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The Size Distribution for the A_gRB_{f-g} Model of Polymerization

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This paper gives the equilibrium distribution of polymer sizes for Flory's A_gRB_{f-g} model of polymerization. In this model, the polymers are composed of structural units with g functional groups of the type A and $(f-g)$ functional groups of the type B. Reaction is subject to three conditions: (1) Functional groups of the type A react only with those of type B, and vice versa. (2) Intramolecular reactions do not occur [and therefore only branched-chain (noncyclic) polymers and formed]. (3) Subject to conditions (1) and (2), all functional groups are equally reactive. The derivation employs Stockmayer's statistical mechanical method (first used on Flory's RA_f model), coupled with a recursion giving the number of distinct polymers which may be assembled from k units of the A_gRB_{f-g} type. We also give distributions for a limiting case of the A_gRB_{f-g} model, the so-called A_gRB_∞ model. This paper completes the solution of the Smoluchowski coagulation equation (monodisperse case) for the kernels $a_{ij} = A + B(i+j) + Cij$. The proof will be given in another publication.

KEY WORDS: Polymerization; coagulation equation; RA_f model; A_gRB_{f-g} model; random polycondensation.

1. INTRODUCTION

This paper gives the equilibrium distribution of polymer sizes for Flory's A_gRB_{f-g} model of polymerization.

The best-known model of polymerization is Flory's[1] RA_f model, also known as the *f-functional random polycondensation model.* In this model, each structural unit of a polymer has f functional groups of the type A. Reaction is subject to three conditions:

1. Functional groups of the type A react with one another, forming bonds between units. See Fig. 1a.

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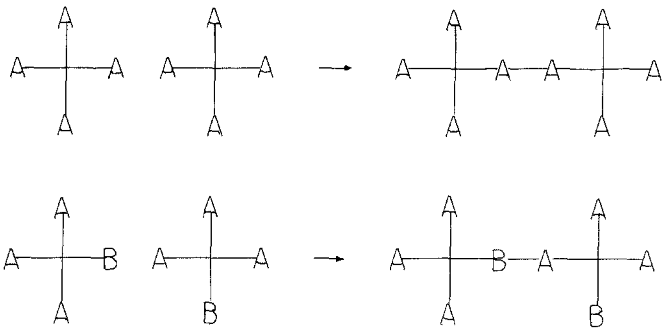


Fig. 1. Reaction of a pair of units: below, for the A_gRB_{f-g} model ($g = 1, f = 4$); above for the RA_f model ($f = 4$).

2. Intramolecular reactions do not occur [and therefore only branched-chain (noncyclic) polymers are formed].

3. *Flory's*[1] *Principle of Equireactivity*: subject to conditions (1) and (2), all unreacted functional groups are equally reactive.

On the other hand, in the A_gRB_{f-g} model, each structural unit has g functional groups of the type A and $(f - g)$ groups of the type B. The conditions on reaction remain unchanged, except that (1) is replaced by (1′): Functional groups of the type A react only with those of type B, and vice versa. See Fig. 1b.

Flory[2] gave the gel point for the RA_f model in 1941. Using statistical mechanics, Stockmayer[3] gave the distribution for the RA_f model in 1943. In Spouge[4] I extended Stockmayer's methods to determine the gel point of the A_gRB_{f-g} model. The extension rested on a combinatoric identity:

$$2(k-1)w_k = \sum_{i=1}^{k-1} \binom{k}{i} w_i w_{k-i} a_{i,(k-i)} \tag{1}$$

w_k is the number of ways of assembling a k-mer (polymer of k units) from its constituent units, and a_{ij} as the number of ways of bonding an i-mer and a j-mer together. We give a proof of (1): the left side is the number of ways of assembling a k-mer, choosing one of its bonds [noncyclic k-mers must have $(k-1)$ bonds], then painting one of the two polymers on either side of the chosen bond black. This equals the right side, which is the number of ways of choosing i units out of k units ($i = 1, \ldots, k-1$), painting the i units black, assembling a painted i-mer and an unpainted $(k-i)$mer, and then bonding the two polymers together.

This identity unified several polymerization models and permitted me to derive and summarize all explicit solutions of the Smoluchowski[5] coagulation equation (monodisperse case) implicit in Drake's[6] review of coagulation. These solutions (as Ziff[7] notes) include the RA_f and A_1RB_{f-1} distributions. They do not include the A_gRB_{f-g} distributions for general g.

