

Gelation in Multiple Link System of the $R-A_g+R-B_{f-g}$ Model: To Find a Neat Solution for Cyclic Concentration

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ABSTRACT: The preceding theory of gelation is extended to the multilink system of the $R-A_g+R-B_{f-g}$ model, where the branching process proceeds forming junction points each comprising of $J/2$ A FU's and $J/2$ B FU's. We show that there exists a neat solution of the ring concentration for this generalized system; the mathematics is identical with the previous finding, but the expression is greatly simplified. Making use of this result together with the random distribution assumption of cyclic bonds, we derive the closed expression of the gel point for this new gelling system which is expected to have wider application. [doi:10.1295/polymj.PJ2006061]

KEY WORDS Neat Solution of Ring Concentration / Random Distribution Assumption / Mixing System / Gel Point /

In this report, we extend the preceding theory of gelation to the multiple link system¹ of the $R-A_g+R-B_{f-g}$ model. In particular, we derive the neat solution of the concentration of cyclic species. The result is identical with the preceding work,² but the mathematical expression is greatly simplified. With the help of this result, we derive the gel point formula, which is expected to have wider application to inorganic polymer systems such as polysilazane as biocompatible materials.

It was observed earlier that primary amines and dichloro silane derivatives undergo the aminolysis to yield cyclic compounds, exclusively. Thus it was expected that the corresponding polyfunctional substances should yield polymeric silazanes comprising of the cyclic structures as junction points (Figure 1). Fink³ showed this, through the synthesis of various Si-N high polymers. This is a typical example of the $R-A_g+R-B_{f-g}$ multilink polymerization to be discussed in this paper.

We re-examine, from new points of view, the fundamental equations which have frequently appeared in the theory of gelation, but have been used without proofs: We will give mathematical proofs to those fundamental

equations and lay those on the solid foundation.

In common with all other papers of this series,² we push forward our discussion on the basis of the following three principles and one assumption:

(1) The gel point is divided into the two terms

$$D_c = D(\text{inter}) + D(\text{ring}). \quad (1)$$

(2) The total ring concentration, $[I]$, is independent of the initial monomer concentration, C , and is a function of D (the extent of reaction) alone.

(3) Branched molecules behave ideally at $C = \infty$.

(4) Assumption I: Cyclic bonds distribute randomly over all bonds. Introducing Assumption I is important, since it reduces an, otherwise, intrinsically insoluble problem of polymer physics to an elementary mathematical exercise, leading us to the simple relations: $D(\text{inter}) = D_{co}$ and $D(\text{ring}) = p_R$, namely,

$$D_c = D_{co} + p_R. \quad (2)$$

In eq 2, D_{co} denotes the Flory's classic gel point⁴ and p_R the fraction of cyclic bonds to the total possible bonds. Since p_R is a function of D_c , eq 2 is an implicit function of D_c . Now the gel point problem is analytic and yields neat solutions. The physical meaning of

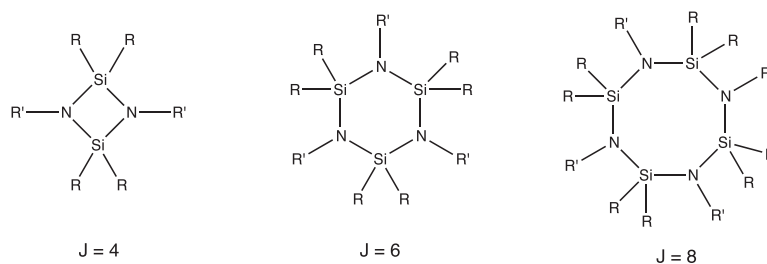


Figure 1. Cyclosilazanes. Typical $R-A_g+R-B_{f-g}$ type junctions.

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eq 2 is very clear: Cyclic bonds simply waste functional units (FU), making no contribution to the growth of molecules, so the gel point is exactly equal to the point where the fraction of intermolecular bonds attains the ideal gel point; *i.e.*, $D(\text{inter}) \rightarrow D_{co}$ as $D \rightarrow D_c$. By eq 2, the problem of finding the gel point reduces to the problem of expressing p_R in terms of D_c .

THEORETICAL

Derivation of Eq 2

Consider a mixing system comprised of two different type of monomer units, $\{g_i M_{A_i}\}$ and $\{(f - g)_j M_{B_j}\}$, where M_{A_i} and M_{B_j} are the mole numbers^{††} of the A and B type monomers, respectively; g_i and $(f - g)_j$ are the corresponding functionalities of the positive integers (1, 2, 3, ...). Let J be the number of FU's necessary to form a junction point on which the two types of the FU's are situated alternately. By the nature of the R-A_g+R-B_{f-g} model, J must be an even integer. Then it follows that unit reaction occurs through the merger of $J/2$ A FU's and $J/2$ B FU's, and $J - 1$ branches arise. The familiar bimolecular reaction corresponds to the special case of $J = 2$.

We seek the probability, α , that a given FU on a R-A_g branching unit leads, *via* R-B_{f-g} units, to the next R-A_g unit. This is an application of the first-success problem in statistics, the general permutation being AA-(BB)_n-AA ($n = 0 \sim \infty$). Let $P(Z|X)$ be a conditional probability defined by $P(Z|X) = P(Z \cap X)/P(X)$, where X is a set of all bonds and Z is a set of all cyclic

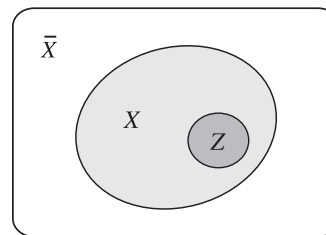


Figure 2. A set of all possible bonds $X = \{\text{all bonds}\}$, $Z = \{\text{cyclic bonds}\}$.

