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A New Look at the Equilibrium Aggregate Size Distribution of Self-Associating Trivalent Molecules[†]

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ABSTRACT: We study the random polycondensation of trivalent monomers. We relax the standard hypothesis of equireactivity of all functional groups and separately treat initiation, elongation, and branching reactions. Via a generating function method we compute the equilibrium aggregate size distribution and the gel point and then examine how both the distribution and gel point change with variations in the initiation, elongation, and branching equilibrium constants. Lastly, we show that to obtain a postgel solution one needs to replace conservation of mass by an equation of state valid in the gel region. We show how particular choices of this equation of state lead to the Flory and Stockmayer postgel aggregate size distributions, how natural modification of these choices leads to generalizations of the Flory and Stockmayer postgel solutions that are valid when functional groups are not equireactive, and how different choices of the equation of state naturally lead to an entire family of postgel solutions.

Introduction

The condensation polymerization of f-valent monomers has been studied theoretically in great detail.[1-19] This simple system involving one type of monomeric unit, each with f functional groups, has become the prototypic example of a system which undergoes gelation at a critical extent of reaction. Theoretical techniques of a wide variety have been used to study this system. Flory[1] utilized a statistical method based upon interpreting the extent of reaction as the probability that a functional group has reacted. Stockmayer[2] and Cohen and Benedek[17] calculated the most probable distribution of polymer sizes using statistical mechanics. Gordon and co-workers[3-7] examined the same problem using a branching process approach developed by Good.[8] The studies of Dusek,[11] Ziff,[12,13] and van Dongen and Ernst[18] centered on the kinetics of the condensation reaction, especially after the gel point had been reached. Donoghue and Gibbs[14-16] examined the consequences of having a finite number of monomers in the system. The original Flory–Stockmayer theory utilized two basic assumptions: (a) equal reactivity of all functional groups and (b) no intramolecular reactions. Assumption b implies that the polymers formed by condensation will contain no loops; i.e., they will have the topological form of a tree. Using these assumptions, all of the various theories predict that gelation occurs at the critical extent of reaction $p_c = 1/(f-1)$. However, for extents of reaction $p > p_c$, differing predictions have been made about the composition of the gel phase.[1,2,13]

Here we compute by a generating function method, rather than the usual branching process method,[3-8] the aggregate size distribution and gel point for the case of trivalent ($f = 3$) monomers when the assumption of equal reactivity is relaxed and first-shell substitution effects[4,6,20] are included. There are some novel features of our method: (1) Rather than dealing with the extent of reaction, our results are stated directly in terms of three equilibrium constants, K_0, K_1, and K_2, and the total concentration of monomer in the system, C_T. (2) By varying the reactivity of a functional group according to how many other functional groups on the same monomer unit are already bound, we explicitly include initiation (K_0), elongation (K_1), and branching (K_2) effects. (3) We characterize polymers by both the number of monomers and the number of branch points they contain. Thus we explicitly keep track of the degree of branching in the system and compute, among other things, the average number of branch points per molecule and the fraction of monomers that are branch points. (4) We study variations in the gel point (measured by C_T*, the critical total monomer concentration needed to gel) as a function of the initiation, elongation, and branching equilibrium constants. We find, for example, that making initiation harder, i.e., lowering K_0, makes it easier to gel; i.e., C_T* is also lowered. (5) Lastly, we show how making different assumptions about the postgel behavior of a generating function, $u(z)$, which arises naturally in our procedure, leads in the case of equireactivity to either the Stockmayer or Flory results for the weight fraction distribution past the gel point. When first-shell substitution effects are present, we show how to generalize the Flory and Stockmayer postgel solutions. We also show that making other assumptions about the postgel form of $u(z)$ leads to an entire family of possible postgel solutions.

Theory

We study a system at equilibrium containing a total concentration C_T of trivalent monomers, of which a concentration C are free (not in aggregates). We characterize the interaction of free sites with each other by three equilibrium constants (see Figure 1): K_0, the initiation constant that describes the binding of a free site on a monomer to a free site on a subunit of an aggregate containing zero bound sites (i.e., another free monomer); K_1, the elongation constant that describes the binding of a free site on a monomer to a free site on a subunit of an aggregate containing one bound site; K_2, the branching constant that describes the binding of a free site on a monomer to a free site on a subunit of an aggregate containing two bound sites. We assume loops cannot form in this system, and hence C_T and the three constants, K_0, K_1, and K_2, can completely characterize the equilibrium aggregate size distribution. Although the equilibrium constants K_0, K_1, and K_2 are defined for monomer addition reactions, we assume polymers grow by both addition and condensation reactions. At equilibrium the concentration of a polymer is independent of the pathway by which it is formed. We use this principle and compute the equilibrium size distribution via a recursive method that relates polymers of sizes that differ by a single monomer unit. Hence we only require the three addition equilibrium constants K_0, K_1, and K_2. The equilibrium constants for condensation reactions involving polymers of size two or greater can be expressed in terms of K_0, K_1, and K_2 via the principle of detailed balance (see Appendix A).

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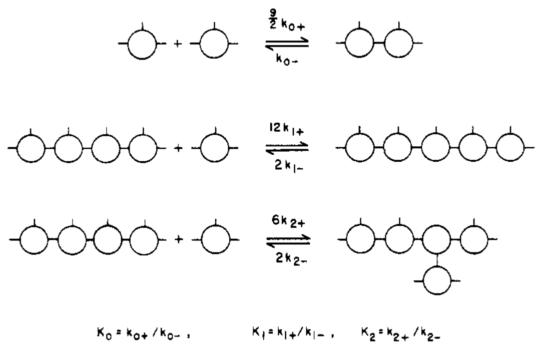

Figure 1. We separate the reactions that occur between free sites on a trivalent monomer and free sites on a polymer into three classes: (1) initiation reactions that involve the reversible binding of a free site on a monomer to a free site on another monomer, with rate constants k_{0+} and k_{0-} and equilibrium constant K_0; (2) elongation reactions that involve the reversible binding of a free site on a monomer to a free site on a polymer subunit that already has one of its sites bound, with rate constants k_{1+} and k_{1-} and equilibrium constant K_1; (3) branching reactions that involve the reversible binding of a free site on a monomer to a free site on a polymer subunit that already has two sites bound, with rate constants k_{2+} and k_{2-} and equilibrium constant K_2. For each class of reaction, the rate constants describe site–site interactions. The statistical factors multiplying the appropriate rate constants describe the number of different ways each reaction can occur. The statistical factors indicated on the diagram are appropriate for the indicated reactions, but may differ for other reactions. This does not present a problem in our calculations (see Appendix B) for we deal with planted trees. If each of the aggregates is planted at its left end, and in the case of the initiation reaction if only one monomer is planted, we find that the equilibrium constants for initiation, elongation of a linear chain, and branching from a linear chain are $6k_{0+}/k_{0-}$, $6k_{1+}/k_{1-}$ and $3k_{2+}/2k_{2-}$, respectively.

To present our theory, it is useful to introduce a nondimensional monomer concentration, $c = C/C_T$, and the following nondimensional parameters that include the statistical factors characterizing the binding of a monomer to an aggregate:

$$\alpha_0 = 6K_0C_T \tag{1a}$$

$$\alpha = 6K_1C_T \tag{1b}$$

$$\beta = 3K_2C_T/2 \tag{1c}$$

Our procedure for calculating the aggregate size distribution is to enumerate and assign the correct statistical weight to all possible treelike aggregates by using a generating function method. The details of this procedure are outlined in Appendix B.

We state our results in terms of the generating function $q(z,\xi)$ for the concentration of treelike aggregates of size n with m branch points.

In Appendix B we prove

$$q(z,\xi) = cz + \frac{\alpha_0 czq_0(z)}{u(z,\xi)^2}\{3u(z,\xi) - 2 + 2[1 - u(z,\xi)]^{3/2}\} \tag{2}$$

where

$$q_0(z) = cz/(1 - \alpha cz) \tag{3}$$

$$u(z,\xi) = 4\gamma\xi q_0(z)^2 \tag{4}$$

and

$$\gamma = \alpha\beta \tag{5}$$

is a branching parameter.