For RA_f polymers obeying classical statistics (so that units and functional groups, though chemically identical, are distinguishable)

$$a_{ij} = [2 + (f-2)i][2 + (f-2)j] \tag{2}$$

(The right side is the product of the numbers of unreacted groups on an i-mer and a j-mer.) For the A_gRB_{f-g} model

$$a_{ij} = 2 + (f-2)(i+j) + 2(g-1)(f-g-1)ij \tag{3}$$

We may consider models where f tends to infinity, yielding the RA_∞ model, for which

$$a_{ij} = ij \tag{4}$$

and the A_gRB_∞ model, for which

$$a_{ij} = i + j + 2(g-1)ij \tag{5}$$

(These are derived from their finite counterparts by selecting the dominant term of a_j as f tends to infinity, then dropping an irrelevant proportionality factor.)

All of theses cases have the form

$$a_{ij} = A + B(i+j) + Cij \tag{6}$$

For these a_{ij}'s the generating function

$$Z = \sum_{k=1}^{\infty} \frac{w_k}{k!} e^{-\beta k} \tag{7}$$

(where β is a parameter yet to be determined) recasts recursion (1) as an ordinary differential equation:

$$2(-Z' - Z) = AZ^2 - 2BZZ' + C(Z')^2 \tag{8}$$

(Z', Z'', etc. denote successive derivatives with respect to β.) To better appreciate the significance of (8), we review Stockmayer's[3] derivation of the RA_f distribution.

In a closed system of M polymers, assembled from N units, the polymer size distribution $(m_1, m_2, m_3, \ldots)$ (i.e., m_1 units, m_2 dimers, m_3 trimers, etc.) satisfies the constraints

$$M = \sum_{k=1}^{\infty} m_k \tag{9}$$

$$N = \sum_{k=1}^{\infty} km_k \tag{10}$$

The total number of ways of producing the size distribution $(m_1, m_2, m_3, \ldots)$, subject to these constraints, is

$$\Omega(m_1, m_2, m_3, \ldots) = N! \prod_{k=1}^{\infty} \frac{1}{m_k!} \left(\frac{w_k}{k!} \right)^{m_k} \tag{11}$$

The proof is standard: Ω equals the number of ways of partitioning the N units into m_1 subsets of one unit, m_2 subsets of two units, etc., multiplied by $w_1^{m_1} w_2^{m_2} w_3^{m_3} \ldots$, the number of ways of assembling the subsets of units into polymers (see Percus[8]).

Treating the system like a microcanonical ensemble, Stockmayer[3] used Lagrange multipliers (the method of most probable distributions from statistical mechanics, e.g., Schrödinger[9]) to maximize (natural) $\log \Omega$, subject to the constraints on M and N. *The most probable size distribution* $(m_1^*, m_2^*, m_3^*, \ldots)$ is given by

$$m_k^* = \frac{w_k}{k!} e^{-\gamma - \beta k} \tag{12}$$

where β and γ are Lagrange multipliers. Equation (12) represents the first term of an asymptotic expansion valid before the gel point (Spouge[4]). Equation (7) gives

$$\frac{m_k^*}{M} = \frac{m_k^*}{\sum m_k^*} = \frac{1}{Z} \frac{w_k}{k!} e^{-\beta k} \tag{13}$$

Determination of β and Z yields the polymer distribution.

Introduce *the separation of the system*:

$$\mu = M/N \tag{14}$$

(μ is the concentration of polymers when the concentration of units is normalized to 1.) In conjunction with (9), (10), (12), and (7), this shows

$$Z = -\mu Z' \tag{15}$$

Combining this with the differential equation (8) gives

$$Z = \frac{2\mu(1-\mu)}{A\mu^2 + 2B\mu + C} \tag{16}$$

Solution of the differential equation (8) for $e^{-\beta}$ in terms of Z, yields the polymer distribution (13) in terms of μ.

For $C = 0$ or $B^2 = AC$, I gave w_k explicitly. In other cases, we can only determine the asymptotics of w_k. Note, however, the exact w_k's are always given by recursion (1).

The next section solves the differential equation for $e^{-\beta}$ in terms of Z, while the section after gives the asymptotics of w_k. The discussion then relates the results to the $A_g RB_{f-g}$ distributions.

2. SOLUTION OF THE DIFFERENTIAL EQUATION

Solve for Z' in equation (8) and separate the variables (Ince[10]), then integrate:

$$-\beta = \int \frac{C}{1 - BZ - \left[1 - 2(B+C)Z + (B^2 - AC)Z^2\right]^{1/2}}\, dZ \tag{17}$$

The cases $C = 0$ and $B^2 = AC$ were solved in Ref. 4 and elsewhere, so we exclude them.

