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Distribution of Cyclic Species in Network Formation: Microscopic Theory of Branching Processes

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General solutions of the distribution of cyclic species are sought in irreversible A–R–B_{f-1} and R–A_f branching processes. With the aid of the concept of an *m* tree, we find the simple explicit solutions as a function of the extent of reaction *D*. In the irreversible processes of a sufficiently concentrated solution,

$$[R_j]_D \simeq \begin{cases} (k_{Rj}/k_L)[(f-1)\,D_B]^j/j & \text{for A–R–B}_{f-1}\text{ model} \\ (k_{Rj}/k_L)[(f-1)\,D]^j/2j & \text{for R–A}_f\text{ model} \end{cases}$$

respectively. Here $[R_j]$ is the concentration of cyclic *j*-mer, k_{R_j} the rate constant of ring *j*-mer formation, and k_L that of interconnection; the subscript B denotes the B functional unit in the A–R–B_{f-1} model. For random flight chains one may replace k_{Rj}/k_L with the Kuhn cyclization probability $(3/2\pi\langle r_j^2\rangle)^{3/2}$ ($\langle r_j^2\rangle$ is the mean square distance), which yields the known exponential law as in the case of the linear theory: $[R_j] \propto j^{-5/2}$. Hence this theory corresponds to the generalization of the Jacobson–Stockmayer linear theory ($f=2$).

KEY WORDS: Random polycondensation; branching process; *m* tree; distribution of cyclic species.

1. INTRODUCTION

This paper deals with the distribution of cyclic species in branching processes. The microscopic theories$^{(1-3)}$ of the branching process, including the mean link probability approach,$^{(4-6)}$ have suffered from a major problem in their inability to picture the correct critical behavior, which has frequently been criticized as a fundamental flaw of the classical theories. It has been pointed out by de Gennes$^{(7)}$ and Stauffer$^{(8)}$ that the deviation

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from the correct critical behavior could be attributed to disregarding the ring production and the distortion of reactivity of unreacted functional units (ufu). Despite a number of ingenious ideas, so far the problem has not been sufficiently improved.(5,9,12)

Here we shall reexamine the distribution of cyclic species in network formation to deduce the explicit solutions on the assumption of equal reactivity.(10)

2. THEORY

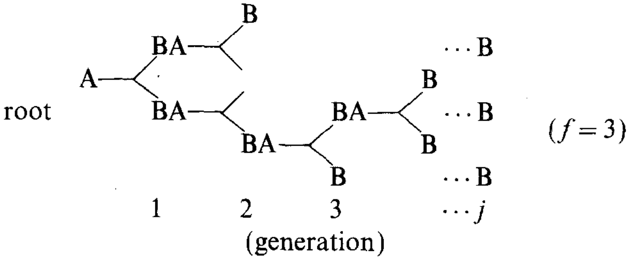
We shall confine ourselves to irreversible processes of a concentrated solution such as a nonsolvent system, where the interconnection rate exceeds the cyclization rate.

2.1. A–R–B_{f-1} Model

Let an unreacted A functional unit (fu) on a mean x-sized cluster be the root, so that the average number of unreacted B's in the jth generation on the same cluster becomes

$$N(B_j) = [(f-1)D_B]^{j-1}(f-1)(1-D_B) \qquad (1)$$

where f denotes the functionality and D_B the extent of reaction of B fu; we have



Let M_0 and D_A be the total number of units and the extent of reaction of A fu, respectively. Then, there are $M_0(1-D_A)$ such clusters. Let i be the number of successful collisions to jump into chemical bond formation, which are called transitions in a statistical sense.(11) For a sufficiently concentrated solution, one may approximate the transition probability P_i of cyclization in $(i-1) \rightarrow i$ as

$$\begin{aligned} P_i &= \text{cyclization rate} \\ &\quad \times (\text{interconnection rate} + \text{cyclization rate})^{-1} \\ &\simeq \text{cyclization rate/interconnection rate} \end{aligned}$$

which is equivalent to the variation of the number of ring j-mers. Hence, one may write the variation in the form[11]