Concentration of *n*-Mers. From the generating function $q(z,\xi)$ we can obtain an expression for the nondimensional concentration of aggregates of different sizes and with different degrees of branching. Let c_n be the nondimensional concentration of n-mers. The previously introduced variable c, the concentration of monomer, is c_1. Further, let $c_{n,m}$ be the nondimensional concentration of n-mers with m branch points. The generating function $q(z,\xi)$ is defined in terms of $c_{n,m}$ as

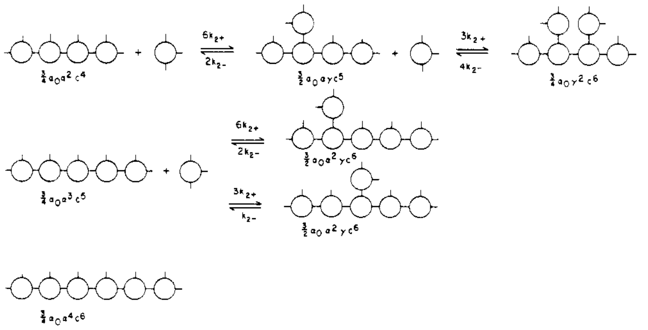

Figure 2. The concentration of aggregates, using the law of mass action, as constructed directly from chemical reactions agrees with those predicted by eq 7. We illustrate for aggregates composed of six monomers. The concentration c_6 is a sum of three terms corresponding to the three types of aggregates six monomers can form: aggregates with two, one, or no branch points. We show how to obtain those concentrations starting from the known concentrations for linear aggregates.

$$q(z,\xi) = \sum_{n=1}^{\infty}\sum_{m=0}^{\infty} c_{n,m}z^n\xi^m \tag{6}$$

From eq 2 we obtain the following power series:

$$q(1,1) = c + \frac{3\alpha_0}{4}[c^2 + \alpha c^3 + (\alpha^2 + 2\gamma/3)c^4 + (\alpha^3 + 2\alpha\gamma)c^5 + (\alpha^4 + 4\gamma\alpha^2 + \gamma^2)c^6 + (\alpha^5 + 20\gamma\alpha^3/3 + 5\gamma^2\alpha)c^7 + (\alpha^6 + 10\gamma\alpha^4 + 15\gamma^2\alpha^2 + 2\gamma^3)c^8 + ...] \tag{7}$$

Since $c_{n,m}$ is proportional to $c^n\gamma^m$, we can pick out the values of $c_{n,m}$ from eq 7. For example, $c_{8,3} = (3/2)\alpha_0c^8\gamma^3$.

It is easy to see where each term in eq 7 comes from. In Figure 2 we show how the $n = 6$, $m = 0$, 1, and 2 terms arise. The direct enumeration illustrated in Figure 2 also shows that our tree-counting procedure gives rise to the same statistical weights as derived directly from chemistry.

Using expansion techniques discussed by Wiegel and Perelson,[21] we obtain the general term in the power series expansion of $q(z,\xi)$

$$c_{n,m} = \frac{3\alpha_0\alpha^{n-2m-2}\binom{n-2}{2m}\binom{2m}{m}\gamma^mc^n}{2(m+1)(m+2)}, \qquad n \geq 2 \tag{8}$$

Thus, for $n \geq 2$

$$c_n \equiv \sum_m c_{n,m} = \frac{3\alpha_0\alpha^{n-2}c^n}{2}\sum_m\frac{\binom{n-2}{2m}\binom{2m}{m}(\gamma/\alpha^2)^m}{(m+1)(m+2)}$$

When $K_0 = K_1 = K_2$ (i.e., when all sites on the monomer are equireactive), this sum can be explicitly evaluated. For this case, $\alpha_0 = \alpha = 4\beta$, $\gamma = \alpha^2/4$, and hence

$$c_n = \frac{3}{2}\alpha^{n-1}c^n\sum_m\frac{2^{-2m}\binom{n-2}{2m}\binom{2m}{m}}{(m+1)(m+2)} \tag{9}$$

Performing the sum, one finds

$$c_n = \frac{3}{(n+1)(n+2)}\binom{2n}{n}\left(\frac{\alpha}{2}\right)^{n-1}c^n, \qquad n \geq 2 \tag{10}$$

After the concentration of monomer, c, is determined below, we shall show that eq 10 is in agreement with the classical Flory–Stockmayer[1,2] distribution for systems in a pregel state.

Concentration of Polymers with m Branch Points. A new feature in our model of random polycondensation is the explicit accounting of the degree of branching in a polymer. Let b_m denote the nondimensional concentration of polymers with m branch points, i.e.

$$b_m \equiv \sum_{n=2m+2}^{\infty} c_{n,m} + \delta_{m,0}c$$

then, from eq 8

$$b_m = \frac{3\alpha_0\gamma^m\binom{2m}{m}c^{2m+2}(1-\alpha c)^{-(2m+1)}}{2(m+1)(m+2)} + c\delta_{m,0} \quad (11)$$

Thus, for example, the concentration of linear chains

$$b_0 = \frac{3\alpha_0 c^2(1-\alpha c)^{-1}}{4} + c$$

That this is correct can easily be seen from eq 7, the power series expansion of q.

Sum Rule. To calculate explicitly the size distribution, we must first find c, the free monomer concentration. Up to the gel point, conservation of mass can be expressed by the sum rule

$$1 = \sum_{n=1}^{\infty}\sum_{m=0}^{\infty} nc_{n,m} = z\frac{\partial q(z,\xi)}{\partial z}\bigg|_{z=1,\xi=1} \quad (12a)$$

Using eq 2, the sum rule becomes

$$1 = q(1 - 3q_0/c) + 3q_0 + 3\alpha_0[1 - (1-u)^{1/2}]/2\alpha\beta \quad (12b)$$

where

$$q_0 \equiv q_0(1) = c/(1-\alpha c) \quad (13a)$$

$$u \equiv u(1,1) = 4\alpha\beta q_0^2 \quad (13b)$$

and

$$q \equiv q(1,1) = c + \frac{\alpha_0 c q_0}{u^2}[3u - 2 + 2(1-u)^{3/2}] \quad (13c)$$

Writing q, q_0, and u in terms of c in eq 12b, rearranging, and squaring, we find that c satisfies the following quartic equation:

$$[16\alpha\beta^2 + \alpha_0^2(16\beta - 3\alpha) + 4\alpha_0\alpha(\alpha - 6\beta)]\alpha c^4 - 4[8\beta^2 + \alpha_0(\alpha - 6\beta)]\alpha^2c^3 + 4[4\alpha^2\beta^2 - 3\alpha_0(\alpha - \alpha_0)]c^2 + 4(3\alpha + 2)\alpha_0 c - 8\alpha_0 = 0 \quad (14)$$

Numerical examination of the quartic indicates that below the gel point there is only one real solution whose value lies in the physical range, $0 \le c \le 1$ (see Figure 3). Above the gel point there is no real solution of the quartic with $0 \le c \le 1$ that satisfies eq 12b. As we might expect from an examination of eq 12b, this bifurcation in behavior occurs at the branch point singularity $u = 1$. Below we show by more conventional techniques that $u = 1$ is the criterion for gelation.