The integral is a standard form, and Edwards[11] gives the method of solution. We split the integral into three cases.

Case 1: $B^2 < AC$

Complete the square inside the radical to throw the root into the form

$$a\left[1 - b^2(Z+\gamma)^2\right]^{1/2} \tag{18}$$

where

$$a = \left[\frac{C(A + 2B + C)}{AC - B^2}\right]^{1/2} \tag{19}$$

$$b = \frac{AC - B^2}{\left[C(A + 2B + C)\right]^{1/2}} \tag{20}$$

$$\gamma = \frac{B + C}{AC - B^2} \tag{21}$$

Use the substitution

$$\theta = \arcsin\left[b(Z+\gamma)\right] \tag{22}$$

To rationalize the resulting integrand, we employ

$$V = \tan\tfrac{1}{2}\theta \tag{23}$$

to give

$$-\beta = \int \eta \frac{1 - V^2}{V^2 - 2\delta V + \epsilon} \cdot \frac{dV}{1 + V^2} \tag{24}$$

(22) and (23) yield

$$V = \frac{1 - \left[1 - b^2(Z+\gamma)^2\right]^{1/2}}{b(Z+\gamma)} \tag{25}$$

Note that

$$\delta = \frac{B}{b(1 + B\gamma + a)} \tag{26}$$

$$\epsilon = \frac{1 + B\gamma - a}{1 + B\gamma + a} \tag{27}$$

$$\eta = \frac{2C}{(1 + B\gamma + a)b} \tag{28}$$

Let

$$V^2 - 2\delta V + \epsilon = (V - \alpha_1)(V - \alpha_2) \tag{29}$$

$$\alpha_1 = \delta + (\delta^2 - \epsilon)^{1/2} \tag{30}$$

$$\alpha_2 = \delta - (\delta^2 - \epsilon)^{1/2} \tag{31}$$

Under the assumed conditions, α_1 and α_2 are real and distinct. Partial fraction decomposition gives

$$-\beta = \int \eta \left(\frac{pV + q}{1 + V^2} + \frac{r_1}{V - \alpha_1} + \frac{r_2}{V - \alpha_2} \right) dV \tag{32}$$

where

$$p = \frac{4\delta}{(\epsilon - 1)^2 + 4\delta^2} \tag{33}$$

$$q = \frac{-2(1 - \epsilon)}{(\epsilon - 1)^2 + 4\delta^2} \tag{34}$$

$$r_1 = \frac{1 - \alpha_1^2}{1 + \alpha_1^2} \cdot \frac{1}{\alpha_1 - \alpha_2} \tag{35}$$

$$r_2 = \frac{1 - \alpha_2^2}{1 + \alpha_2^2} \cdot \frac{-1}{\alpha_1 - \alpha_2} \tag{36}$$

Equation (32) may be integrated directly:

$$\begin{aligned} e^{-\beta} &= K \exp\Big\{ \eta \Big[\tfrac{1}{2} p \ln(1 + V^2) + q \arctan V \\ &\qquad + r_1 \ln(V - \alpha_1) + r_2 \ln(V - \alpha_2) \Big] \Big\} \\ &\stackrel{\Delta}{=} \exp h(V) \end{aligned} \tag{37}$$

($\stackrel{\Delta}{=}$ indicates a definition.) K is a constant of integration and exp and ln denote exponentiation and logarithm to the base e, respectively. We now determine K:

$$\lim_{\beta\to\infty}(Ze^{\beta}) = w_1 = 1 \tag{38}$$

[see (7)]. Equation (25) gives

$$Z = -\gamma + \frac{1}{b}\cdot\frac{2V}{1+V^2} \triangleq f(V) \tag{39}$$

Equation (25) shows Z is zero when

$$V = \frac{1-\left[1-b^2\gamma^2\right]^{1/2}}{b\gamma} = \alpha_1 \tag{40}$$

(The second equality is tedious algebra.) We may also verify that $\eta r_1 = 1$. L'Hôpital's rule gives

$$\begin{aligned} K &= \lim_{V\to\alpha_1} Ze^{\beta}K \\ &= \frac{2}{b}\,\frac{1-\alpha_1^2}{\left(1+\alpha_1^2\right)^2}\exp\left\{-\eta\left[\tfrac{1}{2}p\ln\left(1+\alpha_1^2\right) + r_2\ln(\alpha_1-\alpha_2) + q\arctan\alpha_1\right]\right\} \end{aligned} \tag{41}$$

where $1/e^{\beta} = e^{-\beta}$ was introduced as a denominator. The numerator and denominator were differentiated with respect to V [see equations (37) and (39)] and then evaluated for $V = \alpha_1$. Determining K gives the value of $e^{-\beta}$ for fixed μ, since Z, and hence V [equations (16) and (25)] are known functions of μ.