bonds, so that $P(Z|X) = p_R/D_A$ with D_A being the extent of reaction of the A FU (Figure 2). It is clear that for $n = 0$:

$$\alpha_0 = D_A \left(\frac{J}{2} - 1 \right) (1 - P(Z|X)) (\langle g_w \rangle - 1);$$

for $n = \ell$ ($\ell = 1, 2, 3, \dots$):

$$\alpha_\ell = D_A \left(\frac{J}{2} \right) (1 - P(Z|X)) (\langle (f - g)_w \rangle - 1) \times D_B \mathcal{J}^{\ell-1} \left(\frac{J}{2} \right) (1 - P(Z|X)) (\langle g_w \rangle - 1),$$

where $\mathcal{J} = (\frac{J}{2} - 1)(1 - P(Z|X))(\langle (f - g)_w \rangle - 1)D_B$ with D_B being the extent of reaction of the B FU and the symbol $\langle \rangle_w$ represents a weight average quantity defined by, for instance, $\langle g_w \rangle = \sum_i g_i^2 M_{A_i} / \sum_i g_i M_{A_i}$, etc. The probability, α , is obtained by summing up all these terms; *i.e.*, $\alpha = \sum_{\ell=0}^{\infty} \alpha_\ell$. When α exceeds the critical value, $\alpha_c = 1$, an infinite network should arise, so the gel point is

$$\alpha_c = D_A \left\{ \left(\frac{J}{2} - 1 \right) (1 - P(Z|X)) (\langle g_w \rangle - 1) + \frac{\left(\frac{J}{2} \right)^2 (1 - P(Z|X))^2 (\langle g_w \rangle - 1) (\langle (f - g)_w \rangle - 1) D_B}{1 - \mathcal{J}} \right\} = 1. \quad (3)$$

Since $P(Z|X) = p_R/D_A$, eq 3 becomes

$$s(D_{Ac} - p_R)^2 + t(D_{Ac} - p_R) - 1 = 0, \quad (4)$$

with

$$s = (J - 1) (\langle g_w \rangle - 1) (\langle (f - g)_w \rangle - 1) / \kappa,$$

$$t = \left(\frac{J}{2} - 1 \right) \{ (\langle g_w \rangle - 1) + (\langle (f - g)_w \rangle - 1) / \kappa \},$$

and $\kappa = \sum_j (f - g)_j M_{B_j} / \sum_i g_i M_{A_i}$, the relative mole number of B FU to A FU. Solving eq 4, we arrive at the relationship of eq 2:

$$D_{Ac} = \frac{\sqrt{t^2 + 4s} - t}{2s} + p_R. \quad (5)$$

^{††}Monomer number divided by the Avogadro number.

The first term of eq 5 represents the ideal gel point, D_{Ac0} . For $J = 2$, $t = 0$ and we recover the familiar result:²

$$D_{Ac0} = \sqrt{\frac{\kappa}{(\langle g_w \rangle - 1) (\langle (f - g)_w \rangle - 1)}}. \quad (6)$$

Cluster Profile in the R-A_g+R-B_{f-g} Model

We seek the total number of FU's in the n th generation of a mean cluster without rings. First we consider the homogeneous mixture of the R-A_g+R-B_{f-g} model. Consider an m Tree that has m unreacted A-Type FU's on the root (1st generation: Figure 3). Let $N(F)_n$ be the number of FU's in the n th generation. It is clear that

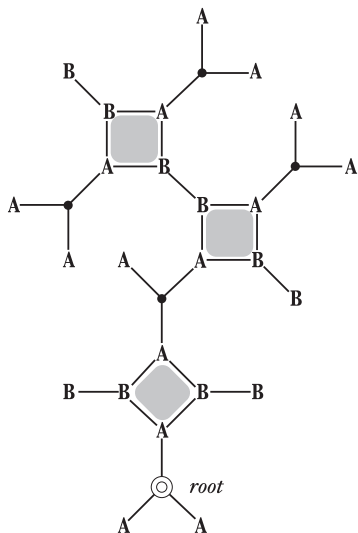


Figure 3. Representation of the $R-A_g+R-B_{f-g}$ multiple branching of $g = 3, f - g = 2$ and $J = 4$. Shaded moieties represent junction points. In this case, $m = 2$.

$$\begin{aligned}
 N(F)_1 &= g - m; \\
 N(F)_2 &= (g - m) \left\{ \left(\frac{J}{2} - 1 \right) (g - 1) + \frac{J}{2} (f - g - 1) \right\}; \\
 N(F)_3 &= (g - m) \left\{ \left(\frac{J}{2} - 1 \right) (g - 1) D_A \left[\left(\frac{J}{2} - 1 \right) \right. \right. \\
 &\quad \times (g - 1) + \left. \left. \frac{J}{2} (f - g - 1) \right] + \frac{J}{2} (f - g - 1) \right. \\
 &\quad \times \left. D_B \left[\frac{J}{2} (g - 1) + \left(\frac{J}{2} - 1 \right) (f - g - 1) \right] \right\}; \\
 &\dots \\
 &\dots
 \end{aligned}$$

In general one can write

$$\begin{aligned}
 N(F)_n &= (g - m) [a_n (g - 1) + b_n (f - g - 1)]; \quad (7) \\
 N(F)_{n+1} &= (g - m) \left\{ a_n (g - 1) D_A \left[\left(\frac{J}{2} - 1 \right) (g - 1) \right. \right. \\
 &\quad \left. \left. + \frac{J}{2} (f - g - 1) \right] + b_n (f - g - 1) D_B \right. \\
 &\quad \times \left. \left[\frac{J}{2} (g - 1) + \left(\frac{J}{2} - 1 \right) (f - g - 1) \right] \right\},
 \end{aligned}$$

or

$$\begin{aligned}
 N(F)_{n+1} &= (g - m) [a_{n+1} (g - 1) \\
 &\quad + b_{n+1} (f - g - 1)], \quad (8)
 \end{aligned}$$

with

$$\begin{aligned}
 a_{n+1} &= \left(\frac{J}{2} - 1 \right) (g - 1) D_A \\
 &\quad \cdot a_n + \frac{J}{2} (f - g - 1) D_B \cdot b_n; \\
 b_{n+1} &= \frac{J}{2} (g - 1) D_A \\
 &\quad \cdot a_n + \left(\frac{J}{2} - 1 \right) (f - g - 1) D_B \cdot b_n. \quad (9)
 \end{aligned}$$

Eq 9 satisfies the matrices:

$$\begin{pmatrix} a_{n+1} \\ b_{n+1} \end{pmatrix} = \begin{pmatrix} \epsilon_{11} & \epsilon_{12} \\ \epsilon_{21} & \epsilon_{22} \end{pmatrix} \begin{pmatrix} a_n \\ b_n \end{pmatrix}. \quad (10)$$