In the special case $\alpha_0 = \alpha = 4\beta$, i.e., when all sites are equireactive, eq 14 can be easily solved and yields one real positive root:

$$c = \frac{(1+2\beta)(1+8\beta)^{1/2} - (1+6\beta)}{16\beta^3} \quad (15)$$

We show in Appendix C that for this special case, c can be expressed in terms of p, the equilibrium extent of reaction. In particular

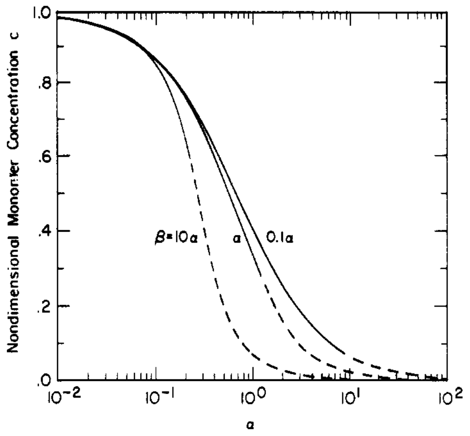

Figure 3. Nondimensional concentration of free monomer, c, vs. α for $\beta = 0.1\alpha$, 1.0α, and 10.0α. Since $\alpha = 6K_1C_T$ and $\beta = 3K_2C_T/2$, this is essentially a plot of the free monomer concentration vs. the total monomer concentration, C_T, for various values of K_2/K_1. In obtaining the graphs we took $\alpha_0 = \alpha$, solved eq. 14, and then checked that the solutions satisfied the sum rule. Although eq 14 yielded a single real root with $0 \le c \le 1$ for all values of α, only the c values corresponding to the solid portions of the curves satisfied the sum rule. The dashed curves correspond to real solutions of eq 14 that do not satisfy the sum rule. The transition from solid to dashed occurs when u reaches 1.

$$c = (1-p)^3 \quad (16)$$

and

$$p = \frac{1 + \alpha - (1+2\alpha)^{1/2}}{\alpha} \quad (17)$$

Further, one finds (see eq C.5)

$$c = \frac{2p(1-p)}{\alpha} \quad (18)$$

It is now a simple matter to show that c_n, given by eq 10, is the Flory–Stockmayer[2] result

$$c_n^{\mathrm{FS}} = \frac{3(2n)!}{n!(n+2)!}\,\frac{(1-p)^2}{p}[p(1-p)]^n \quad (19)$$

(Note c_n^{FS} is called m_n/N by Stockmayer.[2]) Rewriting eq 19 as

$$c_n^{\mathrm{FS}} = \frac{3}{(n+1)(n+2)}\binom{2n}{n}\frac{(1-p)^3}{p(1-p)}[p(1-p)]^n$$

and using eq 16 and 18 to eliminate p, one finds $c_n^{\mathrm{FS}} = c_n$; i.e., eq 10 equals eq 19, as claimed.

Moments of the Aggregate Size Distribution. Let M_0, M_1, and M_2 be the zeroth, first, and second moment of the aggregate size distribution, where size is measured in terms of the number of monomers per aggregate. Then

$$M_0 \equiv \sum_{n=1}^{\infty}\sum_{m=0}^{\infty} c_{n,m} = q \quad (20a)$$

$$M_1 \equiv \sum_{n=1}^{\infty}\sum_{m=0}^{\infty} nc_{n,m} = \left(z\frac{\partial q(z,\xi)}{\partial z}\right)_{z=1,\xi=1} \quad (20b)$$

and

$$M_2 \equiv \sum_{n=1}^{\infty}\sum_{m=0}^{\infty} n^2c_{n,m} = \left[z\frac{\partial}{\partial z}\left(z\frac{\partial q(z,\xi)}{\partial z}\right)\right]_{z=1,\xi=1} \quad (20c)$$

The zeroth moment is a measure of the total number of aggregates in the system. The first moment is the total nondimensional concentration of monomer in finite-size aggregates. If all aggregates are finite, then $M_1 = 1$, as indicated by the sum rule, eq 12.

Criterion for Gelation. A common criterion for having reached the gel point is the divergence of M_2 when $M_1 = 1$. By direct calculation one can show

$$M_2 = M_1 + \frac{6q_0^2}{c}\left(\frac{q}{c} + 1\right) - \frac{9\alpha_0 q_0}{2c\alpha\beta}[1 - (1 - u)^{1/2}] + 6\alpha_0 q_0^3(1 - u)^{-1/2}/c \quad (21)$$

When $u = 1$, eq 12 can still be satisfied, but for $\alpha_0 \neq 0$, $M_2 \rightarrow \infty$. In addition, as was shown in Figure 3, $u = 1$ is the point at which the sum rule begins to break down. Thus we take $u = 1$ as the criterion for gelation. In Appendix D we show this criterion is equivalent to the one found from branching processes.

Examination of Gelation. Consider the special case $K_0 = K_1 = K_2 \equiv K$. For this case $\alpha_0 = \alpha = 4\beta$. From the definitions of u and q_0

$$u = 4\alpha\beta q_0^2 = 16\beta^2 c^2(1 - 4\beta c)^{-2} \quad (22)$$

Thus at the gel point when $u = 1$

$$c^* = (8\beta)^{-1}$$

where we use a superscript asterisk to indicate the value of a variable or parameter at the gel point.

If we substitute this critical value of c into the sum rule, eq 12, and set $u = 1$, we find $\beta^* = 1$, and hence $c^* = {}^1/_8$ at the gel point. Thus at the gel point, ${}^7/_8$ of the monomers are in aggregates and ${}^1/_8$ are free, a result that agrees with Stockmayer.[2] Futher, from the definition of β, eq 1c, we see that there exists a critical monomer concentration $C_T^* = 2/(3K)$ such that, for systems with $C_T < C_T^*$, gelation can never occur.

As a second example we consider the case where $K_0 = K_1 \neq K_2$. We set

$$r \equiv K_2/K_1 \quad (23)$$

so that $\alpha_0 = \alpha = 4\beta/r$. Now from the definitions of u and q_0, when $u = 1$, we have

$$1 = r\alpha^2 c^2/(1 - \alpha c)^2 \quad (24)$$

Solving eq 24, we find that the only physical root is

$$c^* = \frac{1}{\alpha(1 + r^{1/2})} \quad (25)$$

If we substitute this value of c into the sum rule with $u = 1$, we find α takes on the value α^* given by

$$\alpha^* = 1/r^{1/2} + 3/r \quad (26a)$$

Hence

$$c^* = r/(r + 4r^{1/2} + 3) \quad (26b)$$

In Figure 4 we plot u as a function of α. Note that u monotonically increases from 0 to 1, reaching the critical value one at $\alpha = \alpha^*$. As predicted by eq 26a, $\alpha^* = 0.62$, 4.0, and 33.16 when $r = 10$, 1, and 0.1, respectively.

The critical monomer concentration $C_T^* = \alpha^*/(6K_1)$. If branching is favored over elongation so that $r > 1$, then $\alpha^* < 4$, $C_T^* < 2/(3K_1)$, and $c^* > {}^1/_8$. In the limit that $r \rightarrow \infty$, $C_T^* \rightarrow 0$ and $c^* \rightarrow 1$. Thus in this limit of an infinite branching equilibrium constant, a pure sol phase is not stable. In Figure 5 the dependence of C_T^* on r is given, and the sol and gel regions are indicated.

Finally, we consider the general case $K_0 \neq K_1 \neq K_2$. Because of our nondimensionalization, we need only specify $r = K_2/K_1$, and

$$R \equiv K_0/K_1 \quad (27)$$

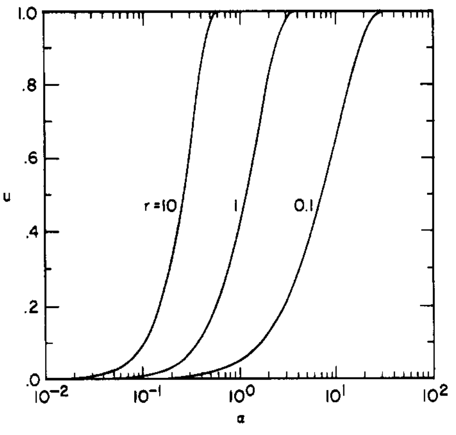

Figure 4. Plot of u vs. α with $\alpha_0 = \alpha$ and $r = 0.1$, 1, and 10. To obtain these graphs we solved eq 14 for the root with $0 \leq c \leq 1$ that satisfied the sum rule. This value of c was then substituted into eq 13a and 13b.