$$\delta N_{\mathrm{R}j} \simeq k_{\mathrm{R}j} \cdot M_0(1-D_{\mathrm{A}})(f-1)(1-D_{\mathrm{B}})[(f-1)\,D_{\mathrm{B}}]^{j-1} \times \{k_L \cdot [(f-1)\,M_0 - i](M_0 - i)/V\}^{-1} \tag{2}$$

where $N_{\mathrm{R}j}$ is the number of the ring j-mers to be formed, $k_{\mathrm{R}j}$ the rate constant of ring j-mer formation, k_L that of interconnection, and i the number of reacted units. For large i and M_0, one may approximate Eq. (2) with a differential equation:

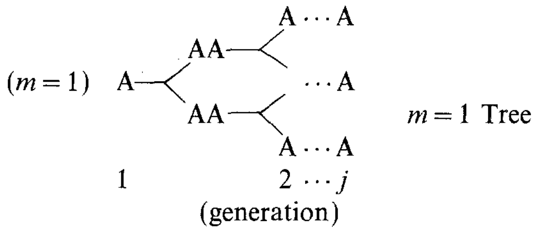
$$dN_{\mathrm{R}j} \simeq \{k_{\mathrm{R}j} \cdot M_0(1-D_{\mathrm{A}})(f-1)(1-D_{\mathrm{B}})[(f-1)\,D_{\mathrm{B}}]^{j-1} \times [k_L \cdot (f-1)\,M_0(1-D_{\mathrm{B}})\,M_0(1-D_{\mathrm{A}})/V]^{-1}\}\,di \tag{3}$$

With $dD_{\mathrm{A}} = di/M_0$ and $D_{\mathrm{A}} = (f-1)\,D_{\mathrm{B}}$, integrate Eq. (3) with respect to D_{A} or D_{B}, the result being

$$[\mathrm{R}_j] = N_{\mathrm{R}j}/V \simeq \begin{cases} (k_{\mathrm{R}j}/k_L)\,D_{\mathrm{A}}^j/j \\ (k_{\mathrm{R}j}/k_L)[(f-1)\,D_{\mathrm{B}}]^j/j \end{cases} \tag{4}$$

2.2. R–A$_f$ Model

Choose the root from one of the units with m unreacted A's on a mean x cluster. We call such a tree an m tree:



Let D be the extent of reaction of A functional units. Then one finds m ufu in the first and $(f-m)[(f-1)\,D]^{j-2}\,(f-1)(1-D)$ ufu in the $j(\geqslant 2)$th generation. The fraction of the m tree is equal to the probability of finding m ufu from f fu in a single monomer unit, so that there are

$$M_0 \binom{f}{m} (1-D)^m\, D^{f-m} = M_0 \langle X^m \rangle_{\mathrm{AV}}$$

such m trees in the same system.

A. Ring Monomer. In a single m tree there are $m(m-1)/2$ chances of cyclic monomer formation, so that the variation of the ring monomer number may be written as in the transition of $i-1 \to i$,

$$dN_{\mathrm{R}1} \simeq \left\{ \frac{1}{2} k_{\mathrm{R}1} \sum_{m=2}^{f} m(m-1)\, M_0 \binom{f}{m} (1-D)^m D^{f-m} \right.$$
$$\left. \times \left[\frac{1}{2} k_{\mathrm{L}} (fM_0 - 2i)^2 / V \right]^{-1} \right\} di \tag{5}$$

where $D = 2i/fM_0$, is the number of transitions, and hence $2i$ the number of reacted A's. Replacing di with $(fM_0/2)\, dD$, and with the help of the theorem

$$\sum_{m=2}^{f} \binom{f-2}{m-2} (1-D)^{m-2} D^{f-m} = 1$$

we can integrate the above equation with respect to D in the interval $[0, D]$, yielding