Here

$$\begin{aligned}
 \epsilon_{11} &= \left(\frac{J}{2} - 1 \right) (g - 1) D_A; \quad \epsilon_{12} = \frac{J}{2} (f - g - 1) D_B; \\
 \epsilon_{21} &= \frac{J}{2} (g - 1) D_A; \quad \epsilon_{22} = \left(\frac{J}{2} - 1 \right) (f - g - 1) D_B,
 \end{aligned}$$

and

$$\begin{aligned}
 (a_2, b_2) &= \left(\frac{J}{2} - 1, \frac{J}{2} \right); \\
 (a_3, b_3) &= \left(\left(\frac{J}{2} - 1 \right)^2 (g - 1) D_A + \left(\frac{J}{2} \right)^2 (f - g - 1) \right. \\
 &\quad \times \left. D_B, \frac{J}{2} \left(\frac{J}{2} - 1 \right) [(g - 1) D_A + (f - g - 1) D_B] \right);
 \end{aligned}$$

Let us write eq 10 in the form:

$$\mathbb{N}_{n+1} = \mathbb{A} \cdot \mathbb{N}_n. \quad (11)$$

To find the solution, transform eq 11 as

$$\mathbb{N}_n = \mathbb{A}^{n-2} \cdot \mathbb{N}_2. \quad (12)$$

Applying the Cayley-Hamilton theorem to eq 12, one has

$$\begin{pmatrix} a_n \\ b_n \end{pmatrix} = \begin{pmatrix} \left(\frac{J}{2} - 1 \right) \left[\frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{11} + \frac{\alpha^{n-2} \beta - \alpha \beta^{n-2}}{\beta - \alpha} \right] + \left(\frac{J}{2} \right) \frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{12} \\ \left(\frac{J}{2} - 1 \right) \frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{21} + \frac{J}{2} \left[\frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{22} + \frac{\alpha^{n-2} \beta - \alpha \beta^{n-2}}{\beta - \alpha} \right] \end{pmatrix}, \quad (13)$$

where α and β are the eigenvalues of the determinant: $\det(\mathbb{A} - \lambda \mathbb{E}) = 0$, and $\alpha \geq \beta$. From eq 7, the total number of FU's of the tree, therefore, can be expressed in the form:

$$N(F) = \sum_{n=1}^{\infty} N(F)_n = \frac{c_1}{1 - \alpha} + \frac{c_2}{1 - \beta}. \quad (14)$$

Clearly an infinite gel must appear at $\alpha = 1$ or $\beta = 1$, but it can be proven rigorously that β is a negative quantity ($\beta \leq 0$) for all $J \geq 1$, so that the gelation should occur at

$$\alpha = \frac{1}{2} \left[\epsilon_{11} + \epsilon_{22} + \sqrt{(\epsilon_{11} + \epsilon_{22})^2 - 4(\epsilon_{11}\epsilon_{22} - \epsilon_{12}\epsilon_{21})} \right] = 1, \quad (15)$$

which gives $\epsilon_{11} + \epsilon_{22} - \epsilon_{11}\epsilon_{22} + \epsilon_{12}\epsilon_{21} = 1$. With the help of eq 10 and $D_A/D_B = \kappa$, one has

$$(J-1)[(g-1)(f-g-1)/\kappa]D_{Ac}^2 + \left(\frac{J}{2} - 1\right) \times [(g-1) + (f-g-1)/\kappa]D_{Ac} - 1 = 0. \quad (16)$$

Eq 16 is the critical condition for the ideal tree model with no rings, and corresponds to the $P(Z|X) = 0$ (no rings) case in eq 4. The result also agrees with the Tanaka finding for a more general case,¹ if we identify our notation with his:

Table I. One-to-one correspondence of notation

Tanaka	This work
f_w	$\langle g_w \rangle$
g_w	$\langle (f-g)_w \rangle$
$\bar{\mu}_{A,A}$	$1 - D_A + (\frac{J}{2})D_A$
$\bar{\mu}_{B,B}$	$1 - D_B + (\frac{J}{2})D_B$
$\bar{\mu}_{A,B}$	$1 - D_A + (\frac{J}{2} + 1)D_A$
$\bar{\mu}_{B,A}$	$1 - D_B + (\frac{J}{2} + 1)D_B$

As expected, for $J = 2$, eq 16 reduces to the familiar result:

$$[(g-1)(f-g-1)/\kappa]D_{Ac}^2 = 1. \quad (17)$$

The extension of the above discussion to the mixing system of $\{g_i M_{A_i}\}$ and $\{(f-g)_j M_{B_j}\}$ is easy; *i.e.*, it can be accomplished simply by the transformation:

$$g - m \rightarrow g_i - m; \quad g \rightarrow \langle g_w \rangle; \quad f - g \rightarrow \langle (f-g)_w \rangle. \quad (18)$$

The extension to the system with ring formation is also straightforward. Note that the D_{Ac} in eq 16 represents the ideal gel point, while by eq 2, $D_{co} = D_c - p_R$. Thus substituting this into eq 16 together with the use of eq 18, one has

$$s(D_{Ac} - p_R)^2 + t(D_{Ac} - p_R) - 1 = 0, \quad (19)$$

which is just eq 4 in the preceding section, with s and t having the same meanings as given in eq 4.

