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Distribution of Cyclic Species in Network Formation: Microscopic Theory of Branching Process in A_g–R–B_{f-g} Model

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The distribution of cyclic species is explored for an irreversible A_g–R–B_{f-g} model on the basis of the concept of the "m tree" which was introduced in a preceding report by the authors. On the assumption of equal reactivity, the explicit solution is derived; i.e., for a sufficiently concentrated solution the concentration of cyclic j-mers can be expressed as $[R_j] = (k_{Rj}/k_L)[(f-g)D_B]^j\omega_j/j$, where k_{Rj} and k_L are the rate constants of cyclic j-mer formation and interconnection, respectively, and

$$\omega_j = \sum_{k=0}^{[j/2]} \binom{j}{2k} \alpha^k$$

where $\alpha = (g-1)(f-g-1)/g(f-g)$ and $[j/2]$ is the Gauss' symbol. For $g \to 1$, $\omega_j \to 1$, so that the solution reduces to the A–R–B_{f-1} case. At a critical point one observes the strong divergence of the chances $\sum \phi_j$ of cyclization.

KEY WORDS: Network theory; A_g–R–B_{f-g} model; m tree; distribution of cyclic species; divergence of cyclization.

1. INTRODUCTION

This paper deals with the distribution of cyclic species in the A_g–R–B_{f-g} model. The microscopic theory$^{(1-6)}$ of the branching process has suffered from the two major problems of cyclic formation and the distortion of reactivity, which have been thought to be the origins of the incorrect critical behavior$^{(7,8)}$ of the classical theories. Here we explore the problem of cyclic formation. More specifically, we want to extend the theory of the A–R–B_{f-1} model into a more general theory of the A_g–R–B_{f-g} model, which was unsolved in a preceding report$^{(9)}$ because of its complexity. As

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in the preceding report,$^{(9)}$ we assume the principle of equal reactivity and no excluded volume effects, which still confines the presented theory within the framework of a mean field theory. With this restriction in mind, in the following we shall derive the explicit solution for the model of interest under the concept of an "*m* tree."

2. THEORY

Consider an irreversible process in a sufficiently concentrated solution where the interconnection rate exceeds the cyclization rate. A-type functional units (f.u.) can react with only B-type f.u.. Note A-type f.u. and consider a mean shaped tree with m unreacted A f.u. in the first generation (root), which we call an m tree. The first task we must tackle is to find out the mean number of unreacted B f.u. in the jth generation, namely, the number average of the unreacted B's, for then one will find the total chances of cyclization as a result of the product

$$(m \text{ A's}) \times (\text{unreacted B's})$$

Let the total chances of cyclic j-mer formation be ϕ_j, and write it in the form

$$\phi_j = M_0 g(1-D_A)(1-D_B)[(f-g)^j D_B^{j-1}]\omega_j \tag{1}$$

where M_0 denotes the total unit number in a reaction bath, D_A and D_B are the extents of reaction of A f.u. and B f.u., respectively, and g and $f-g$ are the functionalities of the respective f.u. The reason for writing this in such a form will become clear in the following. Hence the problem of finding ϕ_j reduces to that of finding a general form of ω_j.

The probability that one finds m unreacted A's from g A's is equal to

$$\binom{g}{m}(1-D_A)^m D_A^{g-m}$$

so that there are $M_0\binom{g}{m}(1-D_A)^m D_A^{g-m}$ "m trees" in the system. Let $(g-m)\,\xi_A(1-D_B)$ and $\xi_B(1-D_B)$ be the numbers of B-type unreacted descendants in the jth generation whose ancestors are A and B f.u. on the root, respectively. Then, in general, one may write

$$\phi_j = \sum_{m=1}^{g} m[(g-m)\xi_A + \xi_B](1-D_B)\,M_0\binom{g}{m}(1-D_A)^m D_A^{g-m} \tag{2}$$

With the help of the equality

$$\sum_{m=1}^{g-1} m(g-m)\binom{g}{m}(1-D_A)^m D_A^{g-m} = g(g-1)\,D_A(1-D_A) \tag{3}$$

and the equality

$$\sum_{m=1}^{g} m \binom{g}{m} (1 - D_A)^m D_A^{g-m} = g(1 - D_A) \tag{4}$$

one may rewrite Eq. (2) in the form of Eq. (1), that is, with $gD_A = (f - g)D_B$,