$$[\mathrm{R}_1]_D \simeq (k_{\mathrm{R}1}/k_L)(f-1)\, D/2 \tag{6}$$

B. Ring *j*-mer. There are

$$\phi_j = \frac{1}{2} \sum_{m=1}^{f-1} m(f-m)[(f-1)\, D]^{j-2} (f-1)(1-D)\, M_0 \langle X^m \rangle_{\mathrm{AV}}$$

chances of ring j-mer formation in $(i-1) \to i$. Thus the variation of N_{R_j} may be written in the form

$$dN_{\mathrm{R}_j} \simeq \{ k_{\mathrm{R}_j} \phi_j / [(1/2)\, k_L (fM_0 - 2i)^2 / V] \}\, di \tag{7}$$

which leads to

$$[R_j]_D \simeq (k_{\mathrm{R}_j}/k_L)[(f-1)\, D]^j / 2j \tag{8}$$

This happens to include the ring monomer case. Hence, combining Eq. (6) with Eq. (8), we arrive at the general solution of the R–A$_f$ model (Fig. 1).

In summary, in a sufficiently concentrated system we obtain, for all j's,

$$[\mathrm{R}_j]_D \simeq \begin{cases} (k_{\mathrm{R}_j}/k_L)[(f-1)\, D_{\mathrm{B}}]^j / j & \text{for A–R–B}_{f-1}\text{ model} \quad (4) \\ (k_{\mathrm{R}_j}/k_L)[(f-1)\, D]^j / 2j & \text{for R–A}_f\text{ model} \quad (8) \end{cases}$$

respectively. One may put $k_{\mathrm{R}_j}/k_L = (3/2\pi \langle r_j^2 \rangle)^{3/2}$ for random flight chains,(13,14) where $\langle r_j^2 \rangle$ is the mean square distance from the first

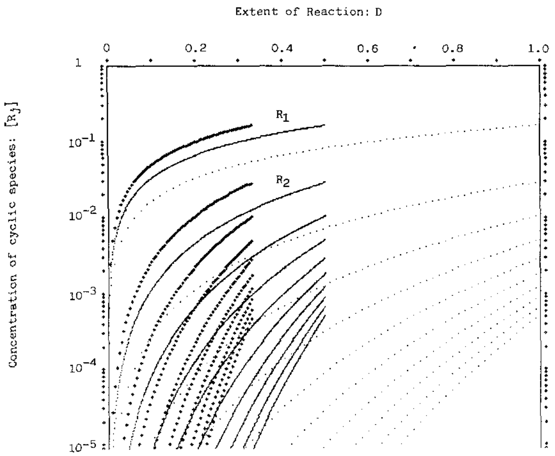


Fig. 1. The distribution of cyclic species: The concentration of cyclics of $j = 1$–10 in a sol fraction is plotted according to the general solution (8) (R–A_f model); $k_{R_j}/k_L = (3/2\pi j)^{3/2}$. Sufficiently concentrated systems, say, nonsolvent systems, are assumed, so that the gel points coincide with $\approx 1/(f-1)$. The results are for $(\cdots)\, f=2$, $(—)\, f=3$, $(**)\, f=4$.

generation to the jth. This result agrees with Spouge's expression⁽¹²⁾ in equilibrium: If we compare our notations with the Spouge's,

$$k_{R_j}/k_L \to p_j$$

$$(f-1)\,D \to \mathbf{m}_2$$

If $f=2$, then the derived solutions rigorously reduce to the linear theory.⁽¹³,¹⁴⁾ Hence one readily sees that the Jacobson–Stockmayer theory is a special case of this theory.

APPENDIX

In the whole system there are

$$\phi_j = \begin{cases} M_0(f-1)(1-D_A)(1-D_B)[(f-1)\,D_B]^{j-1} & \text{for A–R–B}_{f-1}\text{ model} \\ \frac{1}{2}M_0 f(f-1)(1-D)^2\,[(f-1)\,D]^{j-1} & \text{for R–A}_f\text{ model} \end{cases} \tag{A1}$$

chances of cyclic j-mer formation in the respective sol phases, which are equivalent to the combinatorial numbers of j-sized "*chains*."

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[2] In ref. 12 the distribution of cyclic species is described in terms of partition functions.

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