Estimation of Ring Concentration

To derive the concentration of cyclic species in polymer solutions,^{2,5} consider the transition probab-

ity in the unit reaction. Let $p(\text{ring } j)$ be the probability that one functional unit (FU) on a j -chain jumps to form a j -ring, and $p(\text{inter})$ the probability that the FU jumps to form an intermolecular bond, where the j -chain and the j -ring denote a chain and a ring comprised of j repeating units, respectively. Since the reaction must be either the ring formation or the intermolecular reaction, one must have

$$p(\text{inter}) + \sum_{j=1}^{\infty} p(\text{ring } j) = 1. \quad (20)$$

These quantities can be expressed, using the rate equations, say, in the form:

$$\sum_{j=1}^{\infty} p(\text{ring } j) = \sum_{j=1}^{\infty} \left(\frac{v_{R_j}}{v_L + v_R} \right), \quad (21)$$

where v_L denotes the velocity of the intermolecular reaction and v_{R_j} that of the j -ring formation, and $v_R = \sum_j v_{R_j}$, as defined earlier.² Note that the $p(\text{ring } j)$ can be equated with the number fraction of a j -ring to be formed during the unit reaction, δu , and is generally a function of D . The total number of j -rings to be formed is, therefore, calculated by taking the summation:

$$N_{R_j} = \int p(\text{ring } j) \cdot \delta u. \quad (22)$$

We derive the expression of the ring concentration in the asymptotic limit of $C \rightarrow \infty$, where the relative frequency of cyclization to the intermolecular reaction is negligible. Experiments have shown that $v_L \gg v_R$ for sufficient high concentration, so that the approximation

$$p(\text{ring } j) = v_{R_j}/(v_L + v_R) \doteq v_{R_j}/v_L, \quad (23)$$

is valid. Substituting eq 23 into eq 22, one has

$$N_{R_j} \doteq \int (v_{R_j}/v_L) \cdot \delta u. \quad (24)$$

As discussed earlier,² as $C \rightarrow \infty$, the excluded volume effects are expected to vanish, then one can make use of the ideal behavior of branched molecules with no rings and no excluded volume effects (the tree approximation). Note that the reaction proceeds by way of the merger of J FU's; the familiar polymerization reaction is a special case of $J = 2$. Take notice of A-type FU's and one has the equality, $\delta D_A = (J/2)\delta u / \sum_i g_i M_{A_i}$, because for every unit reaction, $J/2$ A FU's are consumed. Thus

$$N_{R_j} = \frac{2 \sum_i g_i M_{A_i}}{J} \int (v_{R_j}/v_L) \cdot \delta D_A. \quad (25)$$

This formula is frequently used as a basic equation to derive a closed solution of the ring concentration.

In order to express v_{R_j} with experimentally measurable quantities, we must evaluate the total number, ϕ_j , of chances of the j -ring formation. Let \mathcal{P} be the probability that one end of a j -chain enters the small volume v around the other end. To avoid complication, let us solve a special case in which an A–A chain and a B–B chain have an equal length and backbone so that one can use the probability, \mathcal{P} , common to all j -chains with different permutations of, say, AA–AA–AA, AA–BB–AA and so forth. Let v_j be the number of cyclic bonds derived from j -ring formation. Clearly the velocity, \dot{v}_j , of the formation is of the form:

$$v_{R_j} = \dot{v}_j \propto \mathcal{P}\phi_j + \mathcal{O}, \quad (26)$$

where \mathcal{O} represents the higher order cyclization (dual, triple, ...) which becomes less probable as $C \rightarrow \infty$. To carry out the rigorous calculation of v_{R_j} , ϕ_j must be evaluated for each chain species, namely, $\phi_j = \phi_{jAA} + \phi_{jAB} + \phi_{jBB}$. According to eqs 7 and 18, it

follows that $N(A)_j = (g_i - m)a_j(\langle g_w \rangle - 1)$. The total number of AA chains is then

$$\begin{aligned} \phi_{jAA} = & \frac{1}{2} \sum_i M_{A_i} \sum_{m=0}^{g_i} m \binom{g_i}{m} (1 - D_A)^m D_A^{g_i - m} \\ & \times (g_i - m)a_j(\langle g_w \rangle - 1)(1 - D_A), \end{aligned} \quad (27)$$

so that

$$\phi_{jAA} = \frac{1}{2} \sum_i M_{A_i} g_i (g_i - 1) a_j (\langle g_w \rangle - 1) D_A (1 - D_A)^2. \quad (28)$$

By the symmetry of AA and BB, we have for ϕ_{jBB}

$$\begin{aligned} \phi_{jBB} = & \frac{1}{2} \sum_k M_{B_k} (f - g)_k ((f - g)_k - 1) \\ & \times b'_j (\langle (f - g)_w \rangle - 1) D_B (1 - D_B)^2, \end{aligned} \quad (29)$$

but b'_j is one of the solutions of the form:

$$\begin{pmatrix} a'_n \\ b'_n \end{pmatrix} = \begin{pmatrix} \frac{J}{2} \left[\frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{11} + \frac{\alpha^{n-2} \beta - \alpha \beta^{n-2}}{\beta - \alpha} \right] + \left(\frac{J}{2} - 1 \right) \frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{12} \\ \left(\frac{J}{2} \right) \frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{21} + \left(\frac{J}{2} - 1 \right) \left[\frac{\beta^{n-2} - \alpha^{n-2}}{\beta - \alpha} \epsilon_{22} + \frac{\alpha^{n-2} \beta - \alpha \beta^{n-2}}{\beta - \alpha} \right] \end{pmatrix}. \quad (30)$$

For ϕ_{jAB} , since $N(B)_j = (g_i - m)b_j(\langle (f - g)_w \rangle - 1)$, we have

$$\begin{aligned} \phi_{jAB} = & \sum_i M_{A_i} \sum_{m=0}^{g_i} m \binom{g_i}{m} (1 - D_A)^m D_A^{g_i - m} (g_i - m) \\ & \times b_j (\langle (f - g)_w \rangle - 1) (1 - D_B), \end{aligned} \quad (31)$$

so that

$$\begin{aligned} \phi_{jAB} = & \sum_i M_{A_i} g_i (g_i - 1) b_j (\langle (f - g)_w \rangle - 1) \\ & \times D_A (1 - D_A) (1 - D_B). \end{aligned} \quad (32)$$

