

We are now in a position to specify the total free energy of the system. For low concentrations (when only rings are present) the free energy is $F = F_{\text{int}} + F_{\text{R}}$ where F_{int} and F_{R} are determined by eqs 3, 8, and 9 and the volume fraction of polymer is $\phi = V_0 c_{\text{R}}$.

At higher polymer concentration the system consists of two basic components—the network and the (finite) rings of different sizes. The free energy is

$$F = F_{\text{int}}(\phi) + F_{\text{R}}(c_{\text{R}}) + F_{\text{N}}(c_{\text{N}}) \tag{16}$$

where F_{N} is determined by eqs 12–14, and the total polymer volume concentration is $\phi = V_0(c_{\text{R}} + c_{\text{N}})$; in this section we set $z = 3$. Of course, the chemical potentials for the network component and for the ring component

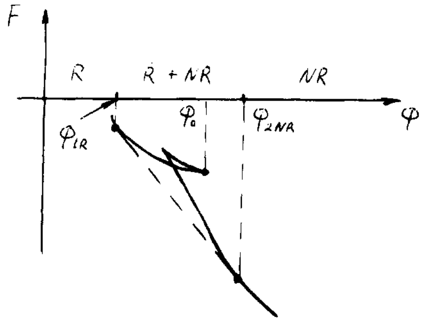

Figure 2. Free energy, F, as a function of polymer volume fraction, ϕ. Phase separation occurs in the region between ϕ_{1R} and ϕ_{2NR}.

must be equal at equilibrium:

$$\frac{\partial F_R}{\partial c_R} = \frac{\partial F_N}{\partial c_N} \tag{17}$$

Equation 17 does not define a binodal but rather is a condition of equilibrium between two components (network and rings) within the same phase. The spinodal corresponding to the onset of thermodynamic instability of the low-concentration (rings) phase can be also easily found. Let us consider the free energy of the system as a function of c_N for a given total concentration $c = c_R + c_N$. In the regime $c < c_0$ and for small $c_N \ll c$ we get using eqs 10 and 13a: $F = \text{const} - \mu c_N - \text{const}\ c_N^{3/2}$, where $\mu < 0$. Obviously c_N cannot be negative; therefore, F increases with c_N, and thus the system is stable in the region $c < c_0$. On the other hand, for $c = c_0$ using eqs 9 and 13a we get $F = \text{const} + \text{const}\ c_N^3 - \text{const}\ c_N^{3/2}$, so that the free energy decreases as the network component appears. Therefore, $c = c_0$ corresponds to the spinodal point (which is independent of $\varkappa$).

A transition from rings (R) to network + rings (NR) is expected in the vicinity of $\phi_0 = c_0V_0 \simeq (\pi/8)(3/2\pi)^{1.5}\zeta(1.5)L^{-0.5}l^{-1.5}$ (see eq 7) which is in fact the largest possible volume concentration for the R phase.

The typical form of the free energy F vs ϕ calculated using eqs 16 and 17 for $z = 3$ is shown in Figure 2. This can be obtained by considering the behavior of the total concentration $c_N + c_R$ as c_N is gradually increased. Equation 17 implies that in the region of interest a decrease of concentration of rings, Δc, is proportional to a fractional power of c_N: $|\Delta c| \propto c_N^{1/4}$. That is why the total concentration first *decreases* and then increases (in the region of large enough c_N). This results in a characteristic "swallow-tail" feature of the plot which always exists so long as cross-links are not suppressed energetically (recall that there is always an entropic suppression of cross-links). This ensures the presence of a first-order transition between R and NR phases. The volume concentrations of polymer in coexisting phases (ϕ_{1R} and ϕ_{2NR}), which can be calculated in a standard way (requiring equal osmotic pressures and chemical potentials of telechelics in both phases), are also shown in Figure 2.