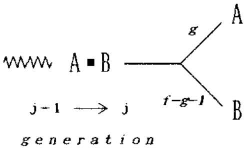
$$\begin{aligned}\phi_j = {} & M_0\, g(1 - D_A)(1 - D_B)[(f-g)^j D_B^{j-1}] \\ & \times \{[(g-1)(f-g)/g] D_B \xi_A + \xi_B\}/\{(f-g)^j D_B^{j-1}\}\end{aligned} \tag{5}$$

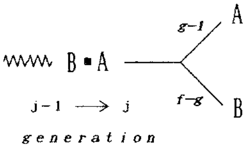
where

$$\omega_j = \{[(g-1)(f-g)/g] D_B \xi_A + \xi_B\}/\{(f-g)^j D_B^{j-1}\} \tag{6}$$

Hence the problem of ω_j reduces to the problem of seeking the total number of B descendants in the jth generation from the respective f.u. on the root.

The number of *B* descendants:





Note a transit from the $(j-1)$th generation to the jth on the m tree. As is seen from the above scheme, a single A f.u. bears g A's and $(f-g-1)$ B's, while a single B f.u. bears $(g-1)$ A's and $(f-g)$ B's. Let $N(A)_j$ and $N(B)_j$ be the numbers of A f.u. and B f.u. in the jth generation, respectively, so that $N(B)_j = (g-m)\xi_A + \xi_B$. Then, one can write the respective numbers in the jth generation as follows: for $j \geqslant 3$,

$$\begin{aligned} N(A)_j &= gD_A N(A)_{j-1} + (g-1)D_B N(B)_{j-1} \\ &= (f-g)D_B N(A)_{j-1} + (g-1)D_B N(B)_{j-1} \\ N(B)_j &= (f-g-1)D_A N(A)_{j-1} + (f-g)D_B N(B)_{j-1} \\ &= [(f-g-1)(f-g)/g]D_B N(A)_{j-1} + (f-g)D_B N(B)_{j-1} \end{aligned} \tag{7}$$

where

$$\begin{aligned} N(\mathrm{A})_1 &= g-m \\ N(\mathrm{B})_1 &= f-g \end{aligned} \tag{8}$$

and

$$\begin{aligned} N(\mathrm{A})_2 &= (g-m)\,g+(g-1)[(f-g)D_\mathrm{B}] \\ N(\mathrm{B})_2 &= (g-m)(f-g-1)+(f-g)[(f-g)D_\mathrm{B}] \end{aligned} \tag{9}$$

Substituting Eq. (9) for the $(j-1)$th term of Eq. (7), one obtains

$$\begin{aligned} N(\mathrm{A})_3 &= (g-m)\,g[(f-g)D_\mathrm{B}](1+\alpha)+(g-1)[(f-g)D_\mathrm{B}]^2\cdot 2 \\ N(\mathrm{B})_3 &= (g-m)(f-g-1)[(f-g)D_\mathrm{B}]\cdot 2 \\ &\quad +(f-g)[(f-g)D_\mathrm{B}]^2(1+\alpha) \end{aligned} \tag{10}$$

where

$$\alpha=(g-1)(f-g-1)/g(f-g) \tag{11}$$

The iteration of the same operation yields

$$\begin{aligned} N(\mathrm{A})_4 &= (g-m)\,g[(f-g)D_\mathrm{B}]^2(1+3\alpha)+(g-1)[(f-g)D_\mathrm{B}]^3(3+\alpha) \\ N(\mathrm{B})_4 &= (g-m)(f-g-1)[(f-g)D_\mathrm{B}]^2(3+\alpha) \\ &\quad +(f-g)[(f-g)D_\mathrm{B}]^3(1+3\alpha) \\ &\ \ \vdots \end{aligned} \tag{12}$$

By induction one may suppose the jth term to be

$$\begin{aligned} N(\mathrm{A})_j &= (g-m)\,g[(f-g)D_\mathrm{B}]^{j-2}z_{j-1}+(g-1)[(f-g)D_\mathrm{B}]^{j-1}\sum_{k=0}^{j-2} z_k \\ N(\mathrm{B})_j &= (g-m)\left\{(f-g-1)[(f-g)D_\mathrm{B}]^{j-2}\sum_{k=0}^{j-2} z_k\right\} \\ &\quad +\{(f-g)[(f-g)D_\mathrm{B}]^{j-1}z_{j-1}\} \\ &\equiv (g-m)\xi_\mathrm{A}+\xi_\mathrm{B} \end{aligned} \tag{13}$$

where

$$z_0=z_1=1 \qquad \text{and} \qquad z_j=z_{j-1}+\alpha\sum_{k=0}^{j-2} z_k \tag{14}$$

for $j\geqslant 2$.