Case 2: $B^2 > AC,\ A \neq 0$

In this case, the square root in (17) becomes

$$a\left[b^2(Z-\gamma)^2 - 1\right]^{1/2} \tag{42}$$

where

$$a = \left[\frac{C(A+2B+C)}{B^2-AC}\right]^{1/2} \tag{43}$$

$$b = \frac{B^2-AC}{\left[C(A+2B+C)\right]^{1/2}} \tag{44}$$

$$\gamma = \frac{B+C}{B^2-AC} \tag{45}$$

The serial substitutions

$$\theta = \operatorname{arccosh}\left[-b(Z-\gamma)\right]$$
$$V = \tanh \tfrac{1}{2}\theta$$

[where "h" indicates the hyperbolic analog of the corresponding trigonometric function (Edwards[11])], yield

$$-\beta = \int \eta \frac{2V}{V^2 - 2\delta V + \epsilon} \cdot \frac{dV}{1 - V^2} \tag{46}$$

where

$$V = \left[\frac{-b(Z-\gamma)-1}{-b(Z-\gamma)+1} \right]^{1/2} \tag{47}$$

and

$$\delta = \frac{ab}{B - b + Bb\gamma} \tag{48}$$

$$\epsilon = \frac{B + b - Bb\gamma}{B - b + Bb\gamma} \tag{49}$$

$$\eta = \frac{-2C}{B - b + Bb\gamma} \tag{50}$$

When α_1 and α_2 are given by (30) and (31), and $A \neq 0$; α_1, α_2, and ± 1 are all real and distinct. Hence

$$-\beta = \int \eta \left\{ \frac{p}{1-V} + \frac{q}{1+V} + \frac{r_1}{\alpha_1 - V} + \frac{r_2}{\alpha_2 - V} \right\} dV \tag{51}$$

where

$$p = \frac{1}{(1-\alpha_1)(1-\alpha_2)} \tag{52}$$

$$q = \frac{-1}{(1+\alpha_1)(1+\alpha_2)} \tag{53}$$

$$r_1 = \frac{-2\alpha_1}{(\alpha_1 - \alpha_2)(1 - \alpha_1^2)} \tag{54}$$

$$r_2 = \frac{-2\alpha_2}{(\alpha_2 - \alpha_1)(1 - \alpha_2^2)} \tag{55}$$

Integration gives

$$e^{-\beta} = K\exp\{\eta[-p\ln(1-V) + q\ln(1+V) - r_1\ln(\alpha_1 - V) - r_2\ln(\alpha_2 - V)]\}$$
$$\triangleq \exp h(V) \tag{56}$$

We determine K as before

$$Z = \gamma - \frac{1}{b}\cdot\frac{1+V^2}{1-V^2} \triangleq f(V) \tag{57}$$

Z is zero for

$$V = \left[\frac{b\gamma - 1}{b\gamma + 1}\right]^{1/2} = \alpha_2 \tag{58}$$

Using l'Hôpital's rule as before (with α_2 in place of α_1, and $\eta r_2 = -1$ instead of $\eta r_1 = 1$), we get

$$K = \frac{4\alpha_2}{b(1-\alpha_2^2)^2}\exp\{-\eta[-p\ln(1-\alpha_2) + q\ln(1+\alpha_2) - r_1\ln(\alpha_1 - \alpha_2)]\} \tag{59}$$

Case 3: $B^2 > AC,\ A = 0$

All proceeds as in Case 2, up to the partial fraction decomposition (51). When $A = 0$, $\alpha_1 = 1$, which introduces a double root into the denominator. Hence

$$-\beta = \int \eta\left[\frac{p}{(1-V)^2} + \frac{q}{1+V} + \frac{r_1}{1-V} + \frac{r_2}{\alpha_2 - V}\right]dV \tag{60}$$

$$p = \frac{-1}{1-\alpha_2} \tag{61}$$

$$r_1 = \frac{-(1+\alpha_2)}{2(1-\alpha_2)^2} \tag{62}$$

and q and r_2 are as before [(53) and (55) with $\alpha_1 = 1$].