The characteristic width of the swallow tail can be easily estimated by eqs 13a and 9 as

$$\Delta\phi \sim \varkappa^{2/3}/l^2L$$

The assumption of an ideal (unswollen) network is valid if $\Delta\phi \gg 1/l^3$ (see condition (15)). Thus, the mean-field theory is applicable if

$$\varkappa \gg \varkappa_{\min} = (L/l)^{3/2} \tag{18}$$

For $\varkappa \sim \varkappa_{\min}$ the two-phase region is narrow: $(\phi_{2NR} - \phi_{1R}/\phi_{1R} \sim \Delta\phi/\phi_0 \sim (L/l^3)^{1/2} \ll 1$ (see inequality (2)). In the region $\varkappa < \varkappa_{\min}$ the transition is even weaker and the network appearing at the transition point is very dilute and thus is swollen; this regime is briefly considered in the Discussion.

Here we focus instead on the regime $\varkappa \gg \varkappa_{\min}$ for which the mean-field approach is valid. If, in addition, $\varkappa \ll \varkappa_1 \equiv L$, then the volume concentration of rings in both phases is close to ϕ_0. Phase equilibrium between the ring (R) and network with rings (NR) phases can be analyzed in a standard way: one needs to equate the chemical potentials and osmotic pressures in both phases. The predicted total concetrations in the R and NR phases are

$$\phi_{1R} \simeq \phi_0 - \frac{1}{4}\left(\frac{3}{2\pi}\right)^{1/2}\frac{\varkappa}{(Ll)^{3/2}} \tag{19}$$

$$\phi_{2NR} = \phi_{2N} + \phi_{2R}$$

The concentration of network in the NR phase is

$$\phi_{2N} \simeq \frac{4}{9\pi}\frac{\varkappa^2}{L^3} \tag{20}$$

and that of rings is

$$\phi_{2R} \simeq \phi_0 - \frac{3}{4}(2\pi)^{-1/2}\frac{\varkappa}{(Ll)^{3/2}} \tag{21}$$

Equations 19–21 are valid in the region $\varkappa_{\min} \ll \varkappa \ll \varkappa_1$. Note that condition $\varkappa \gg \varkappa_{\min}$ ensures that the network concentration at the transition point (eq 20) is high enough, so that both conditions of validity of the present theory, eqs 14 (unsaturated network) and 15 (Gaussian statistics of subchains), are fulfilled.

The relative width of the two-phase region is $w = \phi_{2NR}/\phi_{1R} - 1 \simeq (\varkappa/\varkappa^*)^2$ where $\varkappa^* \sim L^{5/4}l^{-3/4}$. Thus the transition is weak ($w \ll 1$) if $\varkappa \ll \varkappa^*$ and strong if $\varkappa \gg \varkappa^*$ (note that $\varkappa^* \sim (\varkappa_{\min}\varkappa_1)^{1/2}$). Simultaneously, the fraction of rings in the high-concentration NR phase is large when the transition is weak and small in the opposite case. As the concentration of the NR phase is further increased, the volume fraction of rings decreases; it becomes much smaller than ϕ_0 if the total concentration ϕ is much larger than $\phi^* \sim L/\varkappa^2$.

The mean number n_s of telechelics per network subchain is large at the transition point, $n_s \sim L^2/\varkappa^2$ and then decreases as the concentration is increased; in the region $\phi \gg \phi^*$ nearly all strands consist of exactly one telechelic, $n_s \simeq 1$. (This does not necessary violate our assumption of an unsaturated network.) Note that the characteristic maximum (cutoff) number of telechelics per ring, $\tilde{n}$, in the NR phase is always of order n_s; note also that the absolute value of the second (correction) term in the right-hand-side of eq 21 is on the order of the volume fraction of rings with $n \sim n_s$.