Now the unit reaction takes place between $J/2$ A FU's and $J/2$ B's. There are, in general, $\binom{N}{J}$ ways to choose J units from N units. If N is a large number and $N \gg J$, then it follows that $\binom{N}{J} \cong N^J / J!$. And thus

$$\begin{aligned} \dot{v}_{jAA} = & I \mathcal{P} \phi_{jAA} \frac{\left\{ \sum_i g_i M_{A_i} (1 - D_A) \right\}^{J/2-2}}{\left(\frac{J}{2} - 2 \right)!} \\ & \times \frac{\left\{ \sum_j (f - g)_j M_{B_j} (1 - D_B) \right\}^{J/2}}{\left(\frac{J}{2} \right)!} \left(\frac{v}{V} \right)^{J-2}, \end{aligned} \quad (33)$$

$$\dot{v}_{jAB} = I \mathcal{P} \phi_{jAB} \frac{\left\{ \sum_i g_i M_{A_i} (1 - D_A) \right\}^{J/2-1}}{\left(\frac{J}{2} - 1 \right)!}$$

$$\times \frac{\left\{ \sum_j (f - g)_j M_{B_j} (1 - D_B) \right\}^{J/2-1}}{\left(\frac{J}{2} - 1 \right)!} \left(\frac{v}{V} \right)^{J-2}, \quad (34)$$

$$\begin{aligned} \dot{v}_{jBB} = & I \mathcal{P} \phi_{jBB} \frac{\left\{ \sum_i g_i M_{A_i} (1 - D_A) \right\}^{J/2}}{\left(\frac{J}{2} \right)!} \\ & \times \frac{\left\{ \sum_j (f - g)_j M_{B_j} (1 - D_B) \right\}^{J/2-2}}{\left(\frac{J}{2} - 2 \right)!} \left(\frac{v}{V} \right)^{J-2}, \end{aligned} \quad (35)$$

where I is a constant and v/V represents the probability that a FU enters a small volume, v , around another FU. The v_L , on the other hand, has the form:

$$\begin{aligned} v_L = & I \frac{\left\{ \sum_i g_i M_{A_i} (1 - D_A) \right\}^{J/2}}{\left(\frac{J}{2} \right)!} \\ & \times \frac{\left\{ \sum_j (f - g)_j M_{B_j} (1 - D_B) \right\}^{J/2}}{\left(\frac{J}{2} \right)!} \left(\frac{v}{V} \right)^{J-1}, \end{aligned} \quad (36)$$

It is clear that one can put $a_j = \mu_{a_j} D_A^{j-2}$, $b_j = \mu_{b_j} D_A^{j-2}$

and $b'_j = \mu b'_j D_A^{j-2}$, with μ being a constant independent of D . Since, as $C \rightarrow \infty$,

$$p(\text{ring } j) \rightarrow \frac{\dot{v}_j}{v_L},$$

where $\dot{v}_j = \dot{v}_{jAA} + \dot{v}_{jAB} + \dot{v}_{jBB}$, substituting the above relations into eq 25 and putting $[\Gamma] = \sum_{j=1}^{\infty} N_{R_j}/V$, one obtains

$$[\Gamma]_{C \rightarrow \infty} = \sum_{j=1}^{\infty} \varphi_j \frac{1}{2j} \left\{ \left(\frac{1}{2}t - \sqrt{s + \left(\frac{1}{2}t\right)^2} \right)^j + \left(\frac{1}{2}t + \sqrt{s + \left(\frac{1}{2}t\right)^2} \right)^j \right\} D_A^j, \quad (37)$$

where $\varphi_j = \mathcal{P}/v$ is the relative cyclization frequency introduced earlier.⁵ One can check the soundness of eq 37. As soon as the gel point is passed, the production of rings is expected to diverge. Thus, taking account of the boundary condition, $0 \leq D_A \leq 1$, one has for $D_A = D_{Ac}$

$$\left(\frac{1}{2}t + \sqrt{s + \left(\frac{1}{2}t\right)^2} \right) D_{Ac} = 1 \quad (38)$$

which gives

$$D_{Ac} = \frac{\sqrt{t^2 + 4s} - t}{2s}, \quad (39)$$

in agreement with the result mentioned in eqs 5 and 16. When $J = 2$, $t = 0$. Then altering the index of the relative cyclization frequency as $\varphi_{2k} \rightarrow \varphi_k$ (see Appendix 1), eq 37 reduces to the known result:^{2,5}

$$[\Gamma]_{C \rightarrow \infty} = \sum_{j=1}^{\infty} \varphi_j \frac{1}{2j} [(\langle g_w \rangle - 1) \times ((f - g)_w - 1) D_A^2 / \kappa]^j. \quad (40)$$

It will be useful to examine the functional behavior of the term $\{\cdot \cdot \cdot\}$ in eq 37. To do so, let $\zeta(j) = \frac{1}{2} \{\cdot \cdot \cdot\} D_A^j$. In Figure 4, $\zeta(j)$ is plotted as a function of D_A and j (generation) for a special case of $J = 4$, $\langle g_w \rangle = 3$, $\langle (f - g)_w \rangle = 2$, and $\kappa = 1$. As one can see, $\zeta(j)$ is finite for all j 's for $D_A \leq D_{Ac} = \frac{1}{12}(-3 + \sqrt{33})$, but diverges strongly for $D_A > D_{Ac}$. Important is the fact that eq 37 is convergent at $D_A = D_{Ac}$.

The physical meaning of Figure 4 is comprehensible from the mathematical form of $\zeta(j)$. As $D_A \rightarrow D_{Ac}$, it follows that

$$\zeta(j) \rightarrow \frac{1}{2} \left[\left(\frac{\frac{1}{2}t - \sqrt{s + \left(\frac{1}{2}t\right)^2}}{\frac{1}{2}t + \sqrt{s + \left(\frac{1}{2}t\right)^2}} + 1 \right)^j \right]. \quad (41)$$

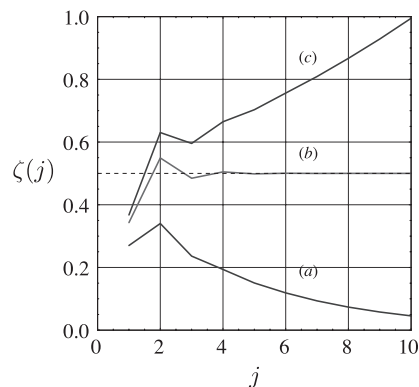


Figure 4. Plot of $\zeta(j)$ as a function of D_A and j (generation) for $J = 4$, $\langle g_w \rangle = 3$, $\langle (f - g)_w \rangle = 2$ and $\kappa = 1$. (a): $D_A = 0.18$; (b): $D_A = D_{Ac}$; (c): $D_A = 0.245$.