Integration gives

$$e^{-\beta} = K\exp\left\{\eta\left[\frac{p}{1-V} + q\ln(1+V) - r_1\ln(1-V) - r_2\ln(\alpha_2 - V)\right]\right\}$$
$$\triangleq \exp h(V) \tag{63}$$

Equations (57) and (58) still hold, so l'Hôpital's rule gives

$$K = \frac{4\alpha_2}{b\left(1-\alpha_2^2\right)^2}\exp\left\{-\eta\left[\frac{p}{1-\alpha_2}+q\ln(1+\alpha_2)-r_1\ln(1-\alpha_2)\right]\right\} \tag{64}$$

3. ASYMPTOTICS OF THE COEFFICIENTS

While the recursion (1) for w_k, coupled with the formulas for $e^{-\beta}$, determines the terms of Z, it says little about their asymptotic behavior. This is dependent on the behavior of $w_n/n!$ as n tends to infinity, which we now determine.

In all cases

$$Z = f(V) \tag{65}$$

and the $w_n/n!$ are the coefficients of $f(V)$, expanded as a power series in

$$e^{-\beta} = \exp h(V) \tag{66}$$

If α denotes α_1 in Case 1, or α_2 in Cases 2 and 3, then $e^{-\beta}$ approaches zero as V approaches α. By Lagrange's formulas for expansion of one function in powers of another (Whittaker and Watson[12]) (i.e., Z in powers of $e^{-\beta}$)

$$\frac{w_n}{n!} = \frac{d^{n-1}}{dV^{n-1}}\left\{f'(V)\left[\frac{V-\alpha}{\exp h(V)}\right]^n\right\}_{V=\alpha}\frac{1}{n!} \tag{67}$$

The subscript denotes evaluation at $V=\alpha$. By Cauchy's integral formula for derivatives (Whittaker and Watson[12])

$$\frac{w_n}{n!} = \frac{1}{2\pi i n}\oint_{(\alpha)} f'(V)\exp[-nh(V)]\,dV \tag{68}$$

The subscript (α) indicates the integral is taken counterclockwise along a contour enclosing α, and enclosing no other pole of the integrand. For reasons explained later, we integrate by parts to give

$$\frac{w_n}{n!} = \frac{1}{2\pi i n^2}\oint_{(\alpha)}\frac{d}{dV}\left\{\frac{f'(V)}{h'(V)}\right\}\cdot\exp[-nh(V)]\,dV \tag{69}$$

(The other term is evaluated around a closed contour and vanishes.)

In order to give the asymptotics of the integral by the saddle-point method (Carrier, Krook, and Pearson[13]) we deform the contour of integration to pass through a point where $\mathbb{R}\mathrm{e}\,h(V)$ has a minimum, so that (for large n) the greatest contribution to the integral occurs in the neighborhood of the point. Such points are among the saddle-points of $h(V)$, where $h'(V)=0$. $h'(V)$ for the various cases is given by the integrands of (24) [Case 1, where $h'(\pm 1)=0$] and (46) [Cases 2 and 3, where $h'(0)=0$].

Case 1: $B^2 < AC$

$$h''(V) = -\eta\left[\frac{pV^2+2qV-p}{(1+V^2)^2} + \frac{r_1}{(V-\alpha_1)^2} + \frac{r_2}{(V-\alpha_2)^2}\right] \tag{70}$$

At the possible saddle-points

$$h''(\pm 1) = -\eta\left\{\pm\frac{q}{2} + \frac{r_1}{(\pm 1-\alpha_1)^2} + \frac{r_2}{(\pm 1-\alpha_2)^2}\right\} \lessgtr 0 \tag{71}$$

We will deform the contour to pass through $V = 1$, perpendicular to the real axis, since, along the contour, $\mathbb{R}\mathrm{e}\, h(V)$ will then have a local minimum at $V = 1$. The contour may be further deformed to ensure this minimum is global. Using a variant of Laplace's method (Carrier, Krook, and Pearson[13]), we derive

$$\frac{w_n}{n!} \sim \frac{1}{2\pi i n^2}\cdot\left[\frac{-2\pi}{nh''(1)}\right]^{1/2}\cdot\frac{d}{dV}\left\{\frac{f'(V)}{h'(V)}\right\}_{V=1}\cdot\exp[-nh(1)]\cdot i \tag{72}$$

where $\sim$ indicates that the ratio of the two sides approaches 1 as n tends to infinity. Evaluation of the derivative of the quotient gives

$$\frac{w_n}{n!} \sim \frac{1-\epsilon}{b\eta}\left[\frac{-1}{2\pi h''(1)}\right]^{1/2}\exp[-nh(1)]n^{-5/2} \tag{73}$$

The original integrand (68) had a zero at the saddle-point $V = 1$. The integration by parts eliminated the zero, allowing direct application to Laplace's method.