Let us turn now to the regime, $\varkappa \gg \varkappa_1$, where the transition is very strong (the separation region is very wide). Here we find

$$\phi_{1\mathrm{R}} \simeq \frac{9}{32(2\pi)^{1/6}} \exp(2/3) \frac{1}{L^{1/2} l^{3/2}} \left(\frac{L}{\varkappa}\right)^{2/3}$$

$$\phi_{2\mathrm{H}} \simeq \frac{1}{3L}; \qquad \phi_{2\mathrm{R}} \simeq \phi_{1\mathrm{R}} \exp(-2/3) \tag{22}$$

The relative width of the transition is thus $w = \phi_{2\mathrm{NR}}/\phi_{1\mathrm{R}} - 1 \sim (l^3/L)^{1/2}(\varkappa/\varkappa_1)^{2/3} \gg 1$. Note that in both phases the majority of rings consist of only one telechelic; the same is true for the network strands. The total concentration of rings in both phases is much smaller than the concentrations of network; concentration of rings in the second (NR) phase is smaller than that in the R phase by a factor ~ 2.

Let us check now the validity of the above treatment. First, we assumed the ideal (Gaussian) statistics of network strands and of rings (see condition (15)). This assumption is ensured by the inequalities (2) and (18): $L \ll l^3$ and $\varkappa \gg \varkappa_{\min}$. Using the results of eqs 20–22, one can easily check that the same inequalities ensure also that the network that appears after the transition is always unsaturated (that is, the strands on the average are much larger than concentration blobs; see condition (14)).

Finally we need to check if the clusters other than rings (the simplest example is shown in Figure 1c) are important or not. This point is a bit more subtle. Let us first consider the regime $\varkappa_{\min} < \varkappa < \varkappa_1$. The concentration of rings in both phases is on the order of $c_0 \sim 1/(lL)^{-3/2}$. The concentration of triplets (clusters of three telechelics shown in Figure 1c) can be easily estimated as

$$c_3 \sim c_0^{\,3} \varkappa^2 (lL)^{3/2} \tag{23}$$

where the additional factor $\varkappa^2$ accounts for two three-functional junctions. The ratio $c_3/c_0 \sim \varkappa^2/(lL)^{3/2}$ is always small (it attains its largest value $\sim (L/l^3)^{1/2} \ll 1$ for $\varkappa \sim \varkappa_1$) and therefore triplets are negligible. Larger clusters can be shown to be even less probable than triplets.

Obviously small rings (with $n \sim 1$) give the dominant contributions to polymer volume fraction in the R phase. These small rings, however, play only a secondary role for the R → NR phase transition: its characteristics are determined primarily by the longest rings with the maximum (cutoff) number of subunits (telechelics) per ring, $\tilde{n} \sim 1/|\mu| \sim 1/K(\Delta c_{\mathrm{N}})^2$, where μ is the effective chemical potential (see eq 5). As was already mentioned, $\tilde{n} \sim n_{\mathrm{s}} \sim L^2/\varkappa^2$ at the transition point. The total concentration of rings with $n \sim \tilde{n}$ is (see eq 5)

$$\tilde{c} \sim \tilde{n} c(\tilde{n}) \sim c_0/(\tilde{n})^{3/2}$$

Let us estimate the relative contribution of rings with one subchain (as shown in Figure 1d) with the same total number of subunits $n \sim \tilde{n}$ (clusters with more subchains are even less important). Obviously the shortest subchains should dominate since the probability of a subchain of m subunits decreases as $1/m^{3/2}$. The total concentration of these clusters is

$$\tilde{c}_1 \sim \tilde{n} c_0 \varkappa^2 \tilde{c} \tag{24}$$

where the additional factor $\tilde{n}$ accounts for the fact that a subchain breaks the symmetry of the initial ring. The ratio $\tilde{c}_1/\tilde{c} \sim \tilde{n} c_0 \varkappa^2$ is thus much larger than c_3/c_0 (eq 23). Using the above results for $\tilde{n}$, we get $\tilde{c}_1/\tilde{c} \sim (L/l^3)^{0.5} \ll 1$. Therefore, clusters other than rings could be always neglected in the region under consideration ($\varkappa_{\min} < \varkappa < \varkappa_1$): the above estimates imply that it is rings that dominate among clusters of any given molecular weight.