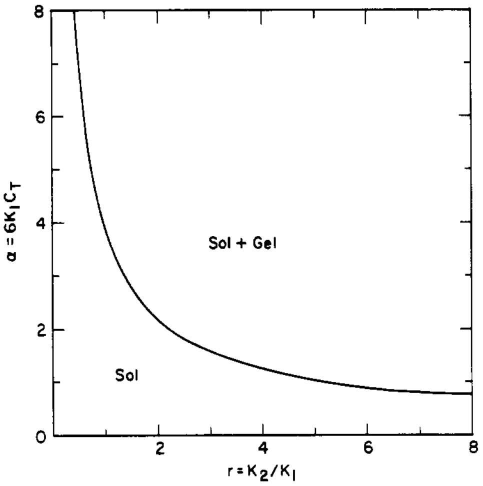

Figure 5. Nondimensional critical monomer concentration $\alpha^* = 6K_1C_T^*$ vs. r (solid line) for $\alpha_0 = \alpha$. For values of $\alpha > \alpha^*$, sol and gel regions coexist, whereas for values $\alpha < \alpha^*$, only sol exists.

Our previous example corresponds to $R = 1$. This general case interests us because we can use it to study the effect of initiation on gelation. We will consider K_1 to be fixed and view variations in $\alpha = 6K_1C_T$ as a variation in C_T and variations in R and r as variations in initiation, K_0, and branching, K_2, respectively.

Since u and q_0 are independent of α_0, eq 24 and 25 still hold. Substituting c^* given by eq 25 into the sum rule with $u = 1$, we find for $\alpha_0 \neq 0$ that

$$\alpha^* = (1 + r^{1/2})^{-1}(1 + R/r^{1/2}) + 3R/r \quad (28a)$$

and

$$c^* = [(1 + R/r^{1/2}) + (3R/r)(1 + r^{1/2})]^{-1} \quad (28b)$$

Because α^* is a monotonically increasing function of R, eq 28a makes the interesting prediction that decreasing the initiation equilibrium constant, K_0, with respect to the elongation equilibrium constant, K_1, decreases α^*. This effect can be substantial. For $r = 1$, $\alpha^* = 4$ when $R = 1$ and decreases to $\alpha^* = {}^1/_2$ when $R = 0$. Since $C_T^* = \alpha^*/(6K_1)$, this means that the critical monomer concentration required for gelation decreases as initiation becomes less likely. Conversely, increasing K_0 increases C_T^*.

In order to understand why gelation occurs at lower values of C_T as α_0 is decreased, we examine the aggregate size distribution, c_n. We first observe that in the limit $\alpha_0 = 0$, only monomer exists; i.e., $c_n = \delta_{n,1}$. For $\alpha_0 > 0$, but small, we can expand the monomer concentration c in a power series around one; i.e., $c = 1 - a_1\alpha_0 + \ldots$. Substituting this series for c into the quartic equation obtained from the sum rule, eq 14, we find a_1 is a positive function of α and β. Now we show that as α_0 decreases, the concentration of n-mer, c_n, for sufficiently large n increases, making gelation more likely. Formally, from eq 8, we can write

$$c_n = \Omega_n \alpha_0 c^n$$

where Ω_n is a function of α and β. Then

$$\frac{\mathrm{d}c_n}{\mathrm{d}\alpha_0} = \Omega_n c^n \left(1 + \frac{n\alpha_0}{c} \frac{\mathrm{d}c}{\mathrm{d}\alpha_0} \right)$$

For small α_0, i.e., when $c \cong 1 - a_1\alpha_0$,

$$\mathrm{d}c_n/\mathrm{d}\alpha_0 \cong \Omega_n c^n (1 - n a_1 \alpha_0)$$

In particular, for $n > N \equiv (a_1\alpha_0)^{-1}$

$$\mathrm{d}c_n/\mathrm{d}\alpha_0 < 0$$

Thus, as $\alpha_0 \rightarrow 0$, polymers of size greater than N grow in concentration, and polymers of size less than N decrease in concentration; i.e., the size distribution becomes bimodal.

As $\alpha_0 \rightarrow \infty$, one can show from eq 14 that $c \rightarrow (3\alpha_0/2)^{-1/2}$. Therefore, $c_n \rightarrow \Omega_n (3/2)^{-n/2} \alpha_0^{-n/2+1}$ for $n > 1$, and the only concentration that remains finite as $\alpha_0 \rightarrow \infty$ is the dimer concentration, $n = 2$. In general, as α_0 increases, small aggregates become favored over large ones. To overcome this and obtain a sol–gel phase transition, C_T must be raised to the value predicted by eq 28a.

Branched Polymers. Here we continue the study of the degree of branching begun earlier. First we calculate the average number of branch points per molecule. Let

$$\langle m \rangle \equiv \frac{\sum_{m=0}^{\infty} m b_m}{\sum_{m=0}^{\infty} b_m} = \frac{\sum_{m=0}^{\infty} m b_m}{q} \tag{29}$$

where b_m is given by eq 11. Although $\langle m \rangle$ can be computed directly by noting

$$\binom{2m}{m} = (-1)^m 2^{2m} \binom{-1/2}{m}$$

and using the identity

$$\sum_{m=0}^{\infty} \binom{2m}{m} x^{2m} = (1 - 4x^2)^{-1/2}$$

we compute $\langle m \rangle$ by generating function methods; i.e.

$$\langle m \rangle = \frac{1}{q(1,1)} \left. \frac{\partial q(z,\xi)}{\partial \xi} \right|_{z=1,\xi=1}$$

and find

$$\langle m \rangle = \frac{1}{q} \left(-2(q - c) + \frac{3\alpha_0 c q_0}{u} [1 - (1 - u)^{1/2}] \right) \tag{30}$$

where q, q_0, and u are defined by eq 13. At the gel point, $u = 1$ and $q = c(1 + \alpha_0 q_0)$. Thus

$$\langle m^* \rangle \equiv \langle m \rangle|_{u=1} = \frac{\alpha_0 q_0}{1 + \alpha_0 q_0} = \frac{R\alpha^* c^*}{1 + (R - 1)\alpha^* c^*}$$

According to eq 25, $\alpha^* c^* = (1 + r^{1/2})^{-1}$ and hence

$$\langle m^* \rangle = R/(R + r^{1/2}) \tag{31}$$

Thus when all sites are equireactive, $R = r = 1$, $\langle m^* \rangle = {}^1/_2$. This value of $\langle m^* \rangle$ is small because it is an average over all molecules in the system. It is therefore heavily influenced by the relatively high concentrations of monomers, dimers, and trimers which have no branch points. A more intuitive measure of the degree of branching is the fraction of polymer subunits that are branch points. In the branching process theory of polymerization this quantity is called p_3, the probability that a monomer has three sites bound.[3] Because we have nondimensionalized all variables by dividing by C_T, p_3 is given by

$$p_3 = \sum_{n,m} m b_m = \langle m \rangle q \tag{32}$$

At the gel point one finds

$$p_3{}^* = \frac{R r^{1/2}}{r + 3R + 4Rr^{1/2}} \tag{33}$$

Thus, with $r = R = 1$, $p_3{}^* = 1/8$; i.e., one out of every eight monomers is a branch point. Greater amounts of branching can be achieved at the gel point in the case of nonequireactivity. We find $p_3{}^*$ has a global maximum of ${}^1/_4$, which obtains in the limit of both r and R large.