Case 2: $B^2 > AC,\ A \neq 0$

$$h''(V) = \eta\left[\frac{p}{(1-V)^2} - \frac{q}{(1+V)^2} + \frac{r_1}{(\alpha_1-V)^2} + \frac{r_2}{(\alpha_2-V)^2}\right] \tag{74}$$

For the saddle-point

$$h''(0) = \eta\left(p - q + \frac{r_1}{\alpha_1^2} + \frac{r_2}{\alpha_2^2}\right) < 0 \tag{75}$$

Similar methods as before yield

$$\frac{w_n}{n!} \sim \frac{1}{2\pi i n^2}\cdot\left[\frac{-2\pi}{nh''(0)}\right]^{1/2}\cdot\frac{d}{dV}\left[\frac{f'(V)}{h'(V)}\right]_{V=0}\cdot\exp[-nh(0)]\cdot(-i) \tag{76}$$

$(-i)$ occurs instead of i at the end because, in contrast to Case 1, integration along the contour passes through the saddle-point from the upper half-plane to the lower half-plane. This is because $0 < \alpha$ in Case 2, whereas $\alpha < 1$ in Case 1. (0 and 1 are the saddle-points for contour deformation.)

This gives

$$\frac{w_n}{n!} \sim -\frac{4\delta}{b\eta}\left[\frac{-1}{2\pi h''(0)}\right]^{1/2} \exp[-nh(0)]n^{-5/2} \tag{77}$$

Case 3: $B^2 > AC,\ A = 0$

$$h''(V) = \eta\left[\frac{2p}{(1-V)^3} - \frac{q}{(1+V)^2} + \frac{r_1}{(1-V)^2} + \frac{r_2}{(\alpha_2 - V)^2}\right] \tag{78}$$

The asymptotics are still given by (77). In (77) the formulas appropriate to Case 3 (for b, δ, η etc.) must then be applied.

4. DISCUSSION

We summarize our results in Table I. The appropriate parts of the paper give the values of the parameters, *which are given by different formulas for different cases.*

These formulas, though lengthy, are practical for computation. The proportion of units found in k-mers is

$$\frac{km_k^*}{N} = \frac{km_k^*}{\sum km_k^*} = \frac{-1}{Z'} k \frac{w_k}{k!} e^{-\beta k} = \frac{\mu}{Z} k \frac{w_k}{k!} e^{-\beta k} \tag{79}$$

[See Eqs. (10), (12), (7), and (15).] Figure 2 graphs the cumulative total,

$$\sum_{n \leqslant k} \frac{nm_n^*}{N} \quad \text{vs.} \quad K \tag{80}$$

for different models and values of μ.

[Models of the type $A_g RB_g$, for which $A = 2$, $B = 2(g-1)$, and $C = 2(g-1)^2$, fall into the case $B^2 = AC$, which was covered in Ref. 4. Hence, neither Table I nor Figure 2 includes them.]

All solutions are equilibrium solutions. (Reference 4 discusses this point in greater detail.) As Ziff[7] notes, the equilibrium distributions for the RA_f and $A_1 RB_{f-1}$ models determine distributions for the corresponding irreversible polymerization processes (this point was known to Stockmayer[3] in 1943 for the RA_f model).

In fact, the solutions given in this paper complete the solution of the coagulation equation (monodisperse case) for a_{ij}'s of the form (6). The proof will be given in a later publication.

Table I. Specific Polymer Distributions for any

$$a_{ij} = A + B(i+j) + Cij: \frac{m_k^*}{M} = \frac{1}{Z}\frac{w_k}{k!}e^{-\beta k}, \qquad Z = \frac{2\mu(1-\mu)}{A\mu^2 + 2B\mu + C},$$

$$2(k-1)\frac{w_k}{k!} = \sum_{k=1}^{k-1}\frac{w_i}{i!}\frac{w_{k-i}}{(k-i)!}a_{i,(k-i)}$$

a_{ij} Classes		Case 1 $C \neq 0, B^2 < AC$	Case 2 $C \neq 0, B^2 > AC, A \neq 0$	Case 3 $C \neq 0\ B^2 > AC, A = 0$
Model		None	A_gRB_{f-g} $(g \neq 1, \frac{1}{2}f, f-1)$	A_gRB_∞ $(b \neq 1)$
a_{ij}	A		2	0
	B		$f-2$	1
	C		$2(g-1)(f-g-1)$	$2(g-1)$
V		$\frac{1-[1-b^2(Z+\gamma)]^2}{b(Z+\gamma)}$	$\left[\frac{-b(Z-\gamma)-1}{-b(Z-\gamma)+1}\right]^{1/2}$	$\left[\frac{-b(Z-\gamma)-1}{-b(Z-\gamma)+1}\right]^{1/2}$