In the region $\varkappa > \varkappa_1$ the cutoff number of subunits in rings is $\tilde{n} \sim 1$. Thus, we do not need to consider clusters of large molecular weight. The concentration of triplets can be estimated in analogy with eq 23:

$$c_3 \sim c^3 \varkappa^2 (lL)^{3/2}$$

where $c \sim \phi_{\mathrm{R}}/L \sim c_0(L/\varkappa)^{2/3}$ is the concentration of small rings (see eq 22). Hence, $c_3/c \sim (\varkappa/\varkappa_2)^{2/3}$, where

$$\varkappa_2 \sim L^{1/4} l^{9/4} \gg \varkappa_1$$

Therefore, triplets again could be neglected in the region $\varkappa < \varkappa_2$, but they are important for $\varkappa > \varkappa_2$. In fact, it is straightforward to show that in the latter region both rings and larger clusters are dominated by triplets near the transition point.

The equilibrium properties of the system in the region $\varkappa > \varkappa_2$ can be considered using the same approach as before. The results are as follows. At very low concentrations, $\phi \lesssim \phi_{\mathrm{RT}} \sim (\varkappa_2/l^3\varkappa)$, the system is a gas of small rings, which transforms to a gas of triplets at $\phi \sim \phi_{\mathrm{RT}}$. The transition from triplets (T) to network + triplets (NT) occurs at

$$\phi_{1\mathrm{T}} \simeq \frac{3}{64\pi} 1.5^{1.5} \exp(2) \frac{1}{l^3} \tag{25}$$

The network concentration in the NT phase is still $\phi_{2\mathrm{N}} \simeq 1/3L$, and the concentration of triplets in the NT phase is lower than that in the T phase; in fact, we find $\phi_{2\mathrm{T}} \sim \phi_{1\mathrm{T}}/\exp(2)$.

4. Discussion

We have considered the equilibrium properties of an athermal system of semirigid telechelic polymers with functional end groups capable of 2-fold and 3-fold association. Since free ends are forbidden (assumed to be very unfavorable), the system is a gas of small rings at low concentrations. We have shown that when the concentration is increased, the system undergoes a first-order phase transition which is accompanied by the formation of a reversible network of telechelic polymers. The volume fraction of network at the transition point, $\phi_{2\mathrm{N}}$, is finite; it is governed by the parameter $\varkappa \sim \exp(E_z - zE_2/2)$, where E_z is the total effective binding energy of a (z=3)-fold junction, and E_2 is the binding energy of a pair of end groups. The results are summarized in the schematic phase diagram shown in Figure 3.

A very dilute network with $\phi_{\mathrm{N}} < \phi_{2\mathrm{N}}$ is thus unstable. This conclusion is similar to that drawn in ref 12 for living networks without rings under various conditions (the main difference, however, is connected with the fact that in the present study the higher concentration phase is a mixture of the network and the rings). In fact, we can use the results of ref 12 in order to extend the present consideration to the region of low $\varkappa$ ($\varkappa < \varkappa_{\min}$, see eq 18) where the mean-field treatment fails. We consider this briefly below.

In the region $\varkappa < \varkappa_{\min}$ both the network and the longest (cutoff) rings are swollen and also the network becomes saturated. Thus, we arrive there at essentially a good-solvent regime. If we neglect additional subtle