Extensions Past the Gel Point. In the sol–gel coexistence region, $c^* \leq c$, a fraction f_s of the monomers will be in the sol phase. Thus, the sum rule, eq 12, which counts the total number of monomers in finite-sized aggregates, becomes

$$f_\mathrm{s} = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} n c_{n,m} = q(1 - 3q_0/c) + 3q_0 + 3[1 - (1 - u)^{1/2}]/2\beta \tag{34}$$

Defining the partition function, statistical factors, the monomer concentration, and the n-mer concentration for the sol phase as

$$q_\mathrm{s} = q/f_\mathrm{s} \tag{35a}$$

$$\alpha_{0\mathrm{s}} = \alpha_0 f_\mathrm{s} \tag{35b}$$

$$\alpha_\mathrm{s} = \alpha f_\mathrm{s} \tag{35c}$$

$$\beta_\mathrm{s} = \beta f_\mathrm{s} \tag{35d}$$

$$c_\mathrm{s} = c/f_\mathrm{s} \tag{35e}$$

$$c_{n\mathrm{s}} = c_n/f_\mathrm{s} \tag{35f}$$

$$c_{n,m\mathrm{s}} = c_{n,m}/f_\mathrm{s} \tag{35g}$$

we find the sum rule, eq 34, becomes

$$1 = q_\mathrm{s}(1 - 3q_{0\mathrm{s}}/c_\mathrm{s}) + 3q_{0\mathrm{s}} + 3[1 - (1 - u)^{1/2}]/2\beta_\mathrm{s} \tag{36}$$

Thus, in the sol–gel region, the description we have developed is still valid when applied only to molecules in the sol phase.

Equation of State for the Sol–Gel Coexistence Region. Past the gel point, the sum rule cannot be used to find the free monomer concentration in the sol, c_s, unless f_s is known. Consequently, an additional equation is needed to define the state of the system. Recall u monotonically increases from 0 as C_T is increased, reaching 1 at the gel point (see Figure 4). Thus, as a first ansatz, we shall assume u remains at 1 throughout the gel region. This we shall show is a generalization of the Stockmayer[2] postgel solution and reduces to it if we make the equivalent site approximation.

(i) Regaining the Stockmayer Postgel Distribution. When u sticks at 1, c_s and α_s stick at their critical values c^* and α^*. Thus, from eq 26

$$c_\mathrm{s} = r/(r + 4r^{1/2} + 3) \tag{37a}$$

and

$$\alpha_s = 1/r^{1/2} + 3/r \qquad (37b)$$

where for simplicity we have taken $\alpha_0 = \alpha$. Since $\alpha_s = \alpha f_s$

$$f_s = \frac{1}{\alpha}\left(\frac{1}{r^{1/2}} + \frac{3}{r}\right), \qquad \alpha > \alpha^* \qquad (38)$$

In Figure 6 we plot f_s vs. α for various values of r.

Once c_s and f_s are known, the aggregate size distribution of sol-phase molecules can be computed from eq 35f and 10.

$$c_{ns} = \frac{3}{f_s(n+1)(n+2)}\binom{2n}{n}\left(\frac{\alpha_s}{2}\right)^{n-1} c_s^{\,n} = \frac{c_n^*}{f_s}, \qquad n \geq 2 \qquad (39)$$

As is the case for the Stockmayer postgel solution, the postgel size distribution is simply a scaled version of the pregel distribution.

The partition function for the sol phase, q_s, satisfies the relationship

$$q_s = q/f_s$$

When $u = 1$, it follows from eq 2 and 35e that

$$q_s = c_s(1 + \alpha_0 q_0)$$

Using eq 3, 37a, and 37b and taking $\alpha_0 = \alpha$, we find

$$q_s = c_s(1 + 1/r^{1/2}) = r^{1/2}/(r^{1/2} + 3) \qquad (40)$$

To compare our results with those of Stockmayer, we need to consider the case when all sites are equivalent; i.e., $K_0 = K_1 = K_2$, or $r = 1$ and $R = 1$. When $r = 1$, eq 37, 38, and 40 imply that $c_s = {}^1/_8$, $\alpha_s = 4$, $f_s = 4/\alpha = 2/(3K_1C_T)$, and $q_s = {}^1/_4$.

In the postgel region Stockmayer[2] showed that

$$f_s = 4(1 - 3p/2) \qquad (41)$$

To obtain this result we must reinvestigate the definition of p, the extent of reaction, in the postgel region. Recall

$$p \equiv \frac{\text{total number of reacted sites}}{\text{total number of sites}}$$

If we let N be the total number of f-valent monomers and M be the total number of molecules in the system, then it is easy to show

$$p = (2/f)(1 - M/N) \qquad (42)$$

In the postgel region, the gel makes a negligible contribution to the value of M/N since M for the gel is of order 1.

In this paper we are only considering trivalent monomers, so $f = 3$. The nondimensional partition function

$$q = \sum_{n,m} c_{n,m} = \frac{\sum_{n,m} C_{n,m}}{C_T} = \frac{M}{N} \qquad (43)$$

Thus, using eq 35a and 42

$$p = (2/3)(1 - q) = (2/3)(1 - q_s f_s) \qquad (44)$$

Since $q_s = {}^1/_4$, in the postgel region

$$p = (2/3)(1 - f_s/4) \qquad (45)$$

This expression can be rearranged to give the Stockmayer result, eq 41. An alternative derivation of eq 45 is given in Appendix C.

(ii) Regaining the Flory Postgel Distribution. Choosing u to be

$$u = 2/(f_s^{\,\sigma} + f_s^{\,-\sigma}) \qquad (46)$$

with $\sigma = {}^1/_3$ gives the Flory[22] postgel solution for the concentration of n-mer in the sol. To show this directly is difficult. Instead, we shall adopt the Flory method of analytically continuing the pregel solution into the postgel region and show that eq 46 results.

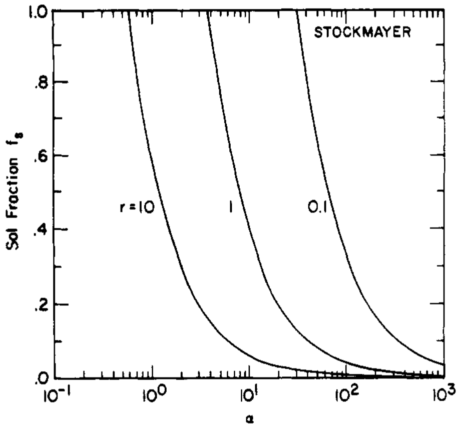

Figure 6. Sol fraction f_s vs. α for the Stockmayer postgel solution. Note that $f_s = 1$ for $\alpha \leq \alpha^*$. The three curves shown correspond to $\alpha > \alpha^*$, $R = 1$, and $r = K_2/K_1 = 0.1$, 1, and 10.

In the Flory procedure one assumes that the pregel equations for the concentration of n-mer apply in the postgel region and that the form of the extent of reaction remains the same. Thus, one assumes the concentration of monomer

$$c = (1 - p)^3 \qquad (47a)$$

with

$$p = 1 + \frac{1 - (1 + 8\beta)^{1/2}}{4\beta} \qquad (47b)$$

Further, the Flory result is based on the equivalent-site approximation: $r = 1$, $\alpha_0 = \alpha$. Under these conditions u is given by eq 22, and hence

$$u^{1/2} = 4\beta c/(1 - 4\beta c) \qquad (48)$$

Solving eq 47b for β and substituting it along with eq 47a into eq 48 give

$$u^{1/2} = \frac{2p(1-p)}{p^2 + (1-p)^2} \qquad (49)$$

Expressing

$$q_0 = c/(1 - 4\beta c)$$

and

$$q = c + \frac{\alpha c q_0}{u^2}[3u - 2 + 2(1-u)^{3/2}]$$

as functions of p and substituting into the sum rule, eq 34, yield

$$f_s = (1-p)^3/p^3 \qquad (50)$$

the result obtained by Flory.[22]

To verify our original claim that u is given by eq 46, substitute the solution of eq 50, $p = (1 + f_s^{1/3})^{-1}$, into eq 49.