The first term of eq 41 satisfies $|(\cdot \cdot \cdot)^j| \leq 1$. For small j 's, it fluctuates around 0 changing the sign, and as $j \rightarrow \infty$, it rapidly approaches 0, so that $\zeta(j) \rightarrow \frac{1}{2}$, in accord with the behavior shown in Figure 4 (curve (b)).

Calculation of p_R

The fraction, p_R , of cyclic bonds to total possible bonds is defined by

$$p_R = \frac{\text{total number of cyclic bonds}}{\text{total number of possible bonds}}. \quad (42)$$

To relate eq 42 with experimentally measurable quantities, consider the simplest case of $J = 3$ of the R- A_f model. In Figure 5, an example of $f = 2$ and $J = 3$ is shown; larger (filled) circles represent monomer units and open circles FU's, where a merger takes place among three FU's to create one junction point (\otimes). Let the statement of this process be $p \Rightarrow q$, where p represents the "merger of the three FU's" and q the "occurrence of k bonds". Our question is, "What is the number of k in this unit reaction?" To answer this question, it is more convenient to ask the contrapositive, $\bar{q} \Rightarrow \bar{p}$, logically equivalent; namely, the question, "How many bond should be broken to split the resultant 3-mer into the original monomer units?" As is seen from Figure 5, there are $3!/2!$ ways to recover the original state; each requires exactly two bond-

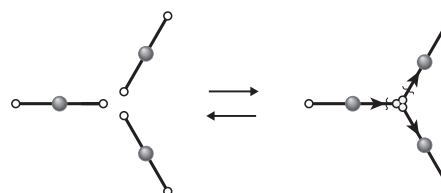


Figure 5. An example of unit reaction of the R- A_f model. Open circles denote functional units and filled circles branching units. The unit reaction takes place by the merger of three functional units.

breaks. Thus the answer is $k = 2$. In general, $J - 1$ bonds arise as a result of the merger of J FU's. Since there are C_f FU's in the system, the total number of possible bonds is $(J - 1/J)C_f$. Recall that every ring has only one cyclic bond. Then the fraction of cyclic bonds to all possible bonds can be expressed as

$$p_R = \frac{J[\Gamma]}{(J - 1)C_f}. \quad (43)$$

For $J = 2$, eq 43 reduces to the known result,² as expected. The result can be easily extended to the multi-link R-A_g+R-B_{f-g} model, where $J - 1$ bonds arise by the merger of $J/2$ A FU's and $J/2$ B FU's. Thus

$$p_R = \frac{J[\Gamma]}{2(J - 1)C_{fA}} = (1 + \kappa) \frac{J[\Gamma]}{2(J - 1)} \gamma_f, \quad (44)$$

where $C_{fA} = \sum_i g_i M_{A_i}/V$ represents the concentration of A FU's, γ_f the reciprocal of the total FU concentration defined by $\gamma_f = 1/C_f = V/(\sum_i g_i M_{A_i} + \sum_j (f - g)_j M_{B_j})$, and κ the relative mole number of B FU's to A FU's as defined in Derivation of Eq 2. Substituting eq 44 into eq 5, we find

$$D_{Ac} = \frac{\sqrt{t^2 + 4s} - t}{2s} + (1 + \kappa) \frac{J[\Gamma]}{2(J - 1)} \gamma_f. \quad (45)$$

An alternative derivation is possible. Let n_A and n_B be the number of reacted A and B FU's, respectively. Expressing eqs 2 and 42 in terms of the total FU number, we have

$$\frac{(n_{Ac} + n_{Bc})}{V} = \frac{(n_{Aco} + n_{Bco})}{V} + \frac{J[\Gamma]}{(J - 1)},$$

since, by the merger of J FU's, $J - 1$ bonds arise. By the nature of the R-A_g+R-B_{f-g} model, it follows that $n_A \equiv n_B$. With the equality $C_f = C_{fA}(1 + \kappa)$ and $D_A = n_A/\sum_i g_i M_{A_i}$ in mind, dividing both the sides of the above equation by C_f , we have

$$\frac{2}{(1 + \kappa)} D_{Ac} = \frac{2}{(1 + \kappa)} D_{Aco} + \frac{J[\Gamma]}{(J - 1)} \gamma_f,$$

which, upon rearranging, leads to eq 45.

Derivation of Gel Point

Only task remained is to unify eqs 37 and 45. We note, however, that eq 37 unfortunately breaks down as soon as the ideal gel point is exceeded; *i.e.*, beyond the gel point, the concentration of rings diverges strongly (see Figure 4). To resolve this problem, we make use of the linear approximation of eq 22. Recall that at high monomer concentration, the concentration of rings is independent of the monomer concentration itself. Since the gelation is a phenomenon characteristic of high concentration, one can approximate $[\Gamma]$ as a function of D alone: At $D_A = D_{Ac}$, one can write

$$[\Gamma] = \mathcal{C}(D_{Ac}) = \frac{2C_{fA}}{J} \sum_{j=1}^{\infty} \int_0^{D_{Ac}} \frac{(v_{R_j}/v_L)}{1 + (v_{R_j}/v_L)} dD_A. \quad (46)$$

Experiments^{6,7} have shown that $[\Gamma]$ is a continuous and monotonic function of D in the interval, $D_{co} \leq D \leq D_c$. Now expand eq 46 with respect to $D_{Ac} = D_{Aco}$ to yield

$$\mathcal{C}(D_{Ac}) = \mathcal{C}(D_{Aco}) + \frac{\mathcal{C}'(D_{Aco})}{1!} (D_{Ac} - D_{Aco}) + \dots \quad (47)$$

Since the system under consideration is in sufficient high-concentration, we may use eq 37 in place of eq 46. Then from eq 47, one has

$$[\Gamma] \cong \sum_{j=1}^{\infty} \varphi_j\{\dots\}/2j + \frac{1}{2D_{Aco}} \sum_{j=1}^{\infty} \varphi_j\{\dots\} (D_{Ac} - D_{Aco}), \quad (48)$$

where $\{\dots\} = 2\zeta(j)$ as given in eq 41. In eq 48, we have made use of eq 38. Substituting eq 48 into eq 45, we arrive at finally

$$D_{Ac} = \frac{\sqrt{t^2 + 4s} - t}{2s} \left\{ \frac{1 - \mathcal{F} \sum_j (1 - 1/j) \varphi_j\{\dots\} \gamma_f}{1 - \mathcal{F} \sum_j \varphi_j\{\dots\} \gamma_f} \right\}, \quad (49)$$

with

$$\mathcal{F} = \frac{(1 + \kappa)J}{4(J - 1)} \left(\frac{1}{2} t + \sqrt{s + \left(\frac{1}{2} t\right)^2} \right). \quad (50)$$