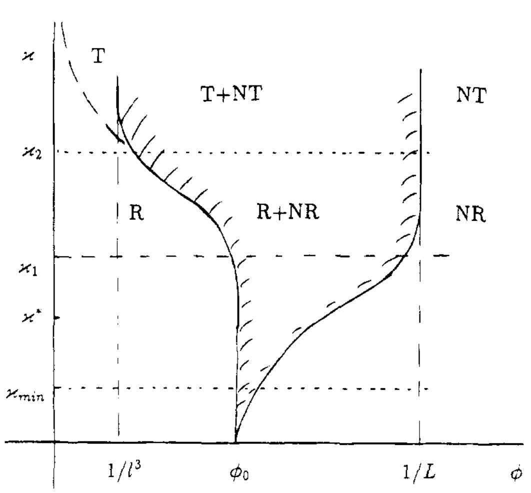

Figure 3. Phase diagram of the system of telechelic chains in variables $\varkappa$ vs ϕ, where ϕ is the volume fraction of the polymer and $\varkappa \sim \exp(E_3 - 3E_2/2)$ is the effective activity of a 3-fold function. Here $\phi_0 \sim 1/(Ll^3)^{1/2}$; the label R corresponds to a gas of polymer rings, T, a gas of triplets, NR, a reversible network mixed with rings, and NT, the network mixed with triplets. The shaded area corresponds to a phase separation.

effects connected to screening by all intermediate rings,[1,22] then the consideration of living networks with excluded volume becomes directly applicable also to the present system at low $\varkappa$ (the presence of rings does not essentially modify the free energy of a network interacting by excluded volume with itself: in fact, small rings do not screen the interactions in a noticeable way, whereas the presence of large rings just changes the excluded-volume free energy by a numerical factor). The minimum volume fraction of the network was predicted[12] to scale as $\phi_{2N} \propto \varkappa^{1/y_3}$, where y_3 is a certain combination of scaling (and correction-to-scaling) exponents characterizing long linear chains in a good solvent. For $z = 3$ and for three dimensions the approximate value is $y_3 \simeq 0.56$.[12] Assuming a smooth crossover between scaling ($\varkappa < \varkappa_{min}$) and mean-field ($\varkappa > \varkappa_{min}$, see eq 20) regimes, we thus get

$$\phi_{2N} \sim \frac{1}{l^3}\left(\frac{\varkappa}{\varkappa_{min}}\right)^{1.79}$$

for $\varkappa < \varkappa_{min}$. Note that the last equation is not much different from the mean-field prediction (eq 20).

We stress that in the specified region defined by conditions (2) and (18) the theory considered above is asymptotically exact. In particular, we proved (rather than merely assumed; see the previous section for a detailed discussion) that in the whole region finite clusters other than rings (clusters with more complicated topology) are negligible: their relative contribution to the free energy and other relevant physical quantities is small. This result can be explained as follows. Obviously clusters other than rings must include 3-fold junction points, and thus their formation is generally suppressed if $\varkappa$ is small. Of course, in the region close to the spinodal point, c_0, complex clusters become entropically very favorable, so that they would be formed if this region were thermodynamically stable. An important point, however, is that a reversible network formation is always coupled with a first-order transition which is strong enough: the region of phase separation is always wider than the region where complex clusters are important, so that the former region includes the latter. The driving force for the first-order transition is the effective attraction between telechelics implied by 3-fold junctions (attraction between three end functional groups gives rise to the same type of effective interaction between polymers). The width of the separation region is determined by the driving force and also by repulsive excluded-volume interaction which oppose the tendency for strong first-order transition. However, for semiflexible polymers considered here ($d \ll l$) excluded-volume interactions are relatively weak (note that in the limit $d \to 0$ excluded volume vanishes), and hence the separation region is wide enough to suppress formation of complex finite clusters.

The free energy of the reversible network considered here (see, e.g., eq 13a) differs not only from the results for permanently cross-linked networks but also from the predictions of classical gelation theories (both percolation and mean-field theories of treelike structures[14]). The main reason for the difference is that our model includes two parameters (E_2 and E_3, effective binding energies for 2- and 3-fold aggregates), rather than a single one (like the probability of bond formation between two functional units) as in classical theories. In fact, we assumed that E_2 is very large, giving rise to a possibility of formation of long linear superchains of telechelics, the possibility of which was not really accounted for by the previous models. It is these long superchains of variable lengths that can form a very dilute reversible network and imply the new scaling concentration dependence of the network free energy, $F_N \propto c_N^{z/2}$.