Our formulation suggests a way to extent the Flory postgel solution to the case of nonequivalent sites. We assume eq 46 holds when $r \neq 1$. Further, when $r \neq 1$, eq 48 becomes

$$u = \left[\frac{r^{1/2}\alpha c}{1 - \alpha c}\right]^2$$

which, when equated to eq 46, yields an equation for c in

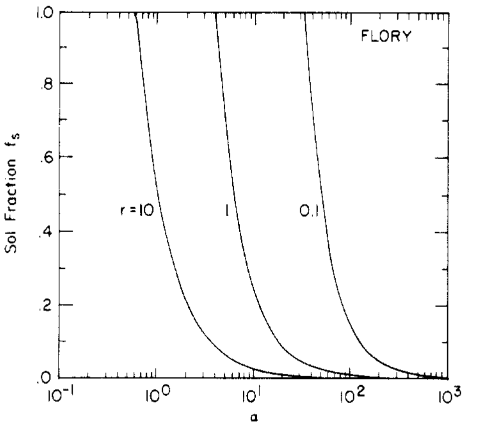

Figure 7. Same as Figure 6 except that the Flory postgel solution is illustrated.

terms of f_s. Substituting this expression for c into the equations for q_0, q, and u, and the sum rule, eq 34, we convert the sum rule into a transcendental equation for f_s and the parameters r and α. By solving this equation numerically, one can obtain f_s as a function of C_T. A graph of f_s vs. α for various values of r is shown in Figure 7.

Discussion

The random polycondensation of f-valent monomers into treelike structures has been thoroughly studied as a model system undergoing a sol–gel transformation. Here we have shown for the case $f = 3$ how one can relax the hypothesis of equireactivity of all sites by including first-shell substitution effects. As in recent work by Wiegel and Perelson[21] and van Dongen and Ernst[24] on rouleau formation and Goldstein and Perelson[23] on antigen–antibody reactions, initiation, elongation, and branching reactions are treated separately via the introduction of three equilibrium constants: K_i, $i = 0$, 1, and 2, where the subscript i denotes a reaction in which monomer binds to a chain subunit with i bound sites. Thus when $i = 0$, monomer adds to monomer; when $i = 1$, monomer adds to a singly bound subunit (i.e., a chain end); and when $i = 2$, monomer adds to a chain subunit bound at two places (i.e., an internal node) and converts it to a branch point.

Using a generating function method, we have explicitly constructed the equilibrium aggregate size distribution as a function of two variables: n, the number of subunits in the chain, and m, the number of branch points. As in the classical RA_3 model, our system exhibits a sol–gel transformation. We have derived a very simple criterion for gelation, $u = 1$, where u is the value of a special chain branching generating function $u(z,\xi)$ at $z = 1$, $\xi = 1$. When all sites are equireactive, $K_0 = K_1 = K_2$, our criterion reduces to the usual Flory–Stockmayer gelation criterion.

To extend our results past the gel point required the introduction of an additional equation of state from which the sol fraction, f_s, was derived. We showed that the hypothesis $u = 1$ throughout the gel region coupled with the equivalent-site hypothesis corresponds to the Stockmayer postgel solution, whereas the assumption $u = 2/(f_s^{1/3} + f_s^{-1/3})$ and the equivalent-site hypothesis leads to the Flory postgel solution. We also showed how both the Stockmayer and Flory postgel distributions can be generalized to systems without equireactivity. Further, our methods allow an entire family of postgel distributions characterized by the equation of state, $u = u(f_s)$.

Although our methods seem rather general, it is not clear how easy it will be to apply them to f-valent polycondensation with $f \geq 4$. For $f = 3$ we needed to solve a quadratic equation to find the generating function for trees with n units and m branch points. In the case of higher valence monomers, higher order algebraic equations will have to be dealt with.

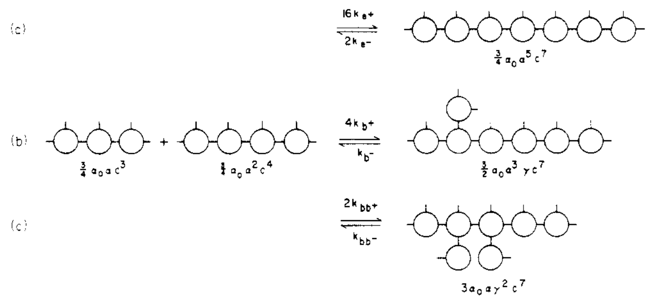

Figure 8. Examples of the three possible condensation reactions. (a) A typical elongation condensation reaction. Any of the four end free sites on the (3,0)-mer can react with any of the four end free sites on the (4,0)-mer. (By an end free site we mean a free site on a node of degree 1.) (b) A branching condensation reaction in which the number of branch points increases by 1. Shown is the case where the internal free site on the (3,0)-mer reacts with any of the four end free sites on the (4,0)-mer. (By an internal free site we mean a free site on a node of degree 2.) (c) A branching condensation reaction in which the number of branch points increases by 2. Shown is the case where the internal free site on the (3,0)-mer reacts with either of the two internal free sites on the (4,0)-mer. The reactions shown in (b) and (c) do not produce all possible (7,1)-mer and (7,2)-mer configurations. Thus the concentrations are not the same as those given in the text for (7,1)- and (7,2)-mers.

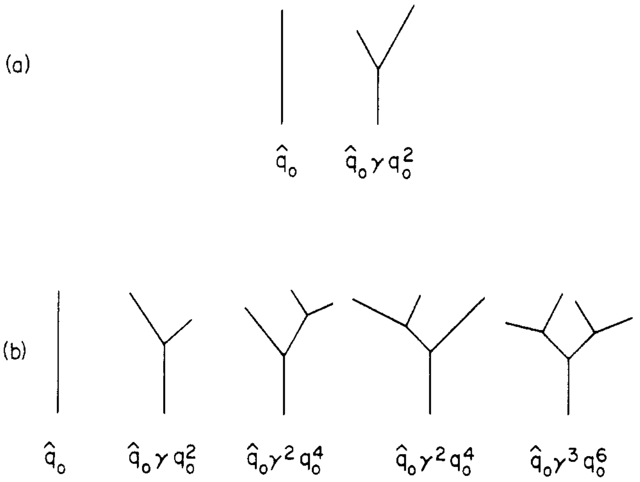

Figure 9. Schematic diagram of (a) trees of order 1 and (b) trees of order 2. Below each tree is written its contribution to the generating function. The trees of order 2 are generated by choosing either a linear chain or a linear chain that bifurcates into two trees of order 1. Using either of the two choices for a tree order 1 on each branch of the bifurcation leads to the four branched structures shown.

Acknowledgment. We thank Mathieu Ernst for his helpful comments on the manuscript.

Appendix A. Equilibrium Constants for Condensation Reactions

Let an (n,m)-mer be a polymer containing n trivalent monomers and having m branch points. Three types of condensation reactions are possible

$$(n,\ m) + (n',\ m') \rightleftarrows (n + n',\ m + m' + i), \qquad i = 0,\ 1,\ \text{and}\ 2$$

When $i = 0$ the number of branch points is conserved. We call this an elongation condensation reaction and denote its equilibrium constant by K_e. When $i = 1$ ($i = 2$) one (two) branch point(s) is (are) created. We call these reactions branching condensation reactions and denote their equilibrium constants by K_b ($i = 1$) and K_{bb} ($i = 2$). From the principle of detailed balance one can show that

$$K_e = K_1^2/K_0 \quad \text{(A.1)}$$

$$K_b = K_2K_1/K_0 \quad \text{(A.2)}$$

and

$$K_{bb} = K_2^2/K_0 \quad \text{(A.3)}$$

An example which makes these relationships clear is given in Figure 8.

When initiation is not distinguished from elongation, addition reactions are simply a special case of condensation reactions; i.e., when $K_0 = K_1$, one finds $K_e = K_1$ and $K_b = K_2$. Reactions in which two branch points are created cannot occur by addition and thus K_{bb} does not reduce to either K_1 or K_2.