Case 1:

$$e^{-\beta} = \exp h(V) \qquad \frac{2}{b}\cdot\frac{1-\alpha_1^2}{(1-\alpha_1^2)^2}\cdot(V-\alpha_1)\cdot\exp\left\{\eta\left[\frac{1}{2}p\ln\frac{1+V^2}{1+\alpha_1^2} + r_2\ln\frac{V-\alpha_2}{\alpha_1-\alpha_2} + q(\arctan V - \arctan\alpha_1)\right]\right\}$$

Case 2:

$$e^{-\beta} = \exp h(V) \qquad \frac{4\alpha_2}{b(1-\alpha_2^2)^2}\cdot(\alpha_2 - V)\cdot\exp\left[\eta\left(-p\ln\frac{1-V}{1-\alpha_2} - r_1\ln\frac{\alpha_1 - V}{\alpha_1-\alpha_2} + q\ln\frac{1+V}{1+\alpha_2}\right)\right]$$

Case 3:

$$e^{-\beta} = \exp h(V) \qquad \frac{4\alpha_2}{b(1-\alpha_2^2)^2}\cdot(\alpha_2 - V)\cdot\exp\left\{\eta\left[-p\frac{\alpha_2 - V}{(1-V)(1-\alpha_2)} - r_1\ln\frac{1-V}{1-\alpha_2} + q\ln\frac{1+V}{1+\alpha_2}\right]\right\}$$

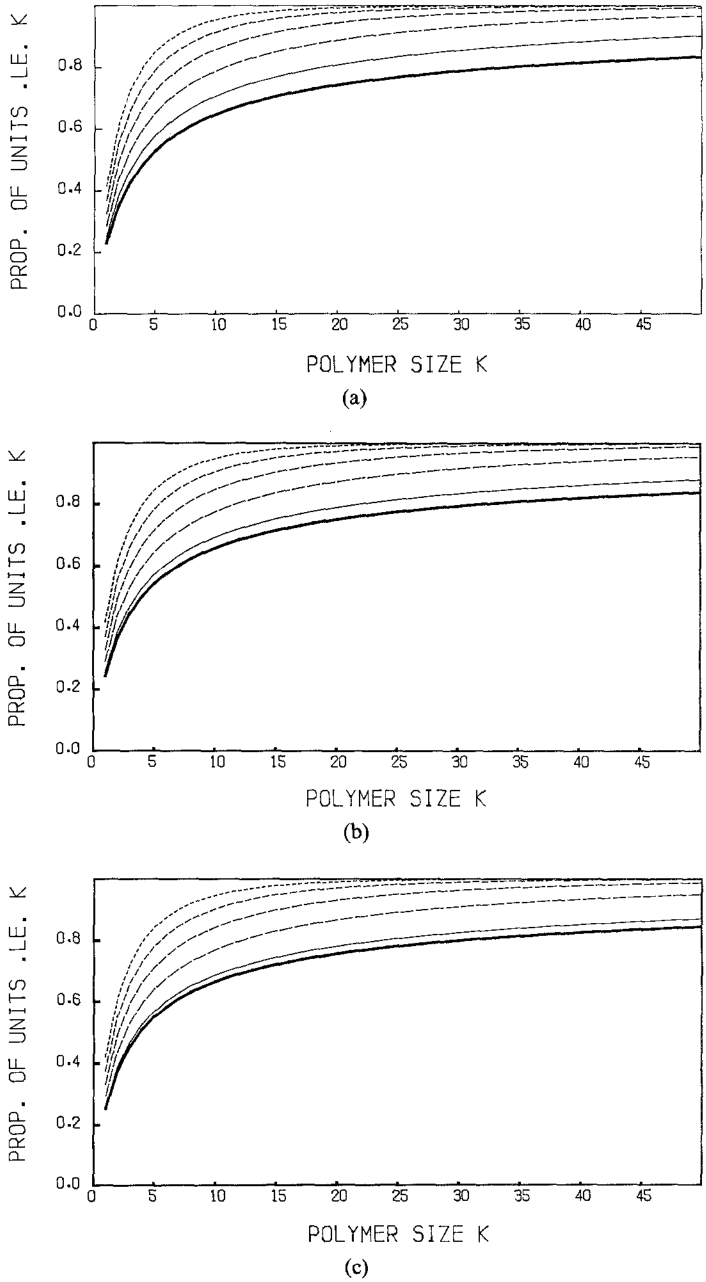
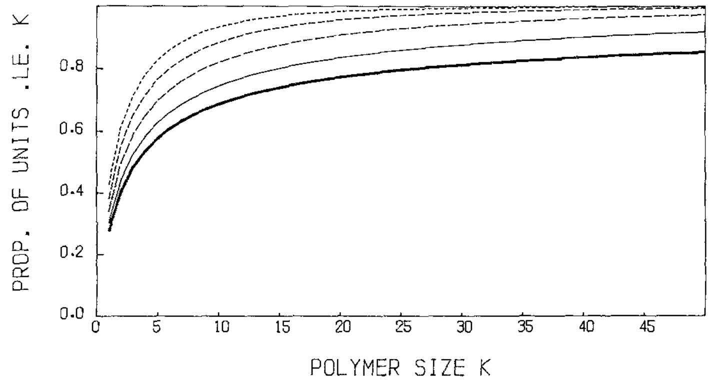
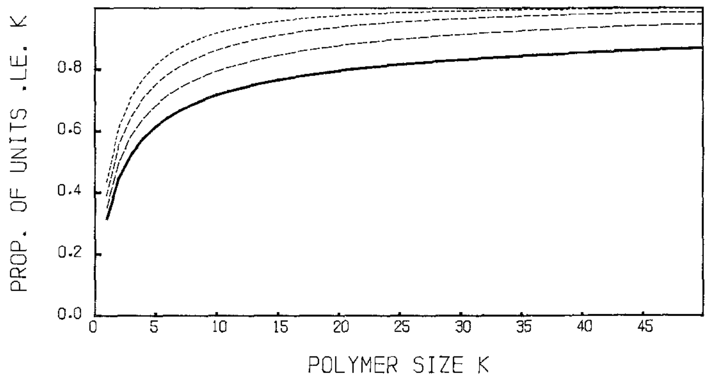