The obtained results can be rather easily generalized for any functionality z, that is, for a system of telechelics with end-groups that could associate either in pairs or in z-aggregates. Since the model with $z > 3$ is physically less important, we mention here the main results only briefly. The behavior of the system with $z = 4$ is qualitatively the same as that for $z = 3$: the system undergoes a reversible gelation via a weak or strong (for large enough $\varkappa$) first-order phase transition. For $z \geq 5$ additional phase separation between gels of different density could occur in a limited region around $\varkappa \sim L^{z-2}$, $\phi \sim 1/L$. For even higher functionalities, $z \geq 6$, the characteristic swallow tail feature of the free energy vs concentration plot (see Figure 2) disappears, and thus the behavior qualitatively changes again: now the gel formation occurs as a second-order phase transition if z-fold junctions are not too favorable, $\varkappa < \varkappa_c \sim L^{z-2}$, and as a first-order transition in the opposite case.

It is also reasonable to apply the obtained results to a system of living polymers (cylindrical micelles in surfactant solutions). Here the end-cap energy might be very large; in this case an effect of free ends could be neglected. Simultaneously the energy of a 3-fold junction (of a cross-link between three cylinders) might be moderate, and thus a living network could be formed.[12] The micelles are normally very rigid, their Kuhn segment being much larger than the diameter, $l \gg d$. Thus the only most obvious difference between a system of telechelics considered above and living polymers is that in the former case a network must consist of subchains of discrete lengths, which are multiples of L. This difference is not important, however, as long as the typical strand length is larger than the Kuhn segment, l, in which case we can simply define the subunit length as the Kuhn segment, i.e., $L \sim l$.

There is another difference: for living polymers (but not for telechelics in the present model) the orientations (tangential unit vectors) must match at ring closure. However, this effect does not modify the phase behavior at all: it results just in an increase of the chemical potential by a constant value, equal in all phases. In fact, the same matching of orientations is implied when a *linear* chain of subunits is creating gradually by attaching the tail of a new subunit to the head of a previous one. Also at a network junction point the orientations of strands must match with orientations of the arms of the junction (of course, we assume that the angle between the arms is fixed and equal to 120° for $z = 3$).

The characteristics of the gelation transition can now be described by eqs 19–21: for $\phi < \phi_0 \sim 1/l^3$ the micelles form rings with typical lengths of order l; the region between ϕ_0 and $\phi_0 + \Delta\phi$ corresponds to a phase separation between rings and a living network mixed with rings, the network volume fraction in the high concentration phase being $\Delta\phi \sim \varkappa^2 d^3/l^3$ (for $1 < \varkappa < l/d$). Thus the formation of a living network with rings is a weak first-order phase transition for $\varkappa < (l/d)^{1/2}$ and a strong one in the opposite case (corresponding to low cross-linking energy). The concentration of the gel phase for $\varkappa \sim l/d$ is of order d/l. The region $\varkappa > l/d$ corresponds to a new regime where the strands are expected to be rodlike, and also a liquid crystalline ordering of micelles is probable.

Reversible gelation has been recently considered theoretically by Tanaka et al.[2–7] for systems of associating polymers with a number of functional groups. It was shown that the gelation being normally a second-order phase transition might also be accompanied by a phase separation. This phase separation, however, is not due to intrinsic properties of the reversible network as in the present treatment but rather simply due to a poor quality of the solvent. It was also shown[2,3] that the region of phase separation shrinks as the probability of cross-linking is decreased. This result is in accordance with the conclusions of the present paper. Note that there is one important difference between the present model and the model considered in refs 2 and 3. In the latter model the probability of formation of a junction between just two primary polymer chains, or between many chains, is governed by the same parameter—the probability of an elementary cross-linking of two functional groups, in contrast with our model where probability of a linear (ring) structure is determined by the energy E_2, whereas branched structures (with 3-fold junctions) are governed by both E_2 and E_3. That is why the model of refs 2 and 3 implies that rings are always dominated by more complex finite clusters, which are entropically more favorable. For the same reason unsaturated networks with long subchains are not likely to appear in that model (at least in a region far from the percolation threshold) in contrast with the predictions for the model considered in the current paper.

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