Appendix B. Obtaining the Generating Function $q(z,\xi)$

In this appendix we show how to enumerate and weight all noncyclic aggregates formed from trivalent monomers. Our procedure, based on generating functions, is a modification of the method used by Goldstein and Perelson[23] for copolymers of bifunctional and trifunctional monomers. The method involves considering a special class of rooted trees, called planted trees (i.e., trees rooted at their ends) that can be drawn in the plane. Once we count and weight plane planted trees, it is an easy matter to count all possible noncyclic aggregates.[23]

In our derivation we will require the following generating functions: $q_0(z)$, the generating function for any linear section of a tree except the trunk (i.e., the planted section) containing $n \geq 1$ monomers; $\hat{q}_0(z)$, the generating function for a planted linear chain containing $n \geq 2$ monomers; $\hat{q}_k(z,\xi)$, the generating function for plane planted trees of order $k \geq 1$ containing $n \geq 2$ monomers and $m \leq 2k - 1$ branch points; $\hat{q}_p(z,\xi)$, the generating function for plane planted trees containing n monomers, $n \geq 2$, and m branch points; $q(z,\xi)$, the generating function for trees containing n monomers and m branch points; and $\hat{q}(z,\xi)$, the generating function for trees containing $n \geq 2$ monomers and m branch points.

We use a recursive method to find $\hat{q}_p(z,\xi)$. Let a plane planted tree of order 0 to be a linear segment, planted at one end, containing $n \geq 2$ monomers. The reason that we consider only trees with two or more monomers will become clear when we analyze branched structures. To count planted linear chains of size two or more, we note that the nondimensional equilibrium concentration of planted dimers is α_0c^2, where $\alpha_0 = 6K_0C_T$ and $c = C/C_T$. In a similar manner, we see that the nondimensional concentration of planted linear m-mers is $\alpha_0\alpha^{n-2}c^n$, where $\alpha = 6K_1C_T$. Thus

$$\hat{q}_0(z) = \alpha_0c^2z^2 + \alpha_0\alpha c^3z^3 + ... + \alpha_0\alpha^{n-2}c^nz^n + ...$$

For $\alpha cz < 1$, the sum converges and

$$\hat{q}_0(z) = \alpha_0c^2z^2/(1 - \alpha cz) \quad \text{(B.1)}$$

Let a plane planted tree of order 1 be either a plane planted tree of order 0 or a plane planted tree of order 0 that branches once, each branch being a linear chain (see Figure 9). To construct the generating function $\hat{q}_1(z,\xi)$ for plane planted trees of order 1, we begin counting with a rooted dimer. Either the chain constantly elongates and hence has generating function $\hat{q}_0(z)$ or it branches. To form a branch point, two monomers must add to the last monomer on an existing linear chain, contributing the factor $(\alpha cz)(\beta cz)$ to the generating function.

This procedure yields a branched structure, provided the initial planted chain is of size two or greater. [If the initial chain is of size 1, a trimer results that is not rooted at an end and hence is excluded from our counting procedure.] The generating function for a linear chain with a branch point having only monomers attached is $\hat{q}_0(z)\cdot\alpha\beta c^2\xi z^2$. Linear chains can grow from the branch point. The weight of an n-mer attached to the branch point is $\alpha^{n-1}c^nz^n$. Thus, the generating function for all plane planted trees with $n \geq 2$ monomers and one branch point is $\hat{q}_0(z)\alpha\beta\xi q_0^2(z)$, where

$$q_0(z) = cz/(1 - \alpha cz) \quad \text{(B.2)}$$

is the generating function for linear chains of size $n \geq 1$ emanating from a branch point. From Figure 9, we see

$$\hat{q}_1(z,\xi) = \hat{q}_0(z)[1 + \gamma\xi q_0^2(z)] \quad \text{(B.3)}$$

where

$$\gamma = \alpha\beta \quad \text{(B.4)}$$

is a *branching parameter.*

We now define a plane planted tree of order k containing $n \geq 2$ monomers to be either a planted linear chain with $n \geq 2$ monomers or a plane planted tree which begins with a planted linear chain of size $n \geq 2$ and then bifurcates into two plane planted trees, each of order $k - 1$ and containing $n \geq 1$ monomers. To illustrate, all plane planted trees of order 2 are shown in Figure 9. It follows from this figure that

$$\hat{q}_2(z,\xi) = \hat{q}_0(z)[1 + \gamma\xi q_0^2(z) + 2\gamma^2\xi^2q_0^4(z) + \gamma^3\xi^3q_0^6(z)] \quad \text{(B.5)}$$

In terms of $\hat{q}_1(z,\xi)$, eq B.3,

$$\hat{q}_2(z,\xi)/\hat{q}_0(z) = 1 + \gamma\xi q_0^2(z)[\hat{q}_1(z,\xi)/\hat{q}_0(z)]^2 \quad \text{(B.6)}$$

In general

$$\hat{q}_k(z,\xi)/\hat{q}_0(z) = 1 + \gamma\xi q_0^2(z)[\hat{q}_{k-1}(z,\xi)/\hat{q}_0(z)]^2 \quad \text{(B.7)}$$

As the index k is increased, plane planted trees with more and more branches are generated. In the limit as $k \to \infty$, all possible plane planted trees with $n \geq 2$ are generated so that

$$\hat{q}_p(z,\xi) = \lim_{k\to\infty} \hat{q}_k(z,\xi)$$

From eq B.7 we find $\hat{q}_p(z,\xi)$ must satisfy the equation

$$q_p(z,\xi) = q_0(z)[1 + \gamma\xi q_p(z,\xi)^2] \quad \text{(B.8)}$$

where

$$q_p(z,\xi) \equiv q_0(z)\hat{q}_p(z,\xi)/\hat{q}_0(z)$$

From eq B.1 and B.2

$$q_p(z,\xi) = \hat{q}_p(z,\xi)/(\alpha_0cz) \quad \text{(B.9)}$$

Of the two solutions to eq B.8 only one approaches $q_0(z)$ as $\gamma \to 0$. This solution, which is the one of interest, when substituted into eq B.9, yields

$$\hat{q}_p(z,\xi) = \frac{\alpha_0cz\{1 - [1 - 4\gamma\xi q_0(z)^2]^{1/2}\}}{2\gamma\xi q_0(z)} \quad \text{(B.10)}$$

To obtain $\hat{q}(z,\xi)$, we must correct $\hat{q}_p(z,\xi)$ for certain degeneracies. First, since we could have chosen any of the three sites on the initial monomer as the root, we multiply $\hat{q}_p(z,\xi)$ by three. Second, an aggregate planted at any site on a terminal subunit corresponds to the same physical object. We thus divide the statistical weight for a planted tree with m branch points by $2(m + 2)$, the number of free sites on terminal subunits that have been chosen as roots by our generating function method. This means that

$$\hat{q}(z,\xi) = \frac{3}{2\xi^2}\int_0^{\xi} \xi' \hat{q}_p(z,\xi')\,d\xi' \qquad (B.11)$$

Performing the integration, we find

$$\hat{q}(z,\xi) = \frac{3}{4}\frac{\alpha_0 cz}{\gamma\xi q_0(z)}\left\{1 - \frac{1}{6\gamma\xi q_0^{\,2}(z)}(1 - [1 - 4\gamma\xi q_0(z)^2]^{3/2})\right\} \qquad (B.12)$$

Finally, $q(z,\xi)$, the generating function for all aggregates with n monomers and m branch points is simply $\hat{q}(z,\xi)$ plus the monomer state, i.e.

$$q(z,\xi) = \hat{q}(z,\xi) + cz \qquad (B.13)$$

Introducing

$$u(z,\xi) = 4\gamma\xi q_0(z)^2 \qquad (B.14)$$

in eq B.12, we obtain eq 2 of the text.