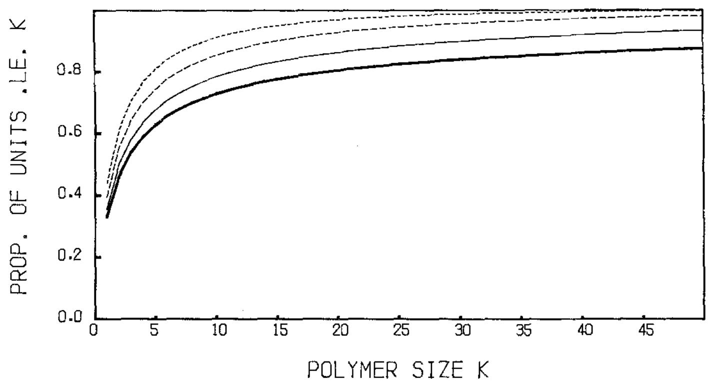
Fig. 2. Proportion of units found in polymers of size less than or equal to k against the polymer size k. Ordinates have been plotted for integral k, then joined by a smooth curve. In all the figures, the curves given are for fixed values of μ. The highest curves are for $\mu = 0.6$; the curves beneath represent decrements of 0.05 in μ (decrements in μ indicate the formation of larger polymers). The lowest curves (in heavy line) represent the polymer distribution just before the formation of an infinite polymer (which occurs at the critical value of μ, μ_c). The μ



(d)



(e)



(f)

for the lowest curves is μ_c, accurate to 6 decimals, but rounded up. The model and rounded μ_c accompany each figure. The ordinates for fixed μ and k decrease from (a) to (f), whereas the ordinates for μ_c (different for each model) and fixed k increase from (a) to (f). Such comparisons may have generalizations. (a) A_2RB_3 $\mu_c = 0.366026$; (b) A_2RB_4 $\mu_c = 0.379797$; (c) A_2RB_5 $\mu_c = 0.387427$; (d) A_2RB_∞ $\mu_c = 0.414214$; (e) A_3RB_∞ $\mu_c = 0.449490$; (f) A_4RB_∞ $\mu_c = 0.464102$.

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