Proof. Assume that the solution, Eq. (13), is true for $j = p$ ($\geqslant 2$). Transform Eq. (13) according to the operation of Eq. (7). With Eqs. (11) and (14), the respective numbers in the $(p+1)$th generation become

$$\begin{aligned} N(\mathrm{A})_{p+1} &= (g-m)\,g[(f-g)D_{\mathrm{B}}]^{p-1}z_p + (g-1)[(f-g)D_{\mathrm{B}}]^p \sum_{k=0}^{p-1} z_k \\ N(\mathrm{B})_{p+1} &= (g-m)(f-g-1)[(f-g)D_{\mathrm{B}}]^{p-1} \sum_{k=0}^{p-1} z_k \\ &\quad + (f-g)[(f-g)D_{\mathrm{B}}]^p z_p \end{aligned} \tag{15}$$

which are equivalent to Eq. (13). Therefore, if Eq. (13) is true for $j = p$, then it is true for $j = p+1$. On the other hand, Eq. (13) is true for $p = 2$ and 3 [see Eqs. (9), (10)]. Hence it is true for all p's larger than 2.

Substituting ξ_{A} and ξ_{B} of Eq. (13) into Eq. (6), one finds

$$\omega_j = z_{j-1} + \alpha \sum_{k=0}^{j-2} z_k \equiv z_j \tag{16}$$

The subtraction of z_{j-1} from z_j and subsequent rearrangement yields

$$z_j - (1-\alpha^{1/2})z_{i-1} = (1+\alpha^{1/2})[z_{j-1} - (1-\alpha^{1/2})z_{j-2}] \tag{17}$$

According to common convention and making use of $z_0 = z_1 = 1$, we solve the above equation, with the result

$$z_j \equiv \omega_j = (1/2)[(1-\alpha^{1/2})^j + (1+\alpha^{1/2})^j] \tag{18}$$

which satisfies Eq. (14), including the $j = 1$ case. All odd powers of $(1 \pm \alpha^{1/2})^j$ should cancel out, so Eq. (18) may be rewritten as

$$\omega_j = \sum_{k=0}^{[j/2]} \binom{j}{2k} \alpha^k \qquad \text{for all } j\text{'s} \tag{19}$$

where $[j/2]$ denotes the Gauss' symbol, namely, the maximum integer not exceeding $j/2$. With this information we can derive the distribution of cyclic species which we first sought.

Consider one transition in an irreversible process in which the ith collision occurs from the $(i-1)$th state. The transition must be either an interconnection or a cyclization. Then for a sufficiently concentrated solution, one may put the variation of cyclic j-mer number into the form

$$\delta N_{Rj} \simeq \frac{k_{Rj} M_0\, g(1-D_{\mathrm{A}})(1-D_{\mathrm{B}})[(f-g)^j D_{\mathrm{B}}^{j-1}]\,\omega_j}{k_L(gM_0 - i)[(f-g)M_0 - i]/V} \tag{20}$$

where k_{Rj} is the rate constant of cyclic j-mer formation and k_L is that of interconnection.

With $D_A = i/gM_0$ and $D_B = i/(f-g)M_0$, Eq. (20) reduces to

$$\delta N_{Rj} \simeq (k_{Rj}/k_L)\ V[(f-g)^j D_B^{j-1}]\omega_j/M_0(f-g) \tag{21}$$

This may be approximated by a differential equation for a large i and M_0 (this is the case in a real system!), so that

$$\begin{aligned} d[R_j] &= d(N_{Rj}/V) \\ &\simeq \{(k_{Rj}/k_L)[(f-g)^j D_B^{j-1}]\omega_j/M_0(f-g)\}\ di \end{aligned} \tag{22}$$

With $di = (f-g)M_0\, dD_B$ integrate Eq. (22) with respect to D_B in the interval $[0, D_B]$; the result is

$$[R_j] = (k_{Rj}/k_L)[(f-g)D_B]^j \omega_j/j \tag{23}$$

where ω_j is given by Eq. (19). Equation (23) is the general solution of the distribution of cyclic species in A_g–R–B_{f-g} network formation. For an ideal chain, one may replace (k_{Rj}/k_L) with the Gaussian normalization factor $(3/2\pi\langle j^2\rangle)^{3/2}$ according to Kuhn's insight,(10,11) where $\langle j^2\rangle$ is the mean square distance from the first generation to the jth. If $g \to 1$, $\alpha \to 0$ and therefore $\omega_j \to 1$, hence Eq. (23) exactly converges on the A–R–B_{f-1} case.