Appendix C. Flory–Stockmayer Extent of Reaction

(a) Pregel. To establish the relation between our results and the Flory–Stockmayer results, we need to express the extent of reaction, p, in terms of the nondimensional equilibrium constant α or β. When all sites are equally reactive, $K_0 = K_1 = K_2 \equiv K$, and $\alpha_0 = \alpha = 4\beta$. Let S be the concentration of free sites on aggregates and let S_0 be the total concentration of sites. Then, by definition

$$p = (S_0 - S)/S_0 \qquad (C.1)$$

To find S, we note that

$$dS/dt = -kS^2 + k_-(S_0 - S)$$

and hence at equilibrium

$$KS^2 + S - S_0 = 0 \qquad (C.2)$$

where $K = k/k_-$. Solving eq C.2 and noting $KS_0 = 3KC_T = \alpha/2$, we find

$$\frac{S}{S_0} = \frac{-1 + (1 + 2\alpha)^{1/2}}{\alpha} \qquad (C.3)$$

and hence

$$p = \frac{1 + \alpha - (1 + 2\alpha)^{1/2}}{\alpha} \qquad (C.4)$$

Rewriting eq 15 in the text in terms of $\alpha = 4\beta$

$$c = 4\frac{(1 + \alpha/2)(1 + 2\alpha)^{1/2} - (1 + 3\alpha/2)}{\alpha^3}$$

it is easy to verify that

$$c = (1 - p)^3 = 2p(1 - p)/\alpha \qquad (C.5)$$

as stated in the text.

(b) Postgel. Stockmayer Postgel Extent of Reaction. In the postgel region we write eq C.1 as follows:

$$p = \frac{S_{0s} - S_s}{S_0} + \frac{S_{0g} - S_g}{S_0} \qquad (C.6)$$

where S_{0s} and S_{0g} are the total concentrations of sites in the sol and gel, respectively, and S_s and S_g are the concentrations of free sites in the sol and gel, respectively. Equation C.2 now holds only for the sol, so that eq C.3 becomes

$$\frac{S_s}{S_{0s}} = \frac{-1 + (1 + 2\alpha_s)^{1/2}}{\alpha_s} \qquad (C.7)$$

For an n-mer composed of 3-valent monomers with no rings the ratio of bound sites to total sites is $2(n - 1)/3n$. To describe the gel we take the limit, $n \to \infty$. From this argument it follows that

$$\frac{S_{0g} - S_g}{S_{0g}} = \frac{2}{3} \qquad (C.8)$$

Substituting eq C.7 and C.8 into C.6, we find

$$p = f_s\left[1 + \frac{1 - (1 + 2\alpha_s)^{1/2}}{\alpha_s}\right] + \frac{2}{3}(1 - f_s) \qquad (C.9)$$

where $f_s = S_{0s}/S_0$. In the postgel region, when all sites are equivalent, $\alpha_s = 4$ (cf. eq 37b), and eq C.9 becomes

$$p = \frac{f_s}{2} + \frac{2}{3}(1 - f_s) \qquad (C.10)$$

which is equivalent to eq 45.

Flory Postgel Extent of Reaction. Flory assumes that in the postgel region all sites, whether in the sol or in the gel, remain equally reactive, and hence eq C.4 continues to hold.

Appendix D. A Branching Process Derivation of the Gelation Criterion $u = 1$

The probability generating function $F_0(\Theta)$ for the number of offspring of a unit in the zeroth generation is

$$F_0(\Theta) = \sum_{k=0}^{3} p_k \Theta^k$$

where p_k, $k = 0, 1, 2, 3$, is the probability of a unit having k offspring. Gordon[3] shows that the weight-average degree of polymerization diverges when

$$F_0''(1) = F_0'(1) \qquad (D.1)$$

where the prime denotes differentiation with respect to Θ. Hence the criterion for gelation can be written as

$$p_1 = 3p_3 \qquad (D.2)$$

In order to compare this criterion with the criterion $u = 1$ we note that a tree with m branch points has $(m + 2)$ ends. Hence the fraction of singly bound polymer subunits, p_1, is

$$p_1 = \sum_{m=0}^{\infty} (m + 2)b_m - 2c \qquad (D.3)$$

where b_m is given by eq 11. As noted in eq 29 and 32

$$p_3 = \sum_{m=0}^{\infty} mb_m = \langle m\rangle q \qquad (D.4)$$

and

$$q = \sum_{m=0}^{\infty} b_m \qquad (D.5)$$

Hence

$$p_1 = p_3 + 2(q - c) \qquad (D.6)$$

At the gel point $p_1 = 3p_3$. So

$$p_3^* = q^* - c^*$$

or equivalently

$$\langle m^*\rangle q^* = q^* - c^* \qquad (D.7)$$

Substituting eq 30 into eq D.7, one finds

$$\frac{\alpha_0 c^* q_0}{u^*}(1 - (1 - u^*)^{1/2}) = q^* - c^*$$

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which upon substitution of eq 13c for q becomes

$$2(u^* - 1) + (2 - u^*)(1 - u^*)^{1/2} = 0 \tag{D.8}$$

The only value of u^*, $0 < u^* \leq 1$, which satisfies this equation is $u^* = 1$.

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Surface Pressure of Linear and Cyclic Poly(dimethylsiloxane) in the Transition Region

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ABSTRACT: Surface pressure π has been measured as a function of surface concentration c for monolayers of linear and cyclic poly(dimethylsiloxane) (PDMS) of molecular weight 730–14 800, spread on water and tricresyl phosphate at 26.0 °C. In the transition region where the surface pressure rises much more rapidly than proportional to the surface concentration, the findings for linear and cyclic PDMS were indistinguishable and independent of molecular weight. The findings in this region could be described as power laws with powers corresponding to scaling predictions for the semidilute region of concentrations (coil overlap accompanied by low overall polymer concentration) on near-Θ and fairly good surface solvents, respectively. However, the second virial coefficient of the surface pressure appeared to be negative for both liquid supports. These observations, the fact that the transition region occurred at quite high fractional surface coverage, and the instability of films from small oligomers suggest that recent interpretations of behavior in the transition region in terms of predictions for a semidilute surface solution are invalid in this case. The existence of a semidilute region of concentrations for polymer monolayers is uncertain in principle. In addition, the comparisons of linear and cyclic polymer above the overlap concentration c^* lead to the surprising conclusion that even for three-dimensional semidilute solutions, the ratio c/c^* is not a universal reduced concentration.

Introduction

When an uncharged amorphous high polymer is spread on a liquid support to form a monolayer, a surface pressure exists that is analogous to the osmotic pressure characteristic of three-dimensional solutions. Surface pressure is the amount by which the surface tension is reduced from that of the pure liquid. The dependence of the surface pressure on surface concentration is simpler than that found for many small molecules;[1,2] three regions can be qualitatively distinguished. In the dilute region, molecules interact sufficiently little that the surface pressure can be described by the first few terms of a virial expansion. The surface pressure in this region depends on the density of molecules, and hence on the molecular weight. At concentrations that correspond approximately to full coverage of the surface by polymer, there begins a plateau of relatively constant surface pressure. This is generally interpreted to reflect collapse of the monolayer to a three-dimensional state. Between these extremes, a transition region is observed. Here the surface pressure rises much more rapidly than proportional to the surface concentration and is independent of molecular weight.

In the transition region, the surface pressure π has been found to follow a power-law dependence on the surface concentration c of polymer.[3–5,52] This behavior has been interpreted[3–5,52] as reflecting a scaling law[6,7] for a semidilute region:

$$\pi/RT = kc^m \tag{1}$$

Here R is the gas constant, T the absolute temperature, k a prefactor of unspecified magnitude, and m a power that depends on the quality of what is considered to be the surface solvent. The value of m is $2\nu/(2\nu - 1)$, where ν is the power of molecular weight to which a two-dimensional polymer coil's radius of gyration is proportional at infinite dilution. The power ν is thought to be approximately 0.75 on a good solvent[8] and approximately 0.505 on a Θ solvent.[9] The surface pressure should thus be proportional to approximately the 3rd power of surface concentration when the polymer is spread on a good surface solvent and approximately the 101st power when it is spread on a Θ solvent. Water at 16.5 °C was thus inferred to be a good surface solvent for poly(vinyl acetate) and nearly a Θ solvent for poly(methyl methacrylate),[3] while a transition from Θ solvent to good solvent was reported for water

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