In Figure 6, D_{Ac} is plotted as a function of γ_f and J .^{7,8} In common with all other models, the gel point shifts upward with increasing dilution (γ_f). This is because of the increasing frequency of cyclization with dilution.⁷ Since D_c is restrained by the boundary condition, $0 \leq D(\text{inter}) + D(\text{ring}) \leq 1$, there is a critical

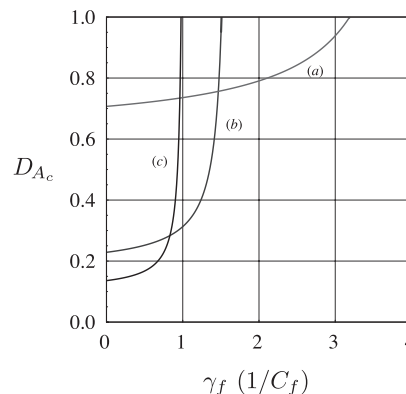


Figure 6. Plot of D_{Ac} as a function of γ_f and J for $\langle g_w \rangle = 3$, $\langle (f - g)_w \rangle = 2$ and $\kappa = 1$. (a): $J = 2$; (b): $J = 4$; (c): $J = 6$.

regime of dilution beyond which $D(\text{inter})$ cannot reach the ideal gel point. This point is the critical dilution, γ_{fc} , the intersections of the $D_{Ac} = 1$ line and the $D_{Ac} - \gamma_f$ curves.² As one can see from Figure 6, the critical dilution occurs abruptly, in direct contrast to the sudden appearance of a macroscopic gel molecule at D_{Ac} .

CONCLUSION

We have derived the closed solution of the concentration of cyclic species in the multifunctional system (eq 37). The result is equal to the formula derived in the preceding paper.² In the present work, however, the mathematical expression has been greatly simplified. Eq 37 is a generalization of the solutions for the $A_g\text{-R-B}_{f-g}$ and $R\text{-A}_g\text{+R-B}_{f-g}$ models.

Our question central to the works of this series is whether Assumption I is correct; *i.e.*, whether or not, eq 2 is mathematically exact. Within the framework of the principle of equireactivity under the athermal condition, there is no way to distinguish cyclic bonds from intermolecular bonds: Once a cyclic bond is formed, all memories of intramolecular bonding are lost. In this sense, the assumption that cyclic bonds distribute randomly over all bonds seems mathematically sound. Only way to settle this problem, however, depends on the extensive examination of the theory by experimental observations.

APPENDIX 1: SPECIAL SOLUTION OF $J = 2$

For $J = 2$, the bond formation between the same FU's is forbidden and $t = 0$, so all odd terms of the sum in eq 49 cancel out, which results in

$$D_{Ac} = \sqrt{\frac{1}{s}} \left\{ \frac{1 - (1 + \kappa)\sqrt{s} \sum_j (1 - 1/2j)\varphi_{2j}\gamma_f}{1 - (1 + \kappa)\sqrt{s} \sum_j \varphi_{2j}\gamma_f} \right\}, \quad (\text{A.1})$$

where $s = (\langle g_w \rangle - 1)(\langle (f - g)_w \rangle - 1)/\kappa$. The relative frequency of cyclization can be expressed by the incomplete Gamma function of the form:

$$\varphi_j = (d/2\pi^{d/2}\ell^d N_A) \int_0^{d/2v_j} t^{d/2-1} e^{-t} dt \quad \text{for ideal molecules,} \quad (\text{A.2})$$

where d is dimension and ℓ the bond length. φ_j is also the function of the quantity v_j (not cyclic bonds) defined by $\langle r_j^2 \rangle = v_j \ell^2$. For ideal chains, it follows that $v_j = C_F \xi j$ where C_F denotes the Flory characteristic constant, ξ the number of bonds within the repeating unit, and j the number of the repeating unit. Through-

out this paper, the repeating unit has been taken as the length of an A-A or a B-B chain within the monomers. However, for the present case of $J = 2$ it is more convenient to take the repeating unit as the length of an A-A-B-B chain. For this purpose, let us transform v_j as $v_j = C_F \xi j = C_F (2\xi)(j/2)$. The 2ξ corresponds to the number of bonds within the newly defined repeating unit, A-A-B-B, and the $(j/2)$ the number of the new repeating unit; *i.e.*, $(\text{A-A-B-B})_{j/2}$, which can be assigned to even terms of φ_j . Thus one can write eq A.1 in the form:

$$D_{Ac} = \sqrt{\frac{1}{s}} \left\{ \frac{1 - (1 + \kappa)\sqrt{s} \sum_x (1 - 1/2x)\varphi_x \gamma_f}{1 - (1 + \kappa)\sqrt{s} \sum_x \varphi_x \gamma_f} \right\}, \quad (\text{A.3})$$

where

$$\varphi_x = (d/2\pi^{d/2}\ell^d N_A) \int_0^{d/2v_x} t^{d/2-1} e^{-t} dt, \quad (\text{A.4})$$

and

$$v_x = C_F \xi' x \quad (x = 1, 2, 3, \dots). \quad (\text{A.5})$$

Now ξ' represents the number of bonds within the new unit length, A-A-B-B, and x the number, so that $(\text{A-A-B-B})_x$. Using further the reciprocal, γ , of the monomer unit concentration^{†††},

$$\gamma_f \rightarrow \frac{\langle (f - g)_n \rangle + \langle g_n \rangle \kappa}{\langle g_n \rangle \langle (f - g)_n \rangle (1 + \kappa)} \gamma, \quad (\text{A.6})$$

with $\langle (\)_n \rangle$ denoting the number average FU defined by $\langle g_n \rangle = \sum_i g_i M_{A_i} / \sum_i M_{A_i}$ etc., eq A.3 reduces exactly to the previous result.²

APPENDIX 2: APPLICATION TO THE ILAVSKY EXPERIMENT

To test the present theory, we want to take up the recent observation by Ilavsky and coworkers.⁹ the polyaddition reaction of tris(4-isocyanatophenyl)-thiophosphate (TI) and poly(oxypropylene)diol (PD) to yield a poly(urethane) network. They carried out the close investigation of the critical molar ratio, κ_c , for gelation at $D_A = 1$, as a function of the dilution, γ_f . In that case, the respective FU's were chosen so that $\kappa = \frac{[\text{OH}]}{[\text{NCO}]} \geq 1$, and therefore $\langle g_w \rangle = 3$ and $\langle (f - g)_w \rangle = 2$.