Critical Point

The only question remaining is whether there exists a critical point(12) of cyclization, and if it exists, where it exists. To answer this question, we must return to the chances of cyclization ϕ_j. If an infinitely large cluster appears, then the sum $\sum \phi_j$ must diverge. From Eqs. (1) and (18), one may write

$$\phi_j \propto [(1-\alpha^{1/2})(f-g)D_B]^j + [(1+\alpha^{1/2})(f-g)D_B]^j$$

If $[\cdots]$ is less than unity, one may perform the summation

$$\sum_{j=1}^{\infty} \phi_j \propto 1/\{1-[(1-\alpha^{1/2})(f-g)D_B]\} + 1/\{1-[(1+\alpha^{1/2})(f-g)D_B]\} \tag{24}$$

Clearly, as $(1 \pm \alpha^{1/2})(f-g)D_B \to 1$, a double divergence of the chances of cyclization occurs. From the stoichiometric theorem, however, it is

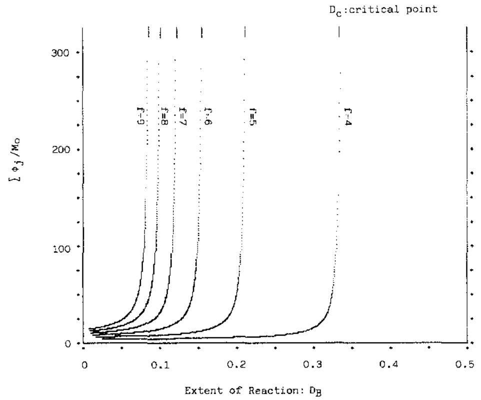


Fig. 1. Critical behavior of the chances $\sum \phi_j$ of cyclization in the A_2–R–B_{f-2} model with varying f, and g fixed at 2. The summation was carried out from $j=1$ to 150 (truncation point). Short bars indicate theretical points from Eq. (25).

impossible that $(1-\alpha^{1/2})(f-g)D_B=1$. So, the physically unrealistic divergence is abandoned. Hence,

$$D_c = 1/[(1+\alpha^{1/2})(f-g)] \tag{25}$$

which is equivalent to Spouge's gel point(12) derived from the average molecular weight, if one alters the definition of the extent of reaction as $i/M_0(f-g) \rightarrow 2i/M_0 f$; i.e., $1/(f-g) \rightarrow 2/f$. This may be reexamined by the

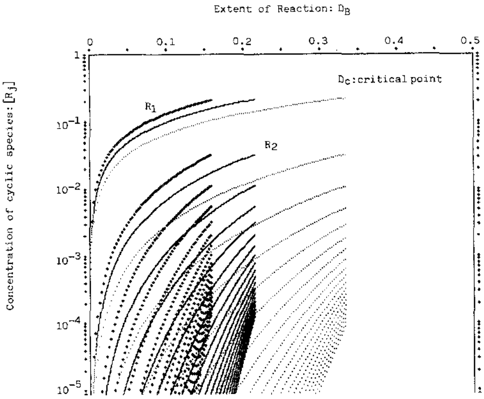


Fig. 2. Distribution of cyclic species in the A_g–R–B_{f-g} model ($g=2$). The concentrations of cyclic species $[R_1]$ to $[R_{20}]$ in sol phases are plotted as functions of f and the extent of reaction of B f.u., D_B, up to the gel points. Chains were assumed to be ideal; i.e., $k_{Rj}/k_L = (3/2\pi j)^{3/2}$. $(\cdots)$ $f=4$, (—) $f=5$, (***) $f=6$.

direct calculation of Eq. (1) with Eq. (19). The results are illustrated in Fig. 1; j is truncated at $j_{\max} = 150$; short bars indicate the theoretical points of Eq. (25). As one sees, at the very points predicted one observes the strong divergence of cyclization (see Figs. 1 and 2).

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