To compare the theory with the experiment, we impose the constraint, $0 \leq D_{Ac} \leq 1$, on eq A.3 to get

^{†††} $\gamma_f = \frac{V}{\sum_i g_i M_{A_i} + \sum_j (f-g)_j M_{B_j}}$, while $\gamma = \frac{V}{\sum_i M_{A_i} + \sum_j M_{B_j}}$.

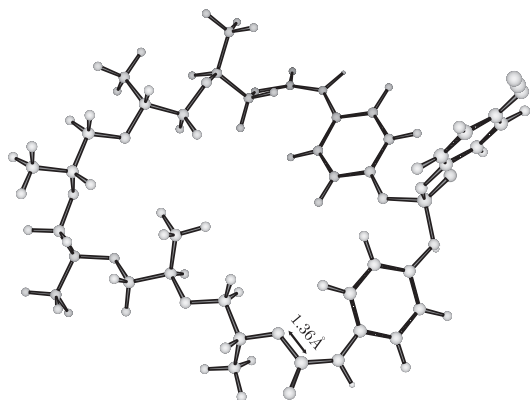


Figure A-1. A 3D view of the smallest ring from Tris(4-isocyanatophenyl)thiophosphate (TI) and poly(oxypropylene)-diol (PD).

$$\gamma_f \leq \gamma_{fc} = \frac{1 - 1/\sqrt{s}}{(1 + \kappa) \sum_x (-1 + \sqrt{s} + 1/2x) \varphi_x}, \quad (\text{A-7})$$

where $s = ((g_w) - 1)((f - g)_w) - 1/\kappa$ is also a function of κ .

To evaluate the value of φ_x , let us introduce the new quantities: the standard bond length, ℓ_s , and the effective bond number, ξ_e .² Note that a real chain has the end-to-end distance of the form:

$$\langle r_x^2 \rangle_\Theta = C_{Fx} \sum_i^{\xi} \ell_i^2 = C_F \xi_e x \bar{\ell}^2, \quad (\text{A-8})$$

for a large x in the Θ state. In practice, however, eq A-8 is not very easy to use. As we can see below, it is convenient to transform this equation as

$$\langle r_x^2 \rangle_\Theta = \nu_x \ell_s^2 = C_F \xi_e x \ell_s^2, \quad (\text{A-9})$$

where ℓ_s represents the C–O bond (1.36 Å) for the present case (see Figure A-1). Now we can write eq A-4 in the form:

$$\varphi_x = (d/2\pi)^{d/2} \ell_s^d N_A \int_0^{d/2\nu_x} t^{d/2-1} e^{-t} dt, \quad (\text{A-10})$$

where $\nu_x = C_F \xi_e x$ and $\xi_e = \xi'(\bar{\ell}^2/\ell_s^2)$. In this way, we have determined all the parameters; the result is shown in Table II. Making use of these values, we have carried out the parametric plot of eq A-7. Experimental points (\diamond) were recalculated according to the equation:

$$\gamma_f = \frac{\langle (f - g)_n \rangle \langle m_{A,n} \rangle + \langle g_n \rangle \langle m_{B,n} \rangle \kappa}{1000 \varrho v \langle g_n \rangle \langle (f - g)_n \rangle (1 + \kappa)}, \quad (\text{A-11})$$

where ϱ is the density of polymer (g/ml), v the volume fraction, and $\langle m_{A,n} \rangle$ and $\langle m_{B,n} \rangle$ are the number average molecular weights of TI and PD monomers, respectively, which are given in Table II. As can be seen in Figure A-2, the experiment supports strongly

Table II. Parameters for the TI-PD Branched Poly(urethane)

parameters	unit	values
molecular weight		TI = 465, PD = 400
$\langle g_w \rangle$		3
$\langle (f - g)_w \rangle$		2
d		3
C_F		4.3
ξ_e		62
ℓ_s	Å	1.36
cyclization frequency		
$\sum_{x=1}^{\infty} \varphi_x$	mol/l	0.1306
$\sum_{x=1}^{\infty} \varphi_x / 2x$	mol/l	0.03366

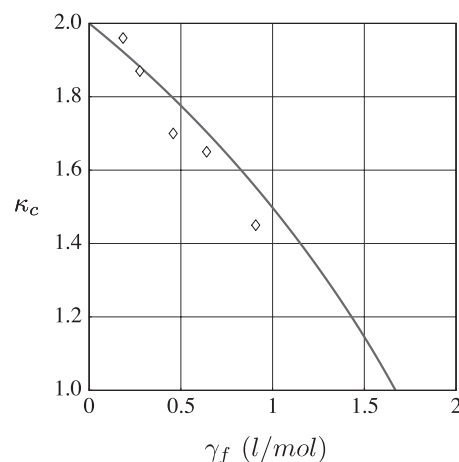


Figure A-2. κ_c plot as a function of γ_f . Solid line: theoretical line by eq A-7; \diamond : experimental points by Ilavsky and coworkers.⁹

the soundness of the theory.

Recall that C_F is not constant, but increases gradually with increasing x , asymptotically approaching a constant as $x \rightarrow \infty$.⁴ Thus it is important to notice that we tend to overestimate the C_F value and thus underestimate the total amount of rings. This may explain the small difference in Figure A-2 between the theoretical line and the experimental points. Quite conversely, if the theory is fully exact, there is a possibility that we can gain the structural information of various branched polymers by fitting the theoretical line to the observed points.

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